A constitutive relationship for electrokinetic dewatering of phosphatic clay slurries

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Abstract

Benchtop experiments were performed, in which an electric field was used to enhance separation of water from phosphatic clay suspensions from a central Florida mine. A constitutive relationship was established that relates the increase in solids content to operating time and the applied electric field. An upper limit to the degree of separation was found to be a function of electric field, and the time required to achieve this limiting value was also a function of electric field. The energy requirement for removal of water ranged from 1.25 to 175 Wh/kg water removed as a function of the electric field. A mathematical model was developed that provided good agreement to the experimental values and served to validate the constitutive relationship.

Key words: Electrokinetic separation, Dewatering, Clay settling areas (CSAs), Phosphate mining

Introduction

Solid-liquid separation represents a significant problem for the phosphate mining industry. A dilute suspension of phosphatic clays is a waste product of the phosphate ore beneficiation (mineral processing). The suspensions, containing initially 3-5 wt% solids, are pumped to large impoundment areas termed clay settling areas (CSAs) (Carrier, 2001). Addition of flocculating agents causes a rapid but partial separation, resulting in a suspension containing roughly 10 wt% solids. Further increase in solids content, however, proceeds very slowly. Hindered settling and self-consolidation of clay requires as much as 25 years to reach a solids content of 40 wt%. In central Florida, CSAs cover over 39 km^2 (150 mi^2), representing 30% of the mined land (Barnett, 2008). The search for enhanced solids-liquid separation is motivated by the need to reduce both the land area dedicated to the storage of phosphatic clay suspensions and the water consumed in the mining operation.

Because it does not require the addition of adulterants that could interfere with future recovery of residual phosphates, application of electrical fields has been proposed as an attractive method to enhance solid-liquid separation. Electrokinetic phenomena involve application of direct electrical current to induce movement of either charged particles or water in a solid matrix with charged surfaces (Newman and Thomas-Alyea, 2004). In dilute suspensions, the electric field induces the movement of particles, which is known as electrophoresis. Upon formation of a solid matrix, the electric field furthers the movement of water via electro-osmosis.

Studies have been reported in which water was removed from clays and other mine tailings through the application of an electric field. Shang and Lo (1997) reported the results of bench-top experiments in which the solids content of phosphate clay suspensions was increased from 13 to 29 wt% in 30 hours using an applied cell potential of 15 V with a distance of 25.4 cm separating the two electrodes. Ho and Chen (2001) reported an increase in solids content of bentonite clay from 9 to 25 wt% in four hours using an applied electric field of 6 V/cm in bench-top experiments with a rotating anode. In a much larger outdoor tank experiment, Fourie et al. (2007) reported an increase in solids content of mine tailings from 39 to 57 wt% under an applied electric field of 0.11 V/cm. Although the literature suggests electrokinetic methods can decrease the time required to remove water from dilute clay suspensions, a constitutive relationship relating the change in solids content with the electric field and operating time has not been established. Identification of this relationship is critical to scale-up and economic analysis of electrokinetic dewatering applications (McKinney and Orazem, 2010).

The objective of this work was to develop a constitutive relationship relating the change in solids content of clay suspensions to the applied electric field and operating time. While the results obtained apply for suspensions from a particular mining operation, the approach should be generally applicable elsewhere.

Experimental

A bench-top cell was built to perform the experiments. Clay slurry samples used for experiments were obtained from the Four Corners phosphate mine located in central Florida, owned and operated by Mosaic Fertilizer, LLC. Details are provided by McKinney (2010).

