SEMICONTINUOUS ELECTROKINETIC DEWATERING OF CLAY SUSPENSIONS

By

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To my parents and friends

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The processing and storage of the phosphatic clay suspensions which result as a waste product from phosphate mining is a longstanding problem. A very long time is required for the gravity-driven settling of clay suspensions with an initial 2-3 wt% solids content, and decades may be required to reach the desired target of 25-30 wt% solids content. In previous work, bench top experiments of electrokinetic dewatering were used to guide the development of a constitutive relationship describing the changes in solids content with time and electric field. In this thesis, a semi-continuous electrokinetic dewatering process was designed and tested. A unique feature of the system is that the electrodes were placed close to each other, leaving a large volume below the electrodes in which the clay could settle. The experimental results showed that electrokinetic dewatering occurs in semi-continuous operation and that the close electrode spacing, which greatly reduced the power requirement, did not impair separation. These results motivated a discussion of how electrokinetic effects could be incorporated into existing thickening equipment. Suggestions are made for future experiments.

CHAPTER 1
INTRODUCTION

Phosphatic clay suspensions are a major waste product of the Florida phosphate mining industry, which raises environmental concerns for phosphate mining companies. The clay slurry, which has an initial solids content of 2-3 wt%, is pumped to large-area disposal ponds for natural settling. This clay settling process takes decades to reach the demanded value of 20-25 wt% solids content. These clay ponds currently cover an area of over 100,000 acres in Florida, which is approximately 30% of the mined land. Thus, there are benefits to developing a technique for phosphatic clay suspension dewatering, two of which are saving land currently used for disposal ponds and recycling water.

Previous bench top experiments performed by Patrick McKinney demonstrated the effects of electrokinetic dewatering. A constitutive relationship was established and power and energy consumption were calculated. The analysis showed that energy consumption was in a reasonable range but power consumption was too high. Thus, in this investigation, a larger scale semi-continuous flow system was designed and implemented to further evaluate the electrokinetic dewatering process.

The separation speed, changes of solids content, and supernatant water turbidity were estimated in this process. The separation results were found to improve considerably with increasing applied potential.

The idea of improving existing thickening instruments by introducing an electric field shall be discussed in Chapter 4. The discussion is focused on optimizing the electrode configuration for maximal efficiency. Horizontal thickeners and inclined surface thickeners are believed to hold promise for incorporating electrokinetic dewatering.

CHAPTER 2
LITERATURE REVIEW

Methods of Clay Dewatering

Numerous methods have been attempted in the search for a better phosphate clay dewatering process. Some of them showed feasibility in laboratory scale experiments and were subsequently tested in large scale, in-situ, environments.

Freeze-Thaw

This method consists of two stages: freeze and thaw. During freezing process clay particles and water are both frozen and separated from each other. Upon thawing, ice melts into water while clay remains dehydrated, allowing for clay particles to settle. Finally, supernatant water was removed from the clay suspension. Although it was reported that the solids content could be increased from 13.7 wt% to 42 wt% in this manner, this method still failed because of the high energy cost [1].

Moving Screen

This technique used the idea of passing a moving screen through the clay suspensions to destroy the structure of the gel-like slurry. The supernatant water was removed periodically. It was found that the solids content increased upon the decreasing speed of the moving screen. However, it is not practical to wait such a long time to reach the required level of dewatering [1].

Sand-Clay Sandwich Process

The sand tailings and clay slurry were stacked layer by layer into a sandwich-like structure. The sand layer simultaneously functioned as a drainage path and also put weight on the lower clay layers to aid dewatering. In this procedure, a sand layer is put on the bottom and a clay layer is placed above it. After the clay layer reaches a sufficiently high density and is stable enough to support another sand layer, the same operation is repeated. However, many problems were seen in the field test. The waiting time between applying different layers was relatively long, thus more ponds were required for this process [1]. Distributing each layer evenly is also a difficult problem when one is dealing with to a large area.

Flocculation Method

This is currently the most widely used method in the mining industry for waste water treatment. The basic idea is to mix clay with flocculants which induce the small clay particles to coagulate, thus forming a larger cluster. These clusters, or ‘flocs’, settle much more readily than untreated suspensions. This method has been used to achieve a 10 wt% solids content starting from 3 wt%.

Electrokinetic Dewatering

The electrokinetic dewatering method uses a direct current applied across two electrodes which are placed on either side of the clay, causing electro-osmosis of the water molecules and electrophoresis of charged clay particles in the colloidal system. The study of this technique began in the 1960’s when the US Bureau of Mines began its pioneering research on the electrokinetic dewatering of tailings. Several successful field applications were reported, but there is still limited understanding of the electrokinetic principles which resulted in the following effects [2]:

- Large variance in the effectiveness of this technique with respect to the material to which it is applied.
- High power consumption in some cases.
- Improperly designed operating systems.

Principles of Electrokinetic Dewatering

Electrokinetic Dewatering Process

A typical electrokinetic clay dewatering process can be divided into two stages: sedimentation and consolidation.

Sedimentation

In the process of sedimentation, suspended clay solids settle under the combined influence of electrokinetic, gravitational, and electrochemical forces. The first of these concerns the motion of electrically charged particles under an applied field. Here we will be concerned primarily with the electrokinetic processes of electrophoresis and dielectrophoresis (see the subsection “Electrophoresis and Electro-osmosis). This effect is used in conjunction with the gravitational force, which causes the clay particles to slowly drift to the bottom of the suspension. Finally, electrochemical forces are important since they determine the rate of interaction and aggregation amongst individual clay particles, and this, in turn, determines how effective the previous two influences are.

A theory of electrokinetic sedimentation has been proposed based on the combined action of electrophoretic, Stokesian, and interparticle forces on fine clay particles suspended in water while under the influence of an external direct current electric field. The theory predicts that the sedimentation velocity of solid suspensions is proportional to the applied current density in the free settling stage and is dominated by the porosity of the suspensions in the subsequent hindered settling stage. A theoretical and experimental study have been conducted to verify this theory [3].

Consolidation

Once a porous soil is formed it is further consolidated; primarily by electro-osmosis. This is the consolidation stage. Mechanical dewatering methods based on gravitational settling, filtration, centrifugation, or hydraulic flow induced by applied pressure or vacuum techniques, all become ineffective in dewatering suspensions of particles smaller than approximately 10 μm in diameter. If the water is initially removed by mechanical methods, the particles move closer together, thus decreasing the size of pores through which the water must flow and drastically diminishing the rate of water removal. Thus, electro-osmotic dewatering becomes the ideal method for the further removal of water trapped in the rather compacted fine clays, because this mechanism is based on the electrostatic effects operating in the electrochemical double layers formed at the clay particle/water interfaces in the wet clays [4].

Electro-osmotic consolidation has two functions: further reducing the soil's water content and balancing electrochemical effects.

Electrophoresis and Electro-Osmosis

Electrophoresis and electro-osmosis are amongst the most important principles in the electrokinetics of clay dewatering, and they have been discussed extensively. The former is the movement of colloidal particles in a direct current electric field, while the latter is the flow of water in porous media due to a direct current electric field.

During the process of electrophoresis and electro-osmosis, the water velocity can be expressed as a function of the applied electric field (E) via:

$$v = \frac{k_e \xi E}{\mu} \tag{2-1}$$

where k_e is the permittivity of water, ξ represents the zeta potential which is the potential at the inner limit of the diffuse layer, and μ is the viscosity of water [5].

The effectiveness of electro-osmotic dewatering is governed by the electro-osmotic permeability k_e, which can be defined by the empirical relation [6]:

$$q_{eo} = k_e A \frac{j}{\sigma} \tag{2-2}$$

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; σ is the electrical conductivity of clay slurry in S/m.

Chemical Reactions on the Electrodes

The issue of chemical reactions on the electrodes is widely discussed in connection with the electrokinetic process. This is because the quality of water collected is one of the primary concerns for investigators, and chemicals released by the electrodes may have an adverse effect. The electrode reactions can be summarized as follows [7]:

At the anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{2-3}$$

$$M_a \rightarrow M_a^{n+} + ne^- \tag{2-4}$$

At the cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2-5}$$

$$M_i^{n+} + ne^- \rightarrow M_i \tag{2-6}$$

$$M_i^{n+} + OH^- \rightarrow M_i(OH)_n \tag{2-7}$$

where M_a represents the anode metal and M_i^{n+} is the dissolved cation species, i, in solution. Equation 2-3 states that the anode hydrolysis generates oxygen and reduces the solution pH value. As a result, a metallic anode will corrode, as shown in Equation 2-4. The solution pH will increase at the cathode and hydrogen will be generated, as shown in Equation 2-5. Cations are driven to the cathode by the electric field where they may reduce to element metals, as shown in Equation 2-6, or, more likely, form hydroxides, as shown in Equation 2-7. With only several exceptions, such as KOH and NaOH, most hydroxides are insoluble at pH > 5 [8]. During the electrokinetic process, the movement of H^+ and OH^- will change the sludge pH drastically. A pH gradient will be generated across the soil as a result of the electrode reactions. The acid front at the anode will advance across the clay suspensions toward the cathode by advection and diffusion effects [9]. The net effect is the decrease of cathode pH in the later stage of treatment.

Factors Influencing the Electrokinetic Process

Discussions about the influential factors during the electrokinetic process include both internal and external factors. The internal or intrinsic factors are the physical and chemical properties of materials, including [2]:

Grain size and mineral type

In materials which have a fine grain size, the surface properties of particles are dominant, and thus electrokinetics works more efficiently. It is particularly effective in brown clay, which is likely a more favorable cover material than what is currently used due to its special properties.

pH value

The electrokinetics is very effective in a high pH environment (pH > 9), but not effective in a low pH environment (pH < 6).

Salinity

Techniques based on electrokinetics are not effective in materials with high salt concentrations [10].

The external factors governing electrokinetic processes are those which are controlled by the experimenter by means an external operation system, including:

Current density

The effective current density in an electrokinetic dewatering process is dependent upon the material properties of the medium under consideration. The magnitude and spatial distribution of the current density are determined by the applied voltage and spacing of electrodes, which are the primary considerations when designing the operation system.

Electrode material

The efficiency, corrosion rate, and lifespan of electrodes are influenced by the materials used. Excluding prohibitively expensive materials such as silver and platinum, iron and copper are amongst the best materials for field applications; being more effective than aluminum, lead and carbon black [11]. Iron or steel electrodes have the advantage of low cost, whereas copper or brass electrodes have higher conductivities.

Electrode layout

This includes the choice of horizontal or vertical configuration for the electrodes. It is preferred to use horizontal electrode configurations for new disposal ponds. For existing tailing ponds, installation of horizontal electrode arrays may not be technically or economically feasible.