Cell design. A cylindrical Plexiglas cell, shown in Fig. 1, was used for the bench-top experiments. The design was adapted from the description of the experimental cell presented by Shang and Lo (1997), Shang (1997), and Lo (1995). The cell was 30 cm in length, with an inner diameter of 9 cm. The cell was oriented vertically, with the cathode placed at the top of the cell and the anode placed at the bottom. With this
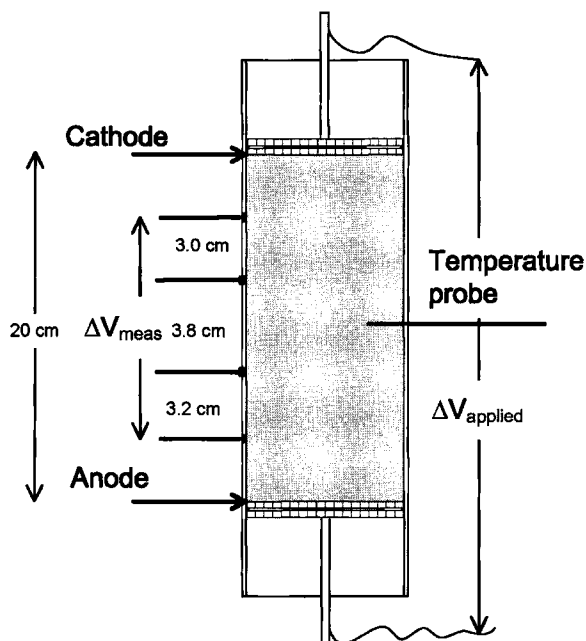
Figure 1 — Schematic representation of a bench-top cell. The darker shaded area within the cell represents the clay slurry loaded for a test.
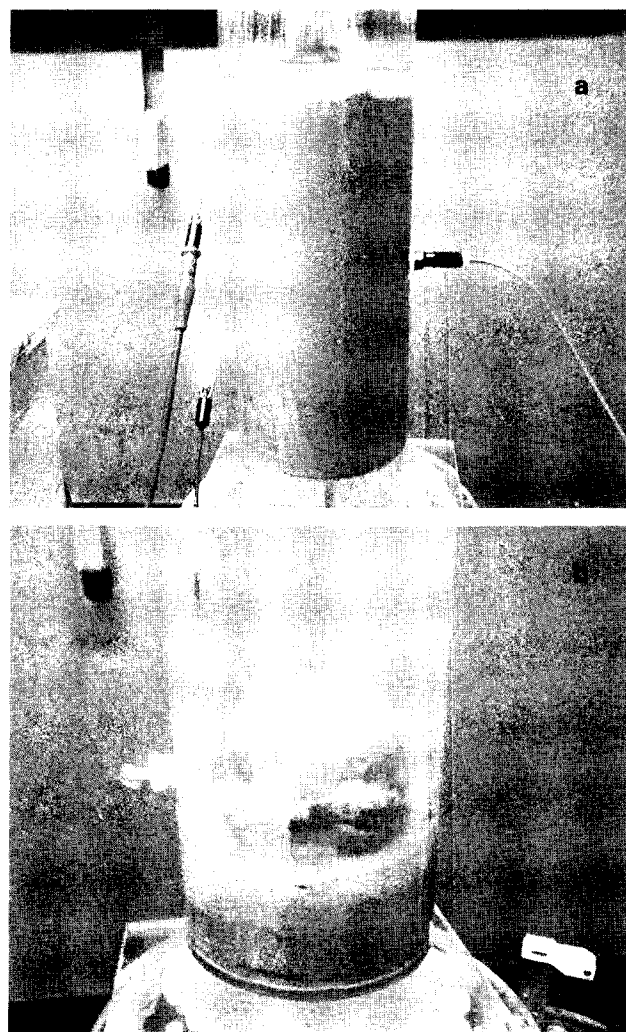

Figure 2 — Photographs of the bench-top test setup: a) before experiment begins, cylinder filled with a 9 wt% solids suspension, and b) after the experiment ended and supernatant water removed, the cell contained a thickened lump consisting of 33.5 wt% solids.

configuration, the electric field applied a downward force on the negatively charged clay particles towards the positively charged anode, while simultaneously attracting the water upwards to the cathode. Thus, the electric field enhanced gravity-driven settling of suspended particles. The parallel disk-shaped electrodes provided a uniform electric field along the radius of the cylinder. The influence of non-uniform electric fields is described separately (McKinney and Orazem, 2010).