Bench-Top Experiment of Electrokinetic Dewatering

McKinney and Orazem [12] performed a series of bench top experiments to examine the effect of the electric field on the phosphatic clay dewatering process. The clay suspensions were sampled from a mine in central Florida. The experimental set up is shown in Figure 2-1.

A Plexiglas cylinder filled with clay suspensions having a solids content of around 10 wt% was used in this experiment. An electric field was added by a pair of mesh electrodes with a top-cathode and bottom-anode configuration. Sensors at different heights were used to evaluate the potential within the cell. The parameters affecting the dewatering process were investigated in both short term and long term experiments. A constitutive relationship describing the dewatering process was formulated as;

$$\Delta w_c = [(0.77tE)^{-n} + (7.1\log_{10}(E) + 16.5)^{-n}]^{-1/n} \tag{2-8}$$

where Δw_c is the change in solids content referenced to the initial composition, t is the elapsed time in hours, E is the electric field in V/cm, and n is a dimensionless parameter that controls the transition from short-time to long-time behavior. Equation 2-8 shows a good agreement with experimental data, indicating the change in solids content can be predicted for a given electric field as a function of elapsed time.

From Equation 2-8, an upper limit on the change in solids content can be found for a given electric field. The upper limit fraction, b, is given by:

$$t_b = \frac{\Delta w_{c,\max}}{0.77E}\left(\frac{b^5}{1-b^5}\right)^{1/5} \tag{2-9}$$

The energy requirement can be expressed by

$$E_{req} = \frac{V_{cell} I t}{\Delta m_w} \tag{2-10}$$

where E_{req} is the energy required (in W-h/kg water removed), V_{cell} is the cell potential, I is the current, t is the operation time, and Δm_w is mass of water removed. The energy requirement for removing water in the McKinney and Orazem experiments ranged from 1.25 to 175 Wh/kg. The calculation result from Equation 2-10 had a good agreement with the experiment values and validated the constitutive relationship.

The constitutive relationship, coupled with a boundary-element model for solving Laplace's equation, was then used to estimate the power requirements for applying electrokinetic dewatering to a large scale settling area. This simulation was conducted with the mathematical model program CP3D [13].

Two types of electrode configuration were investigated, horizontal and vertical. The simulation modeled a clay settling area with the dimensions of 1 mile in width, 1 mile in length and 40 feet in depth.

The simulation results indicated that there was a uniform electric field when utilizing a horizontal electrode configuration and a non-uniform electric field with a vertical configuration. The time and energy required to achieve a 15 wt% increase in solids content when using a non-uniform electric field were both greater than with a uniform electric field.

The notable result of the simulation is the short time required for the separation of water and the huge power requirements. The power required for increasing the solids content of a one-square-mile clay settling area from 10 wt% to 25 wt% was 44,000 MW over 19 hours. While the energy requirement of 8.4×10^8 kWh is moderate, the question was focused on the power requirement. The power is proportional to the square of cell potential and was thus significantly reduced for a smaller electric field.

Equipment Used in Clay Thickening

Based on the success of bench top experiments, electrokinetic dewatering is considered to be a promising method for extension to large scale continuous dewatering operations. However, it is worthwhile to first investigate the existing dewatering techniques which are currently used in the manufacturing industry.

Horizontal Flow Thickener

One traditional way of designing equipment for clay dewatering is to simply use gravity, which means to allow clay particles to settle down under the influence of their own weight. In these kinds of designs, each thickener has an inlet zone, an exit zone, a collection device, and a sludge withdrawal area. Figure 2-2 shows one typical gravity thickener with circular tank. Slurry with low solids content (usually 1-2 wt%) will be pumped through the influent pipe into the tank. During the process of separation, the high density clay particles settle down at the bottom of the thickener, get collected in the hopper, and then scrapped out of the tank through a sludge pipe set at the bottom. The low density water flows up to the top layer and then leaves through the effluent pipe. This apparatus can be operated continuously for clay sedimentation.

Some similar thickener designs are in the form of rectangular tanks [14]. The rectangular tank avoids the short-circuiting problems which frequently occur in circular tanks. If multiple thickeners are used, a rectangular tank will help to save space and materials in construction.

Horizontal flow thickeners are widely used in the separation industry. Its advantages include the low cost of operation and maintenance, easy operation, and thus small operation staffs [15].

However, this method suffers from some shortcomings, which include the long waiting times for settling and less clear supernatant water compared with other methods.

Vertical Flow Thickener

Another thickener has a shape which is similar to the horizontal flow thickener but with a different flow direction. Clay treated by vertical flow thickeners usually flow upward in the tank, through a layer of floc. During this process, heavy clay particles settle down at the bottom and clear water effluent flows out pipe at the top. Vertical flow thickeners are sometimes called ‘solid contact thickeners’ or ‘sludge blanket thickeners’.

This class of thickener usually has a cone shaped unit in the center of thickening tank [16], as shown in Figure 2-3. This area is called the ‘mixing zone’. Slurry enters this area to mix with the flocculants, and then the mixture flows through the suspended layer of sludge near the bottom of tank, entering into the space outside the center cone. This sludge blanket acts as a filter, keeping the flocculate solids in the bulk clay while releasing the water to top. Due to the inverted cone design, the velocity decreases as the fluid flows toward the upper layer. At a certain point, the upward velocity of the water is balanced the downward velocity of solids. The solids become suspended at the bottom and act as a blanket layer to block new flowing sludge. This accelerates flocculation and reduces the amount of coagulants used.

The vertical flow thickener is very efficient for dewatering clay suspensions combined with the chemical flocculants. Furthermore, its special structure prevents the short-circuiting problem often appearing in horizontal flow thickeners. However, due to the unstable property of the sludge, the control of the thickener is very complex. The sludge blanket level is sensitive to changes in coagulant concentration, raw water chemistry and temperature. It needs a very accurate distribution of inlet slurry across the entire tank and precise control of the sludge. The limited compression zone volume is also a disadvantage built into this system.

Inclined Surface Thickener

The inclined surface thickener (also known as 'lamella clarifier') usually consists of a rectangular or circular tank inserted with a bunch of parallel spaced plates or tubes inclined at some specified angle. Taking inclined plates as an example [17], raw slurry flows from bottom to top through these plates. Under the influence of gravity, heavy solids settled down on the lower surfaces of the plates and then slip down along the inclined surface to the hopper of the tank.

As shown in Figure 2-4B, Clay flowing through the inclined surface thickener has a larger settling distance, D, than in the horizontal flow tank. This distance is related to the space between the plates by the relation:

$$D\cos\varphi = d \tag{2-11}$$

where φ is the angle the plates measured from the horizontal; d is the distance between two plates; and D is the settling distance. Thus settling distance is increased by the factor $1/\cos\varphi$. Obviously, the larger the angle is, the smaller the value of $\cos\varphi$, and thus the larger the settlement distance will be. However, the maximum allowed angle is 60° because the angle of inclination must not exceed the angle of repose of the separated solids. Consequently, the maximum settlement distance is twice the distance between the plates.

This type of lamella design is up to 10 times as space efficient as conventional gravity thickener since one may increase the effective area onto which settling may occur. One may see from Figure 2-5 that a reduction of the required floor space is achieved by inclining the plates and stacking them. Using an angle of 45° for heavy particles and 60° for light particles reduces the required horizontal projected area by a factor of $\cos \varphi$. The surface area diagram (Figure 2-5) graphically compares the floor space requirements of an inclined surface thickener with the equivalent horizontal projected settling area [18].

The plate angle are commonly chosen from 45° to 60°. The solids are unlikely to settle down on surfaces with angles larger than this. On the other hand, if the angle is too small, solids will accumulate on the plates instead of sliding down.

Sometimes people use inclined tubes instead of plates. These are specially designed cellular structures consisting of hexagonal tubes and usually designed for use in oil separation pools. The mechanism used is the same as with the lamella above and they both need laminar flow for operation. This requires a Reynolds number of less than 800 [19].

Other Thickeners

There are several thickeners which take advantages of mechanisms other than gravity. These thickeners include belt thickeners, screw thickeners, and centrifuge thickeners.

Belt thickener

The belt thickener is usually composed of a moving belt with a conveying surface arranged horizontally. The initial slurry feeding from one side of the thickener is conveyed to the other side on the surface of the belt. A feeding reactor ensures a uniform distribution over the full width of the continuously moving filter belt. The water filtered through the belt filter cloth is drained off into collection troughs. The volume of initial clay slurry can be reduced by approx 85%. Once the sludge cake has been discharged into the thick sludge collection trough a spray bar then cleans the filter belt [20].

This method is used as a primary clarifier and the resultant thickened clay has a solids content of about 6%.

Screw thickener

The screw thickener, used for wastewater treatment, looks like an inclined baby bottle. In this tank, a screw slowly rotates and conveys the sludge upward through the inclined basket. The thickened clay is collected in another tank at the top of the basket. Water is drained through the basket and flows out from the bottom effluent pipe.

It is reported that the sludge volume reduction can reach to up to 90%. Power consumption is around 35 W/m^3 [20].

Centrifuge thickener

Centrifuges have been applied in wastewater treatment ever since the 1930s. A centrifuge thickener consists of a cylindrical bowl with a scroll inside. Slurry initially flows into the tank and is then separated by the high speed of rotation. As a result, clear liquid flows out from one side and thickened clay is removed from the other end of cylindrical.

This separation is driven by the force due to the rotation of the central scroll. The percent solid output can be varied by changing the operation parameters.

The centrifuge thickener has a low space requirement, and thus it is economical for a small plant. The cleaning work for this instrument is easy, and the operation and maintenance cost is fairly low. However, this thickener still suffers from the disadvantages of high power consumption and capital cost which inhibit its usage in many field applications [21].