Dimensionally stable mesh electrodes made of titanium with a ruthenium oxide coating (Siemens, Inc.) were used for both cathode and anode. The electrodes were machined and fit to work with movable plungers within the cell, which allowed the electrode gap to be adjusted as supernatant water was removed and settlement continued. All experiments began with an electrode gap of 19 or 20 cm. The cell included four Ag/AgCl reference electrodes (In Vivo Metric) to allow measurement of the local Ohmic potential drop. The Ohmic potential drop in the slurry was the dominant contributor to cell potential, as the electrocatalytic properties of the ruthenium oxide coating on the electrodes resulted in small surface overpotentials.

A temperature sensor was used to monitor the temperature during the course of the experiments. For smaller applied potentials, the temperature did not vary significantly during the course of the experiment. The temperature increased for larger applied potentials due to Ohmic resistive heating of the electrolyte. For the experiment shown in Fig. 2, the temperature increased from 23.3 to 73.1° C. Independent experiments conducted without an applied electric field showed that increased temperature did not enhance natural settling.

Instrumentation. The results were obtained using either a Solartron 1286 Electrochemical Interface or an EG&G Princeton Applied Research (PAR) Model 273A Potentiostat/ Galvanostat, under either potentiostatic or galvanostatic control. The potentiostat was operated using CorrWare software

(Scribner Associates, Inc.).

The duty cycle for the experiments included 30 minutes in which the potential was applied (on), followed by two minutes in which the potential was not applied (off). The use of on-off cycles, also implemented by Gopalakrishnan et al. (1996), was intended to allow intermittent relaxation of concentration and hydraulic gradients. No effort was made to optimize the duty cycle. Experiments operated for periods exceeding 12 hours were controlled to operate with the above on-off duty cycle for 12 hours followed by a 12-hour period in which potential was not applied. The time recorded for these experiments represents only the time in which the on-off duty cycle was applied. Upon completion of each dewatering experiment, the cell contents were removed. The clay samples were weighed, placed in an oven to dry completely, and re-weighed to determine the percent solids by weight.

Clay suspensions. The clay suspensions were analyzed by X-ray diffraction and measurements of particle size distribution, conductivity and zeta potentials. The X-ray diffraction patterns generated for the suspended solids revealed the presence of smectite, quartz and trace amounts of palygorskite. Suspensions with a high content of palygorskite tend not to respond well to
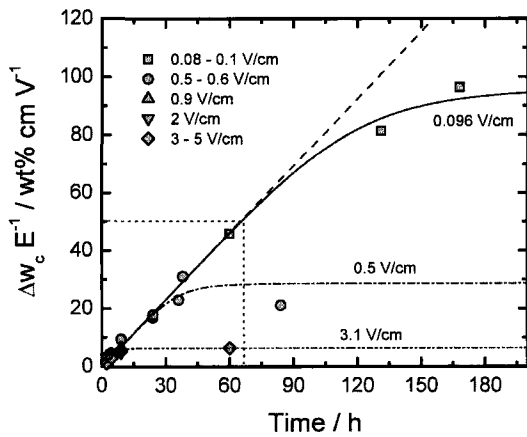
Figure 3 — Increase in solids content scaled by the applied electric field as a function of time, with applied electric field as a parameter. The lines correspond to the constitutive relationship given as Eq. (4). The box represents the range presented in Fig. 4a, and the filled diamond ♦ marks the data point corresponding to the experiment shown in Fig. 2.

electrokinetic treatment, due to palygorskite's small surface charge (Speil and Thompson, 1942; Reddy et al., 2006; Ho and Chen, 2001; Neaman and Singer, 2004). The particle size distribution results indicated that approximately 90% of the clay was finer than 60 microns in diameter and approximately 65% was finer than 2 microns in diameter. The conductivity of the clay suspensions was measured to be 700 μS/cm and the average zeta potential was -20 mV.

The clay slurries, obtained from the Four Corners phosphate mine, were sampled at a point in the process before the phosphatic clays were sent to the CSA. All samples used in these experiments included a proprietary anionic polymeric flocculant that was added to speed the formation of a roughly 10 wt% suspension. Additional *electrokinetic* experiments, performed with samples that were not dosed with the flocculant, but rather allowed to settle naturally to a 9 to 10 wt% solids content, yielded the same results as were obtained with the flocculant.

Results

Experimental results demonstrating proof of concept are presented in Fig. 2. The experiment was conducted for nine hours at an applied cell potential of 80 V. The Plexiglas cell loaded with the clay suspension before the electric field is applied is presented in Fig. 2a. The clay suspension initially contained 9 weight percent (wt%) solids. Upon completion of the experiment, a thickened clay mass was formed, as is shown in Fig. 2b. Supernatant water that formed above the lump was removed before the photograph was taken. The remaining thickened clay in Fig. 2b had a *solids content* of 33.5 wt%. The results presented in Fig. 2 provide a demonstration that application of an electric field can yield substantial solid-liquid separation for clay slurries from the Four Corners mine. In the absence of an electric field, it normally takes 25 years for the clay suspension to reach a solids content of 40 wt%.

Similar experiments were performed using different applied potentials. The results, presented as the change in solids content scaled by the applied electric field $\Delta w_c/E$ as a function of elapsed time, are given in Fig. 3. The solids content of the slurry in units of wt% is defined as
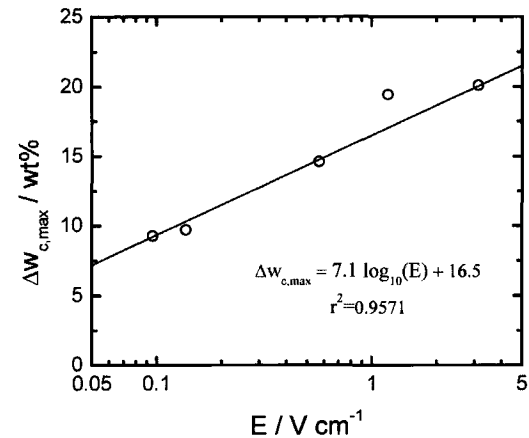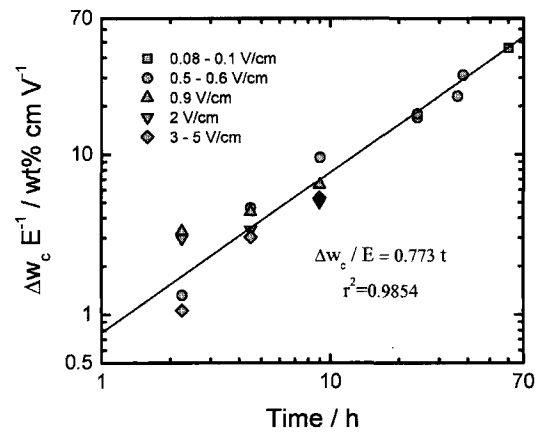

Figure 4 — Limiting behaviors for the data presented in Fig. 3: a) short time behavior for electric fields applied for less than 30 hours. The line is given by Eq. (2), and the filled diamond ♦ marks the data point corresponding to the experiment shown in Fig. 2. b) Maximum change in solids content plotted as a function of the electric field. The line is given by Eq. (3).

$$w_c = \frac{m_c}{m_c + m_w} 100\% \qquad (1)$$

where m_c is the mass of dry clay and m_w is the mass of water present. The change in solids content, Δw_c, is referenced to the initial composition, which was generally between 9 and 11 wt% solids.

Interpolation model

Two types of behavior are evident in Fig. 3. Initially, the increase in solids content scaled by the applied electric field was independent of the electric field strength. This behavior is shown in Fig. 4a. The scaled data follow