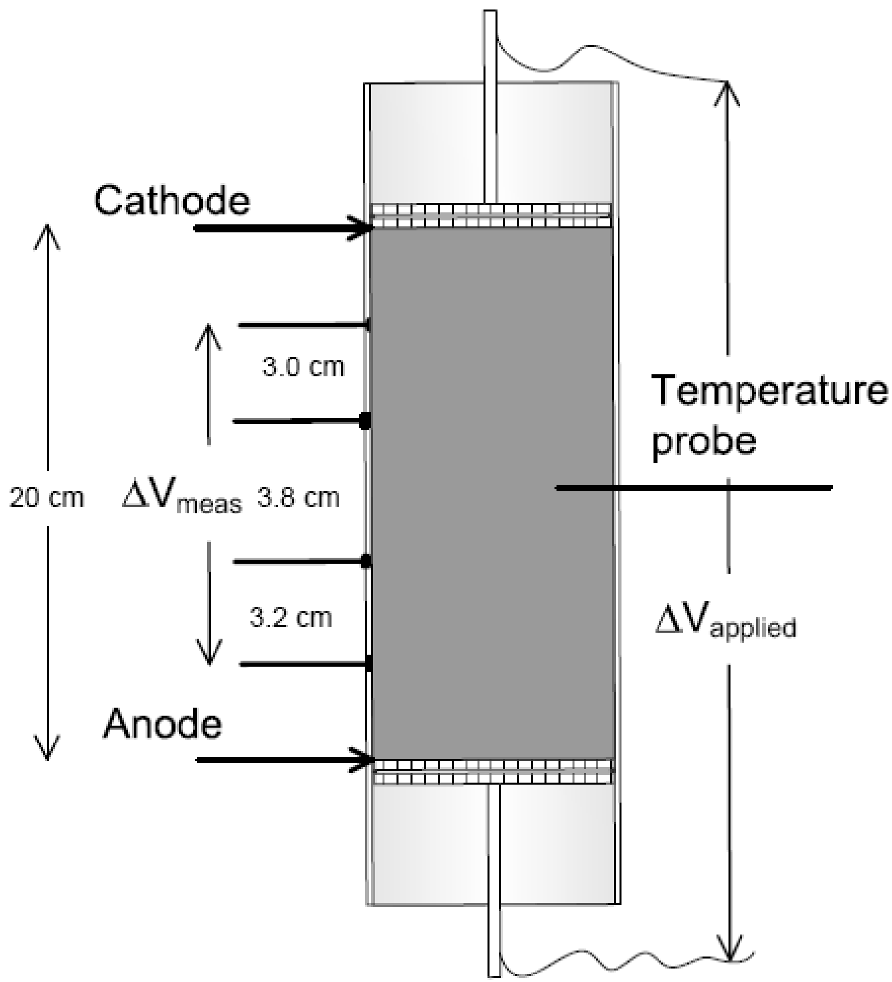


Figure 2-1. Schematic of bench top cell with labeled locations of the electrodes and the temperature and voltage measurements.

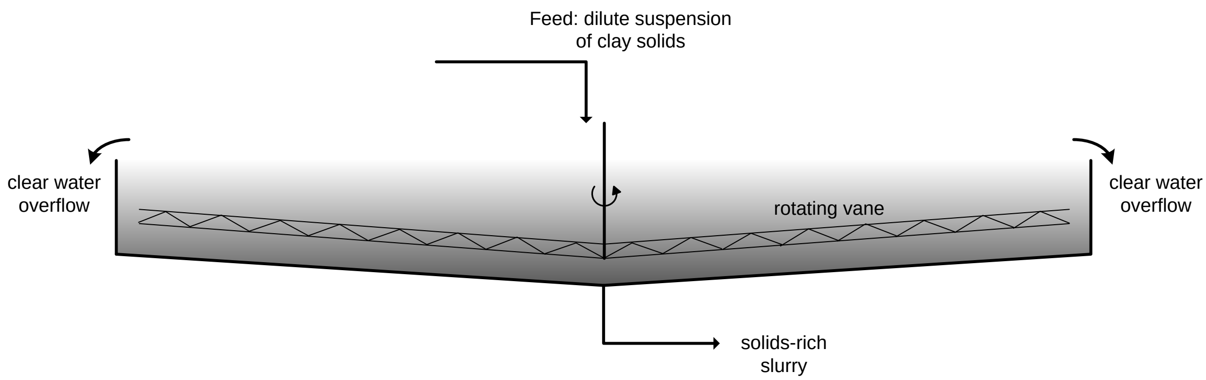


Figure 2-2. Representation of a horizontal flow thickener.

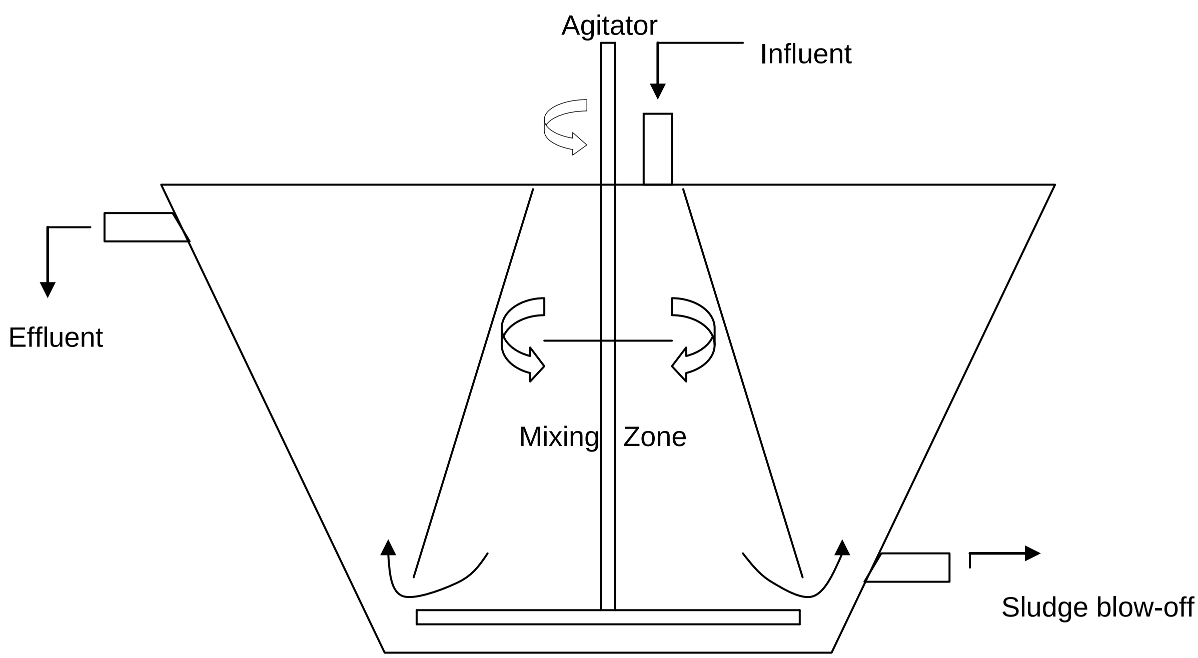


Figure 2-3. Representation of a vertical flow thickener.

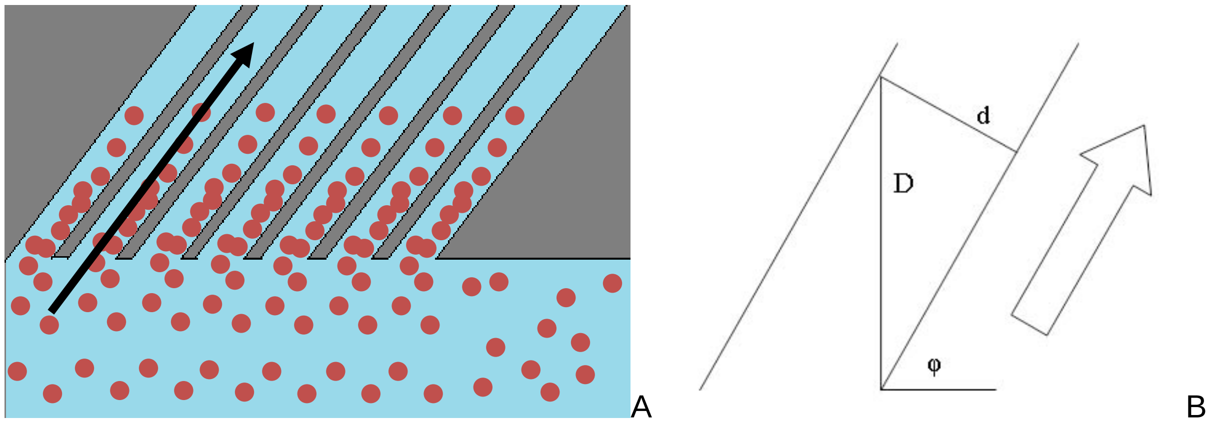


Figure 2-4. Flow direction of clay suspensions in the inclined surface thickener. A) Slurry flow through the inclined plate surface. B) Relation between settling distance and inclined angle.

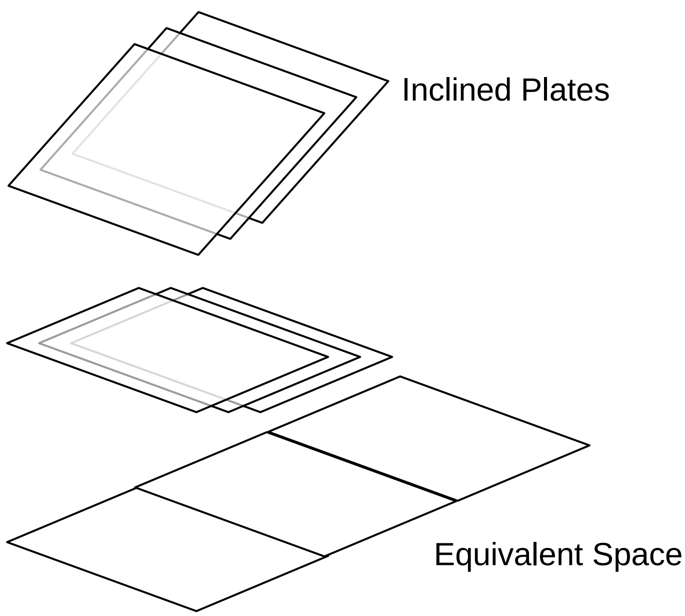


Figure 2-5. Equivalent floor space required by a horizontal flow thickener.

CHAPTER 3
EXPERIMENTAL EVALUATION OF SEMI-CONTINUOUS FLOW OPERATION PROCEDURE

Large Scale Semi-Continuous Flow System

The success of bench-top electrokinetic dewatering has been verified by a series of experiments. However, to adapt this method to mining industry, larger scale equipment with semi-continuous features would be necessary. Thus, in this investigation, a cubic settling tank with large dimensions was designed and evaluated for separation.

Cell Design

The basic separation process is similar to the normal gravity settling process. The initial clay suspensions were pumped into the settling tank and allowed to settle under the influence of an electric field. After separation, water flowed out from the surface effluent pipe and thickened clay accumulated at the bottom of the tank. As shown in Figure 3-1, a plastic storage box with dimensions of 88.3 cm×41.9 cm×15.2 cm was used as a settling tank. Two mesh plate electrodes made of titanium with a ruthenium oxide coating (Siemens, Inc.) were set horizontally in the tank with a top-cathode and bottom-anode configuration. The distance between the electrodes was 10 cm. Each mesh plate electrode was connected to a potentiostat instrument by a titanium wire. The wire was sealed in a silicon tube to prevent exposure to water.

Two PVC tubes were used to conduct the influent and effluent (Figure 3-2). They were kept horizontal to ensure an even distribution of liquid along the whole tube.

Instruments

The influent clay suspensions were controlled by a Masterflex Model 77202-60 digital pump (Cole-Parmer Instrument Company).

The results were obtained using an EG&G Princeton Applied Research (PAR) Model 273A Potentiostat/ Gavanostat, under potentiostat control using CorrWare software (Scribner Associates, Inc.). Operations were conducted during daytime and stopped at night. The duty cycle for the experiments included 30 minutes with potential applied, followed by 2 minutes without potential applied.

Experiment Process

The clay samples were provided by Mosaic Fertilizer, LLC, pretreated by flocculent addition, and allowed to reach an initial solids content of around 11 wt%. The potential was held at 10 V (resulting in an electric field of 1 V/cm) and the flow rate was 20 ml/min. The potentiostat and pump started at t=0. During the separation process, potential and current values were recorded and photos were taken every hour. To minimize the evaporation effect, the tank was covered at night when the operation was suspended.

After the operation, supernatant water was removed thoroughly and clay samples were collected. In the sample collection process, a plastic cylinder of 28 cm in length and 2.6 cm in diameter was used.

The upper opening was covered when the cylinder was inserted straight into the clay. Due to the air pressure, the clay samples remained in the cylinder when it was pulled out of the tank. As electrodes covered nearly the entire surface area of tank, sampling spots could only be selected on one side of the tank. We chose several sampling spots in a straight line at a certain interval.

The solids content of clay samples was obtained by the following method. An empty 200 ml beaker was weighed and the result was labeled as W_1. Clay samples were then transported into the beaker, and the wet clay weight in the beaker was recorded as W_2. Samples were then moved to the oven to dry. After drying, the dry clay weight (including the beaker) was measured and recorded as W_3. The solids content was then calculated with Equation 3-1:

$$w\% = \frac{W_3 - W_1}{W_2 - W_1} \times 100\% \tag{3-1}$$

Clay samples were taken before and after the experiment and compared using the above formula.

To evaluate the separation results, a parallel control experiment was taken under the same conditions. The only difference was that no potential was applied during the process, and gravity was the only force inducing the settling process.

Separation Results

The experiment was terminated after applying the potential for18 hours using the previously described work cycle. The significant change produced during the course of operation (Figure 3-4) indicates the powerful effect of electrokinetic separation on the larger scale basin. Solids content was increased from 11.85 wt% to 19.55 wt%. Clear water was separated from the clay suspensions and moved to the top layer of tank. The surface was divided into two distinct areas, the left part contained clear water which was moving out, and the right part was the influent clay suspensions waiting to settle down. In principle, if the separation speed were lower than the influent speed of the clay suspensions and the process were continuous, the boundary would slowly move from right to left until a steady-state was achieved. Because this is not a completely continuous process, this theoretic steady-state could not be realized. The side view of tank shown in Figure 3-5 gives a clear picture of the results.

A control experiment was taken under the same conditions, and the result is shown in Figure 3-6. In this process, solids content was increased from 11.72 wt% to 14.34 wt%. The operation was terminated when the containers became overfilled. Finally, the whole tank was filled with clay suspensions and no supernatant water was observed.

To further verify the effect of an electric field, a controlled potential of 10 V was added to the separated clay suspensions from the blank experiment. After 6 hours of operation, the solids content was increased from 14.34 wt% to 18.70 wt% and an obvious layer of supernatant water appeared, as shown in Figure 3-7.

Thus, a change in solids of $\Delta w\%$=7.7 wt% was achieved for an electric field of 1 V/cm. In the gravity settling process, the value was $\Delta w\%$=2.62 wt%, indicating a higher efficiency was achieved by applying an electric field. This difference could also be observed from the external appearance of clay suspensions. Supernatant water occupying about 1/3 the height of the tank could be seen after electrokinetic separation. In contrast, in the gravity settling experiment, clay suspensions occupied the whole tank during the entire operation process. Due to the limited tank height, the treatment capacity was too low to support a longer operation. The basin would be filled with clay in 20 hours and the operation would be forced to terminate. Thus, to further estimate the semi-continuous electrokinetics dewatering process, the settling tank was replaced by a deeper one.

Deep Tank Semi-Continuous Flow System

As has been explained, electrokinetic dewatering is more efficient than natural gravity thickening. However, simulations performed using the CP3D software show that applying this process to dewatering ponds with standard dimensions leads to unacceptably high power requirements. To overcome this problem, we studied the efficiency of deep-tank semi-continuous flow systems with a unique feature of suspended electrodes.

Cell Design

Since the shallow tank did not have enough capacity for semi-continuous steady-state operation, a deep tank is needed instead. However, if a deep tank with the same design as before were used, the distance between two electrodes would be too large and the resultant power requirement would be too high. To avoid this problem, the bottom electrode was designed to be suspended in the clay suspensions to reduce the distance. The new electrode configuration is shown in Figure 3-8.

A plastic storage box with the dimensions of 88.9 cm×42.5 cm×32.7 cm was used as the settling tank. This tank had a larger surface area and a height comparable to the bench top cell. Two mesh plate electrodes made of titanium with a ruthenium oxide coating (Siemens, Inc.) were suspended in the tank at an adjustable position. In the following experiments the distance between the two electrodes was adjusted to 10 cm. Thus, the influent clay suspensions experienced two stages in the separation process. In the first step, the clay particles separated from water and moved downward in the tank under the influence of the electric field. When these particles passed the lower electrode, they settled down and accumulated at the bottom by gravity.

The overall flow system is shown in Figure 3-9. Initial clay suspensions in the right bucket were pumped into the tank for settling, and supernatant water flowed out via the left tube to the left bucket.

Instruments

The results were obtained using an EG&G Princeton Applied Research (PAR) Model 273A Potentiostat/ Gavanostat, under potentiostat control by using CorrWare software (Scribner Associates, Inc.).

The influent clay suspensions were controlled by a Masterflex Model 77202-60 digital pump (Cole-Parmer Instrument Company).

The turbidity of supernatant water was measured using a HACH 2100N Laboratory Turbidimeter.

Experimental Process

The tank was filled with clay suspensions provided by Mosaic Fertilizer, LLC, pretreated by flocculent addition and then allowed to reach an initial solids content of around 10 wt%. The operation process was similar to that of the shallow tank.

One bench mode experiment without continuous flow was conducted to evaluate the separation results for different height levels. Two flow-by operations were carried out to compare the result of electrokinetic dewatering and gravity settling.

After the experiment, supernatant water was removed thoroughly and clay samples were collected. To collect clay samples at different heights a device consisting of a glass tube with the inner diameter of 6 mm connected to a syringe was constructed. This tube could be moved to any layer of the clay to collect samples.

Proof of Concept

Two parallel experiments were conducted, one with the constant potential applied between two electrodes and another without potential applied. The control experiment produced results that were similar to what is seen in the settling process as it occurs naturally in a settling pond in mining industry. In this experiment, the advantages of electrokinetic dewatering were seen in the separation speed, changes of solids content, and the turbidity of supernatant water.

Separation speed

At the beginning of the experiments, both tanks were filled with well-mixed clay suspensions. The same operation conditions were used in both cases, with the exception of the applied electric field (Figure 3-10).

After the 5 hours of operation, clear differences between the two suspensions can be observed (Figure 3-11). For the clay suspensions with potential applied, an obscure boundary between water and condensed clay appeared from the side view. In the top view, the clay suspensions became much more dilute; bubbles produced at the electrode surface during the process floated up to the top, and disturbed the supernatant water.

In the control experiment, few changes could be observed from the side view. Some evidence of sedimentation was seen in top view by the clay sheets floating at the water surface.

After 11 hours, significant effects caused by electric field appeared both in the side view and top view. Observing from the top of the system, the supernatant water became so transparent that the top electrode was visible through it. From the side view, a distinct boundary between water and clay was formed as an uneven line. This is because of the accumulation of the influent on the right side of the tank.

The control experiment did not show any changes from the side view. However, from the top view of the tank, the clay displayed an interesting structure containing many narrow cracks.

After 19 hours, in the system affected by electric field, supernatant water became very clear. Condensed clay accumulated at the right side of the tank and forced water to move to the left. A clear boundary was formed in this process, and slowly extended to occupy approximately 1/4 the length of the tank. This system seemed approach steady-state.

In the corresponding control experiment, because the influent flow speed was higher than the settling speed, some clay accumulated at the surface of the effluent pipe and blocked at the edge, which lead the effluent to become mixed with a lot of clay particles.

After 32 hours, the surface boundary moved to the middle of the tank. At this point the operation was terminated and the electric field was removed. Although there was some supernatant water indicating the settling in the control experiment, the significant difference from both top view and side view between the two experiments proved the efficacy of electrokinetics dewatering.

Changes of solids content

Bench mode experimental results are listed in Table 3-1. Nine different locations were selected by dividing the horizontal and vertical directions into three segments. The distance between the clay surface and sampling points were 4 cm, 10.2 cm, and 16.2 cm, in order of decreasing height.

The data indicates that the surface (4 cm) solids content has the lowest value and that there is no significant difference between the middle (10.2 cm) and bottom (16.2 cm) layers. The low solids content in the upper layer might due to the incomplete decant of the supernatant water, which may have remained in the clay structure. Thus, it could be speculated that the solids content is uniform with respect to height.

In the semi-continuous flow experiment, the average initial solids contents were 10.74 wt% and 10.56 wt%, corresponding to the experiments with and without electric field. Final solids content was evaluated by sampling different spots along the horizontal flow direction. The sample locations and results are represented in Figure 3-15. The gray box represents the experimental tank, and the blue cylinders inserted into the box denote the sampling locations and the shape of sampling area. They are marked with the solids content of the final of measurements.

The average solids content with an applied potential was 15.08 wt%, which corresponds to a change in solids content of 4.34 wt%. The result from the constitutive relationship (Equation 2-8) suggested that $\Delta w_{max} = 16.5$ wt% (Changes of solids content) should be achieved when the system reaches steady-state. Thus, the change of solids content from semi-continuous flow system was lower than expected on the basis of the relationship developed from bench-top experiment.

The data shows that the solids content decreases from 16.96 wt% to 13.70 wt% along the flow direction. This result can be explained by the shape of the thickened clay. Because of the inclined surface formed during the accumulation process, water tended to flow to lower levels. Thus, the effluent part of the tank maintained more water both in the bulk and on the surface. As we did not wait a sufficiently long time to decant the surface water thoroughly, this upper portion appeared to have a lower solids content. However, another issue affecting the solids content on the influent side is the evaporation effect from the exposed part of clay. With the boundary line moving from right to left, more and more surface clay was exposed to evaporation. This affected the clay surface up to the mid-point, as this is the final position of the boundary layer. A future experiment that would avoid this evaporation effect was proposed.