$$\frac{\Delta w_c}{E} = 0.77t \qquad (2)$$

where t is the elapsed time in hours and the electric field E is in units of V/cm. Equation (2) shows that, for electric fields applied for less than 30 hours, the time required to achieve a given solids content is inversely related to the applied electric field. The experiments performed for longer periods showed that, even when supernatant water was periodically removed, a limiting value for solids content was reached. The value of
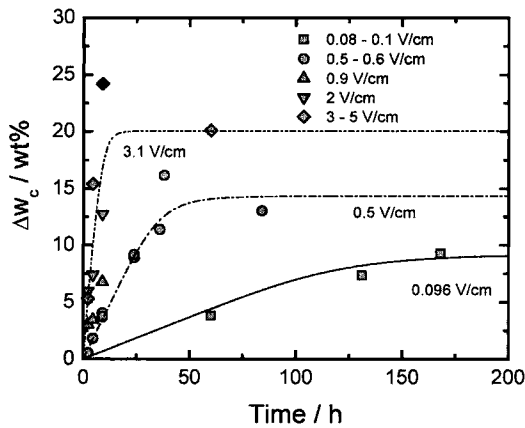
Figure 5 — Increase in solids content as a function of time with applied electric field as a parameter. The lines correspond to the constitutive relationship given as Eq. (4) and the filled diamond ◆ marks the data point corresponding to the experiment shown in Fig. 2.

Figure 6 — Increase in solids content calculated from Eq. (4) as a function of time, with applied electric field as a parameter.

the maximum solids content achievable was found to be a function of the applied electric field, as shown in Fig. 4b. A relationship between the maximum change in solids weight percent $\Delta w_{c,max}$ and the electric field was found to be

$$\Delta w_{c,max} = 7.11 \log_{10}(E) + 16.5 \tag{3}$$

where the electric field E is in units of V/cm.

An interpolation equation was developed to incorporate short and long-time behavior as

$$\Delta w_c = [(0.77tE)^{-n} + (7.1 \log_{10}(E) + 16.5)^{-n}]^{-1/n} \tag{4}$$

where n is a dimensionless parameter that controls the transition from short-time to long-time behavior, E has units of V/cm, and t has units of hours. The comparison of Eq. (4) for $n=5$ to the experimental data for three different applied electric fields are presented in the form of $\Delta w_c/E$ in Fig. 3 and as Δw_c in Fig. 5.

The agreement with experimental data suggests that the change in solids content can be predicted for a given electric field as a function of elapsed time. Equation (4) is presented in Fig. 6 with applied electric field as a parameter. The results indicate that at larger electric fields, the maximum separation is achieved in a shorter time. A time as short as 12 hours is sufficient to achieve maximum separation at an applied electric field of 1 V/cm.

Energy usage model

The energy requirement for water removal can be expressed as

$$E_{req} = \frac{V_{cell} It}{\Delta m_w} \tag{5}$$

where E_{req} is the energy required (in W-h/kg water removed), V_{cell} is the cell potential, I is the current and t is the operating time. The resulting values for a series of experiments are presented in Fig. 7 as a function of applied electric field. The range of experimental values presented in Fig. 7 is in agreement with energy requirements reported in the literature. From the raw numbers reported by Fourie et al. (2007), an energy requirement of 1.25 W-h/kg of water removed was calculated. Larue et al. (2006) reported 700 W-h/kg of water removed. The results presented in Fig. 7 indicate that the energy requirement and associated cost increase with increasing electric field strength.
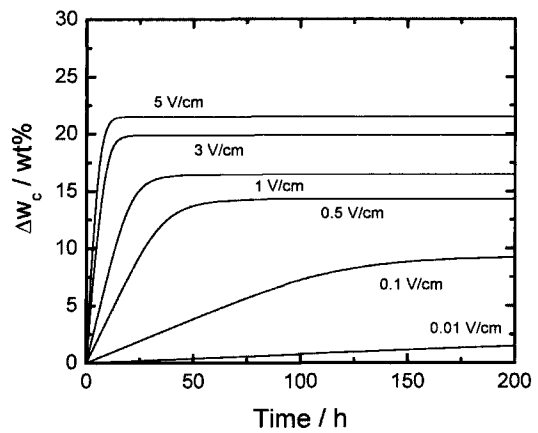
A relationship for the cell potential, V_{cell}, can be obtained by accounting for all the potential losses within the system as

$$V_{cell} = 1.23 + \eta_a - \eta_c - iR_e \tag{6}$$

where η_a is the overpotential at the anode, η_c is the overpotential at the cathode, R_e is the Ohmic resistance of the clay suspension and i is the superficial current density. The value of 1.23 V is the minimum potential required to promote the hydrolysis of water. At the anode, the Butler-Volmer equation provides a relationship between current density and surface overpotential η_a as (Newman and Thomas-Alyea, 2004)