The average final solids content in the control experiment was 13.47 wt%, corresponding to a change in solids content of 2.91 wt%. The solids content displayed no obvious relationship with horizontal positions. This observation was consistent with the result from the experiment with applied potential. Because almost the entire clay surface was exposed to the air, surface water could be distributed evenly everywhere.

Thus, the separation results showed that the changes of solids content achieved by the electrokinetic dewatering process was larger than the gravity-only process but smaller than what is expected according to the constitutive relationship.

Supernatant water

One of the purposes for developing the phosphatic clay dewatering technique is to recycle water, which makes it valuable to examine the quality of supernatant water.

As shown in Figure 3-16, water in the first beaker was collected at the very beginning of the separation process in the experiment with an applied potential. It contained a lot of solids and appeared very turbid. The second beaker contained water collected from the first day. It was less turbid but still had some clay particles accumulated at the bottom of beaker. The third beaker contained the water collected after the first day and it was very clear and transparent. Water in the fourth beaker was collected from the control experiment; it was transparent but light brown in color. From the external appearance of these beakers of water, one may see that the supernatant water became clearer with increasing settling time. Furthermore, the supernatant water from experiments both with and without an applied potential achieved transparency after a sufficient length of time. From the comparison, it is apparent that water removed by an electric field has a higher quality than water from normal gravity settling.

The turbidity values of supernatant water samples were measured and listed in Table 3-2. Two measurements were taken for each sample, the supernatant and the stirred value. The former represented the turbidity after a long settlement time, and the latter represented the turbidity right after sampling. For the experiment with an applied potential, the turbidity decreased with increasing time, which is in consistent with the visual inspection. Results from samples C and D indicate the two methods achieved similar supernatant water turbidity, but the latter had a slightly lower turbidity level.

Table 3-1. List of solids content in different height of clay suspensions.

Length measured from top surface /cm	Solids content near effluent /wt%	Solids content in middle /wt%	Solids content near influent /wt%
4	14.07	13.69	12.29
10.2	15.72	14.98	14.80
16.2	15.26	14.85	15.72

Table 3-2. List of turbidity of different supernatant water samples.

Sample	Supernatant water turbidity/NTU	Stirred water turbidity/NTU
A	44	6635
B	12.2	5170
C	0.460	7.55
D	0.434	3.67

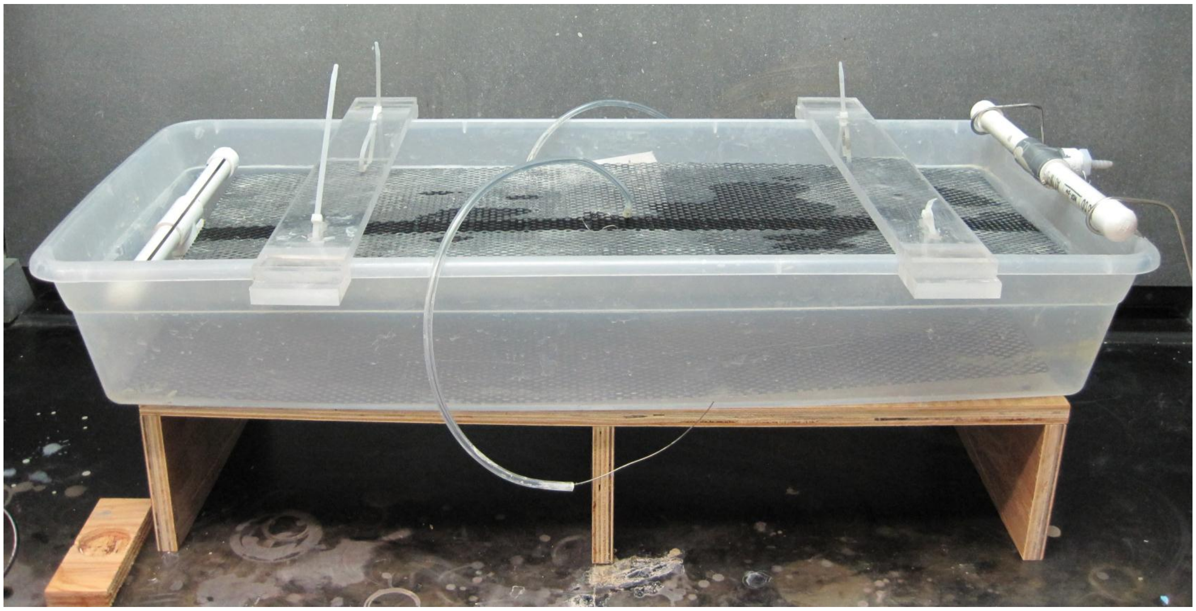
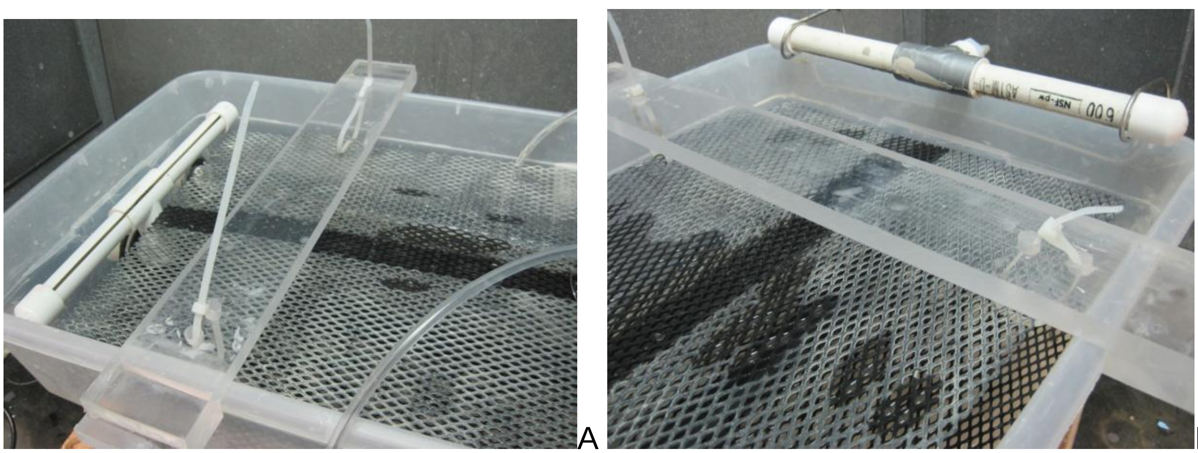


Figure 3-1. Large scale semi-continuous flow system.



A B

Figure 3-2. Top view of large scale semi-continuous flow tank. A) Detail structure of effluent. B) Detail structure of Influent.

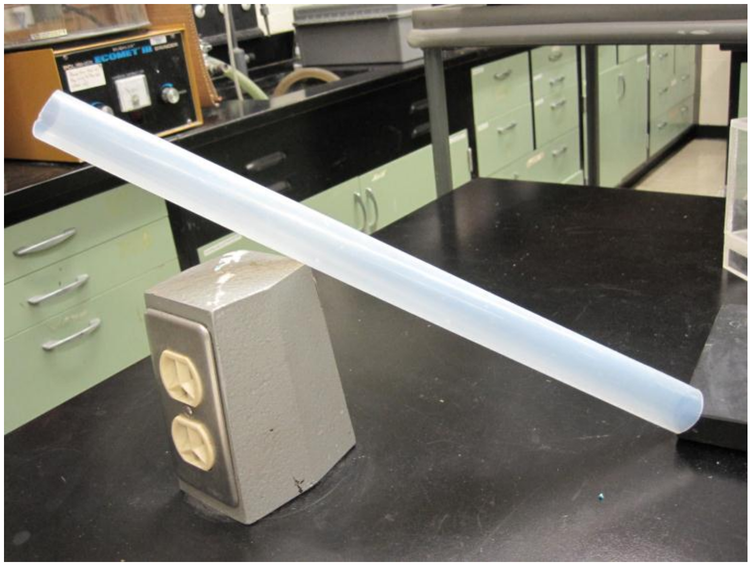


Figure 3-3. Plastic cylinder used for sample collection.

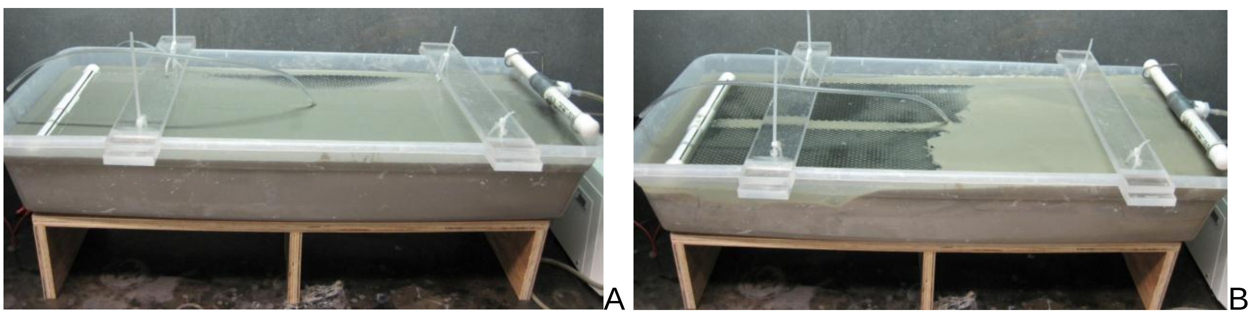


Figure 3-4. Settling tank before and after separation with an applied potential. A) Initial clay suspensions with solids content of 11.85 wt%. B) After separation, with solids content of 19.55 wt%.

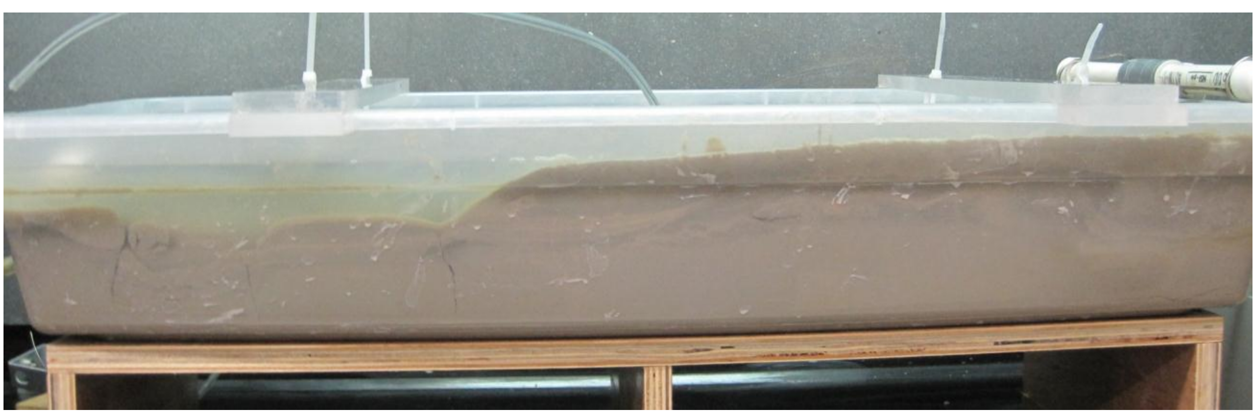


Figure 3-5. Side view of tank after electrokinetic separation (10 V, 18 hours).

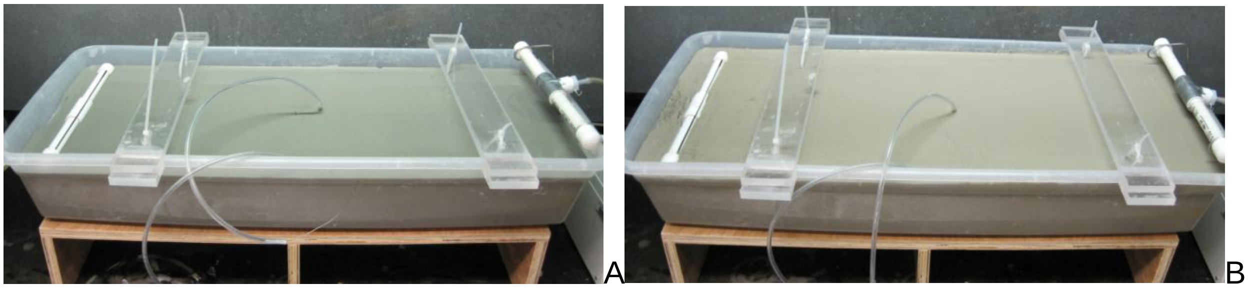


Figure 3-6. Settling tank before and after separation without potential applied. A) Initial clay suspensions with solids content of 11.72 wt%. B) After separation, with solids content of 14.34 wt%.

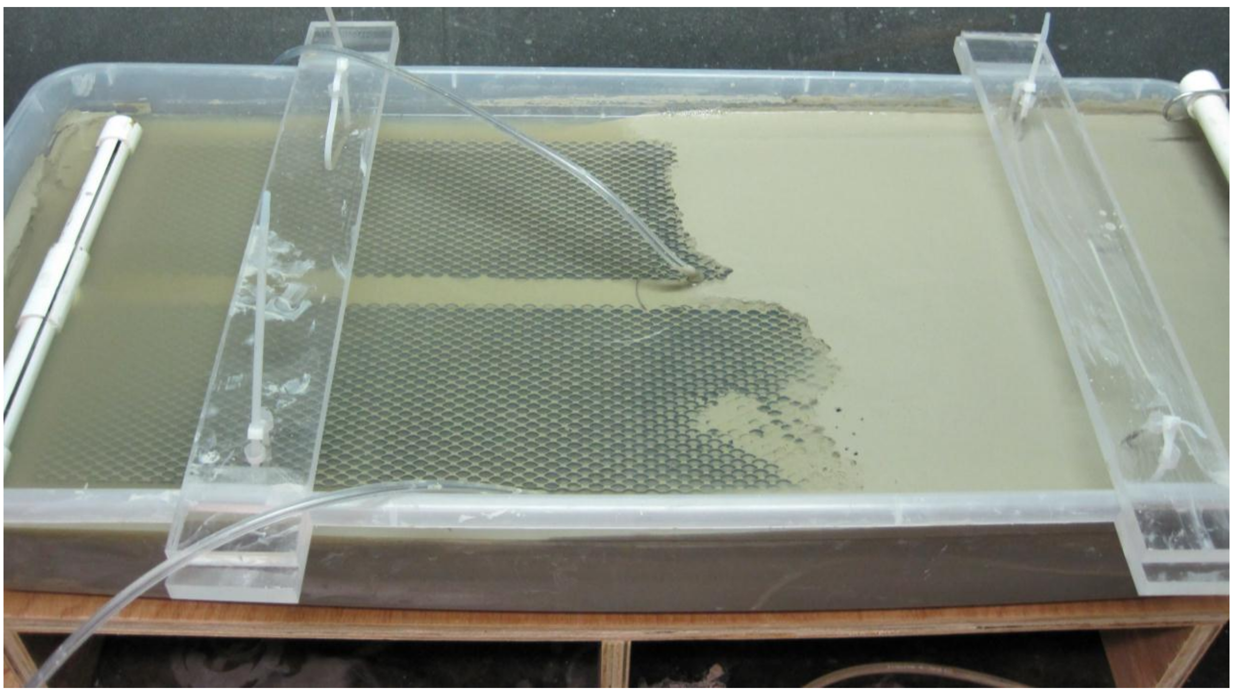


Figure 3-7. Separation result after potential influenced on gravity thickened clay suspensions.

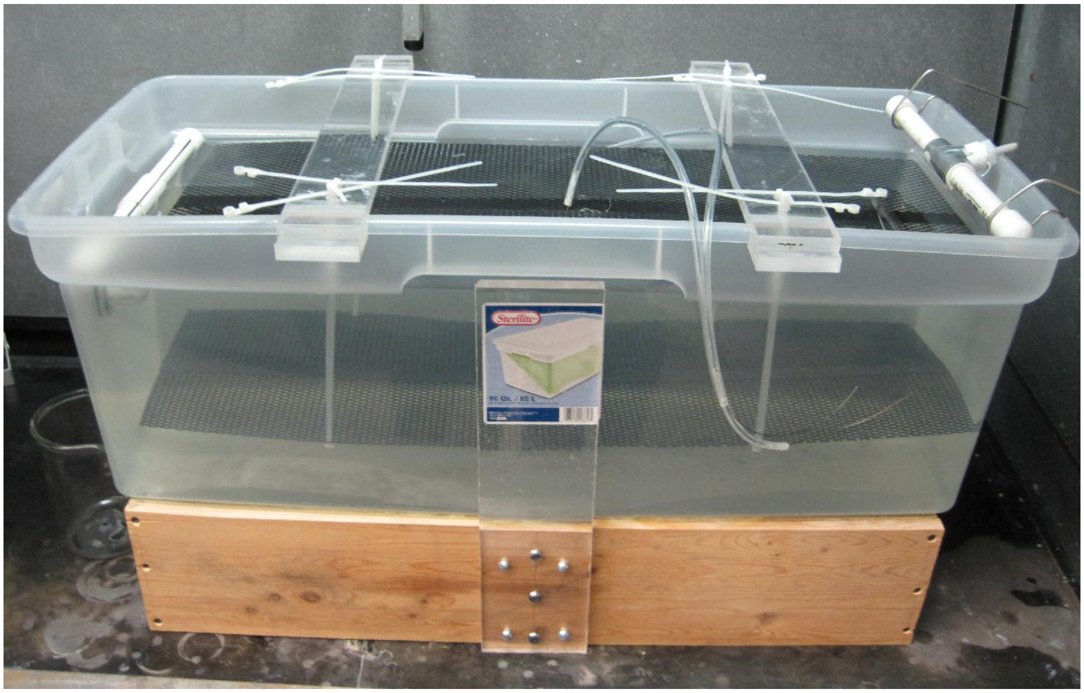


Figure 3-8. Electrode configuration in deep tank semi-continuous flow system.

Figure 3-9. External appearance of whole system in operation.

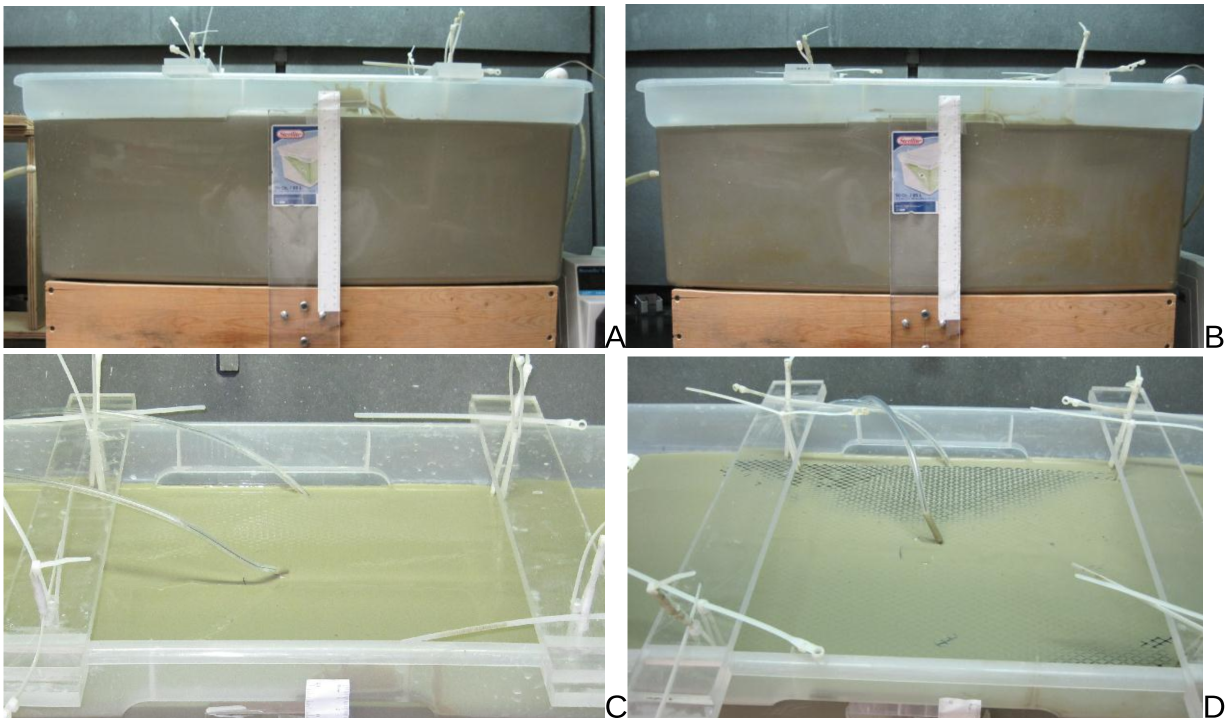


Figure 3-10. Initial clay suspensions at t=0. A) Side view with potential. B) Side view without potential. C) Top view with potential. D) Top view without potential.

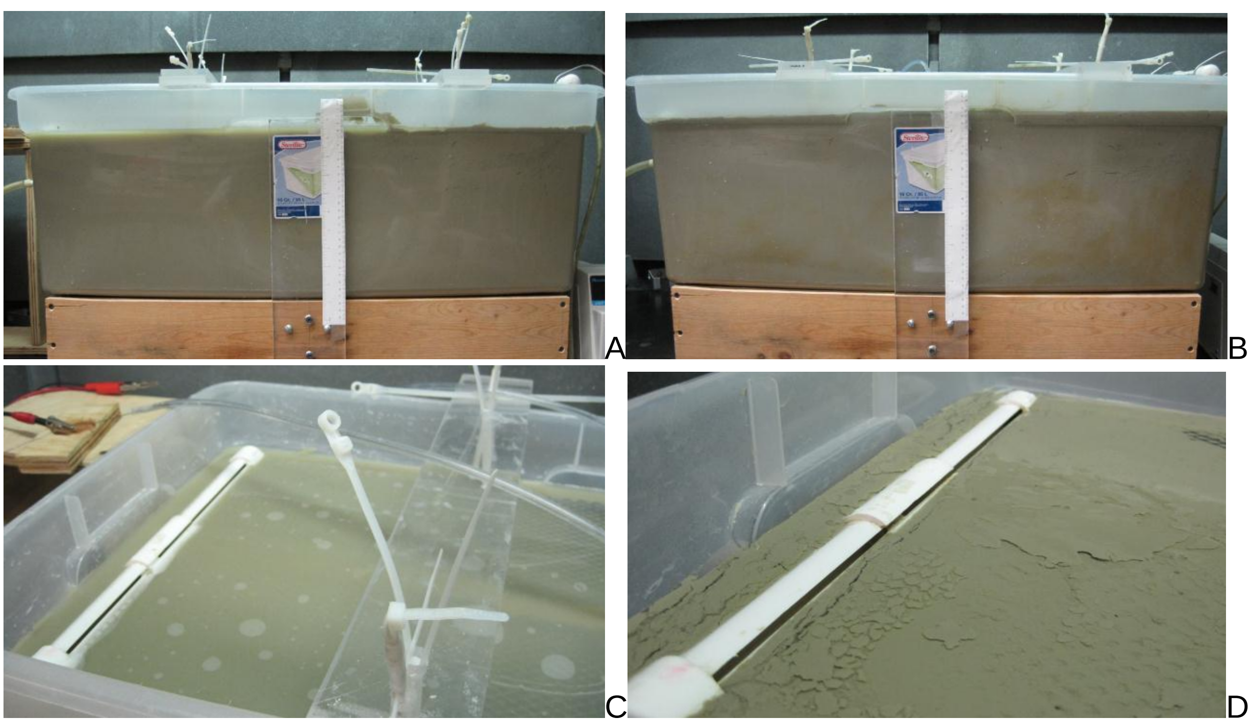


Figure 3-11. Separation after t=5 hours. A) Side view with potential. B) Side view without potential. C) Top view with potential. D) Top view without potential.

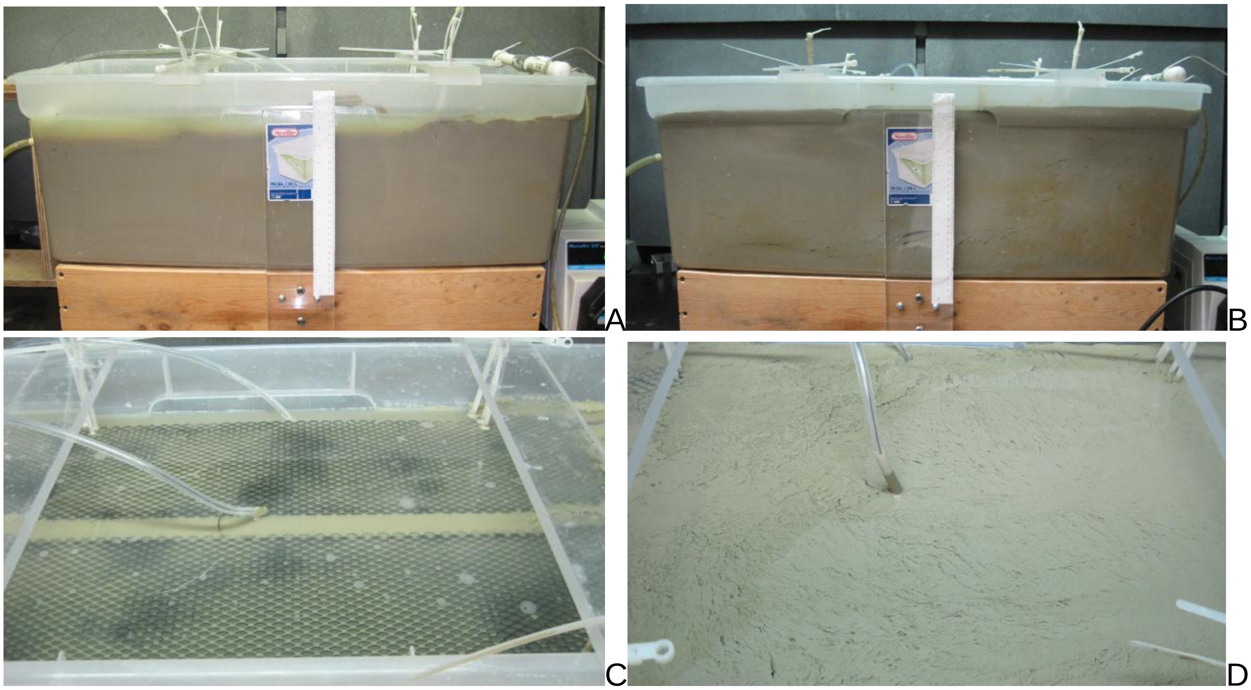


Figure 3-12. Separation after t=11 hours. A) Side view with potential. B) Side view without potential. C) Top view with potential. D) Top view without potential.

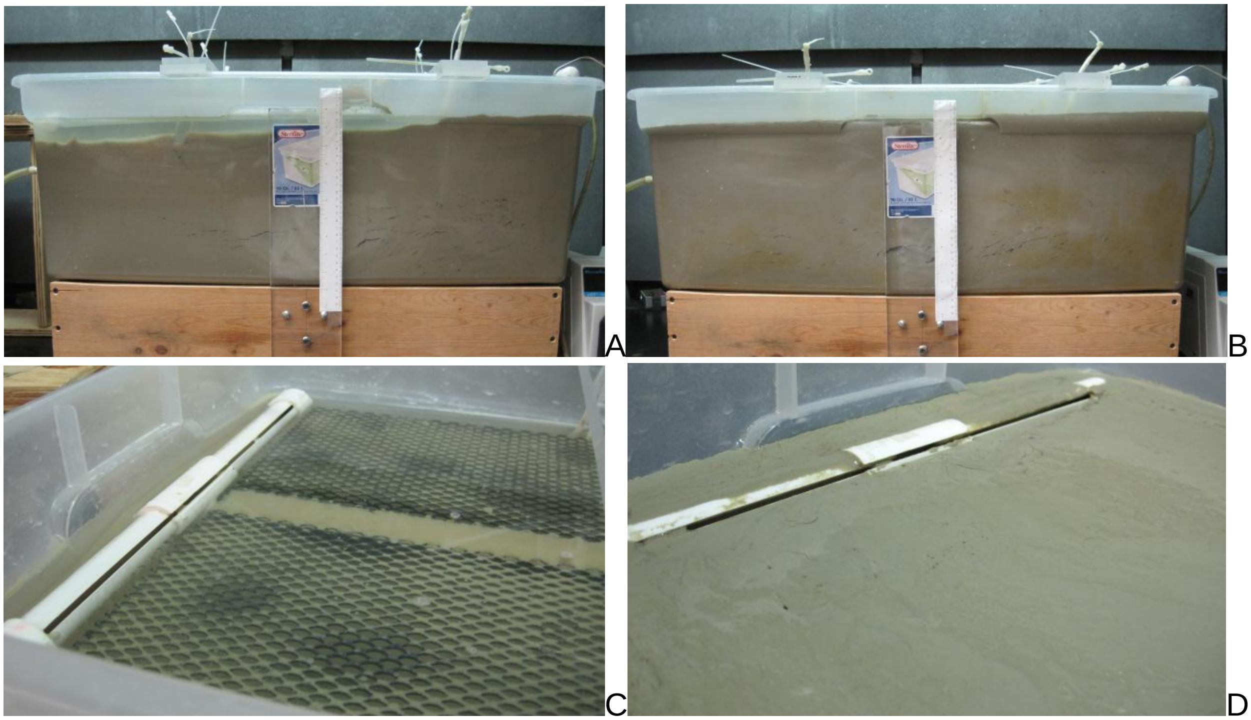


Figure 3-13. Separation after t=19 hours. A) Side view with potential. B) Side view without potential. C) Top view with potential. D) Top view without potential.

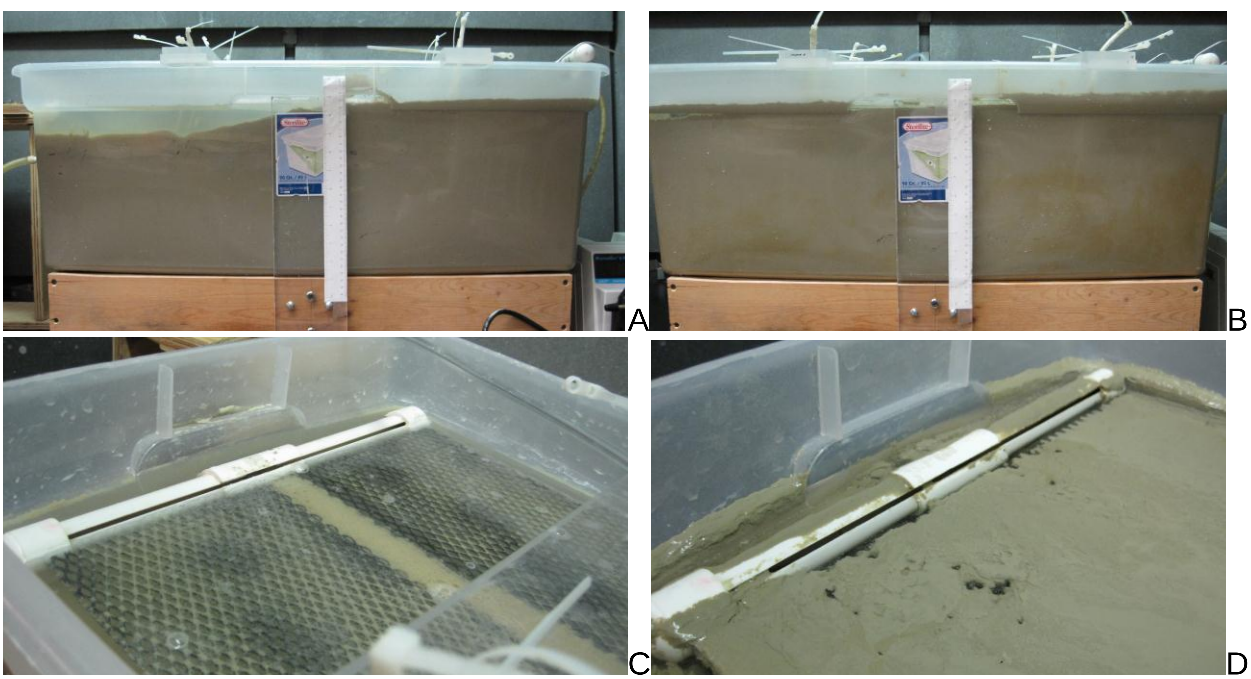


Figure 3-14. Clay suspensions at the end of the experiment. A) Side view with potential. B) Side view without potential. C) Top view with potential. D) Top view without potential.

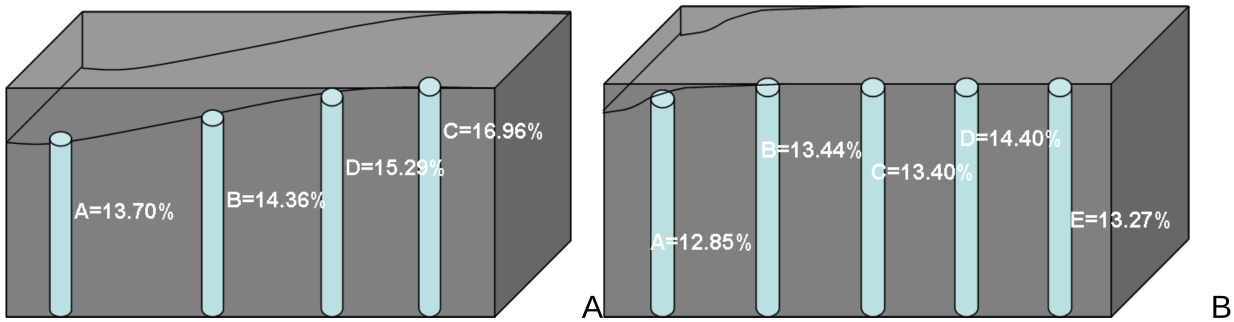


Figure 3-15. Calculation results of solids content after separation. A) With potential. B) Without potential.

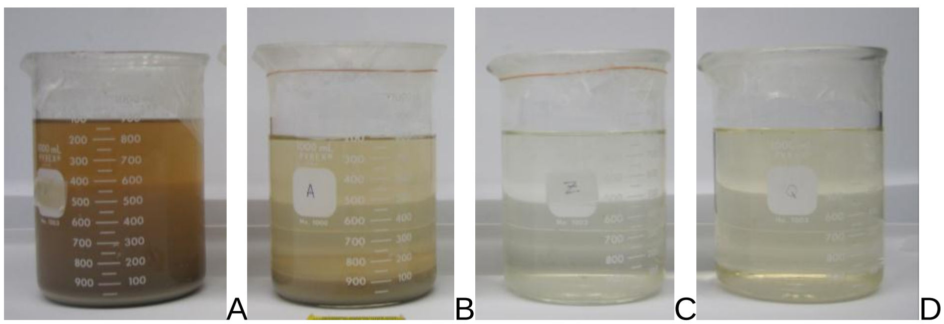


Figure 3-16. Supernatant water collected from different experiments. A) Water from the beginning of separation, with electric field. B) Water from the first day of separation, with electric field. C) Water after the first day, with electric field. D) Water from the blank experiment, without electric field.

CHAPTER 4
APPLICATION OF ELECTROKINETIC SEPARATION TO CONTINUOUS OPERATIONS

Now that we have demonstrated the feasibility of applying an electric field to improve the dewatering efficiency in a larger scale experiment, we shall now discuss the possibility of using electrokinetic separation in continuous flow operations. This discussion is based on the existing instruments used in continuous dewatering; namely, the horizontal flow thickener, vertical flow thickener, and inclined surface thickener.

Horizontal Flow Thickener

To apply electrokinetic dewatering in a horizontal flow thickener, designs similar to the bench top experiments were considered.. Specifically, two ways to add electrodes have been studied. In the first one, an anode is placed at the bottom of the tank and a cathode is positioned at the top surface (Figure 4-1A). In this design there is very limited space in which to set the surface electrode. It is necessary to be extremely careful to avoid the existing devices in the tank such as the center shaft and influent baffle. This structure is actually very similar to an enlarged lab scale experiment. However, because of the scale of the thickener, the distance between two electrodes might be very large, and the electric field between them will be too great to meet power consumption specifications. Thus, a modified design is considered. As shown in Figure 4-1B, the position of the anode is raised to a certain height while the cathode remains at the original position. In this manner, the power cost is significantly reduced. The raw slurry influent will settle down under the effect of both gravity and electric field in the first stage, and accumulate only by gravity after it has passed anode. With this method, we can take advantages of the electric field and avoid wasting energy as much as possible.

If the efficiency of this process could be verified in future experiments, it is likely that this would become an attractive alternative to replace currently used designs.

Vertical Flow Thickener

Although the vertical flow thickener seems very similar to the horizontal flow thickener in shape, it is much harder to design electrode configurations on it. Because of the special mechanisms of vertical flow thickeners, separation efficiency is not determined by gravity alone. Instead, multiple settling conditions should be considered. Obviously it is not proper to simply set the electrodes on vertical flow thickeners the same way as in horizontal flow thickeners. If electrodes are placed above the sludge blanket layer, this method itself becomes meaningless because most solids are locked in the previous process, and not too much effort need be expended at the upper layer. If the electrodes are moved to a slightly lower position, with the cathode remaining above the sludge blanket layer and the anode below it, the existing subtle balance in this complex situation might be broken and a negative effect would appear. Thus, this kind of thickener is not easily modified with an electric field based on our current knowledge.

Inclined Surface Thickener

One reasonable method for introducing electrodes into an inclined surface thickener is to place the electrodes horizontally with the cathode at the top and the anode at the bottom. The selection of different plate materials is worth discussing here. If a conductive material is used (Figure 4-2A), polarization of the plates will occur. This will result in a diminished potential along a segment of the inclined plates and create a free falling zone. This effect will decrease the efficiency of the electrode plates. To avoid this negative effect, non-conductive materials should be considered.

If a non-conductive material is used (Figure 4-2B), the electric field lines will be oriented parallel to the inclined plates. The component of the electric field that is parallel to gravity will act in the same direction as the natural deposition of the solids. The perpendicular component of the electric field will oppose the flow direction of the sludge. This opposition to the flow will delay the settling of the solids, allowing for more time before the sludge reaches the outlet area, which is the result we are seeking for. Thus, if one wishes to upgrade the inclined surface thickener by placing electrodes at the top and bottom, a non-conductive plate material would be a better choice.

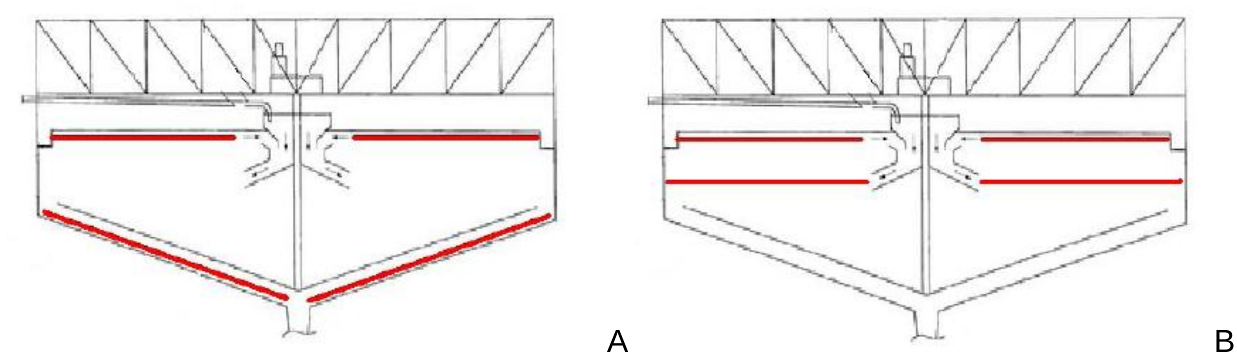


Figure 4-1. Different arrangement of electrodes in horizontal flow thickener. A) Top-cathode and bottom-anode. B) Top-cathode and suspended anode.

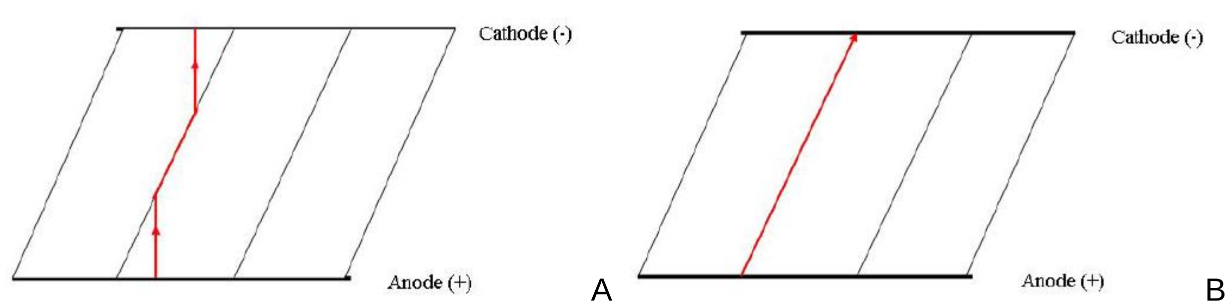


Figure 4-2. Electric field between electrodes when plates are made from different materials. A) Conductive plates. B) Nonconductive plates.

CHAPTER 5
CONCLUSIONS AND FUTURE WORK

Motivated by the success of earlier bench-top electrokinetic dewatering experiments and guided by the constitutive relationship developed therein, we have designed and performed a larger scale electrokinetic dewatering experiment, thus establishing a proof of concept for this technique. As compared to gravity settling, the separation process with a 10 V applied potential was much faster and more efficient. The final solids content with potential was higher than that of the blank experiment. The advantage of the electric field can also be demonstrated by the good clarity of the supernatant water. The water collected from the electrokinetic dewatering process was much clearer after a period of settlement.

Several designs for improving the existing continuous separation instruments with electrokinetic separation were considered. These include several different electrode configurations in the horizontal flow thickener, vertical flow thickener, and inclined surface thickener. The feasibility of these ideas needs to be verified by further efforts.

One of the future studies to be conducted is to apply the bench-top experiment constitutive relationship to the results of the larger scale semi-continuous system. The parameters affecting the dewatering behavior will be estimated by semi-continuous flow experiment results. The residence time will be defined and the time required to reach steady-state will be calculated using the constitutive relationship.

A second future effort involves construction of the equipment proposed for electrokinetic dewatering in continuous flow systems.

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BIOGRAPHICAL SKETCH

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