$$i = i_o (\exp(b_{a,a} \eta_a) - \exp(-b_{a,c} \eta_a)) \tag{7}$$

where

$$b_{a,b} = \frac{\alpha_{a,a} F}{RT} \tag{8}$$

$$b_{a,c} = \frac{\alpha_{a,c} F}{RT} \tag{9}$$

and α is the apparent transfer coefficient for the respective reaction. The Butler-Volmer equation (given by Eq. 7) is written for a reversible reaction with both anodic and cathodic contributions. At large and positive overpotentials, the anodic contribution dominates and the cathodic contribution can be neglected. Thus, Eq. (7) becomes

$$i = i_o (\exp(b_{a,a} \eta_a)) \tag{10}$$

Conversely, when operating at large and negative overpotentials, the cathodic contribution dominates and the anodic contribution can be neglected. This allows Eq. (7) to be simplified to

$$i = -i_o \exp(-b_{a,c} \eta_a) \tag{11}$$

In the present case, due to the electrocatalytic properties of the electrode coating, the surface overpotential was very small. Thus, an iterative method was required. Equation (7) was rearranged to yield

$$\eta_{a,n+1} = \frac{\ln\left(\frac{i}{i_o} + \exp(-\eta_{a,n} b_{a,c})\right)}{b_{a,a}} \tag{12}$$

Parameter	Numerical value
ρ_e	1500 Ωcm
$b_{a,a}$, $b_{a,c}$, $b_{c,a}$, and $b_{c,c}$	19.5 V^{-1}
$a_{a,a}$, $a_{a,c}$, $a_{c,a}$ and $a_{c,c}$	0.5
i_o	1.0 mA/cm^2
A	63.6 cm^2
d	20 cm

Figure 8 — Energy requirement as a function of operating time with applied electric field as a parameter. The vertical lines correspond to the terminal time at which 95% of the maximum increase in solids content is achieved.
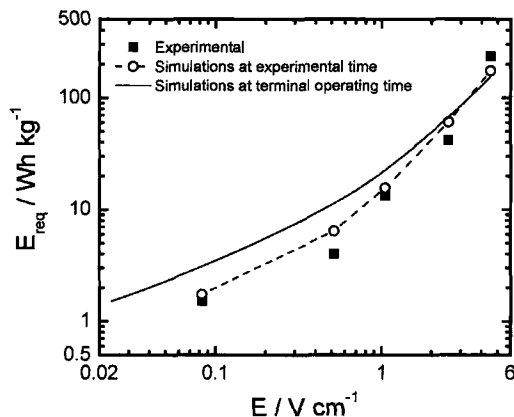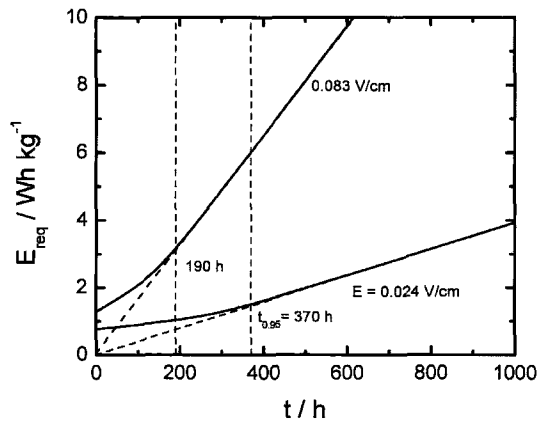

Figure 7 — Energy requirement given as a function of the electric field. Data presented includes experimental and modeled results.

where $\eta_{a,n}$ represents the initial guess for the anodic overpotential. The initial guess (at $n=0$) was obtained from the linear form of the Butler-Volmer equation, i.e.,

$$\eta_{a,0} = \frac{i}{i_o(b_{a,a} + b_{b,c})} \tag{13}$$

The linear form of the Butler-Volmer equation is valid only at very small overpotentials, where neither anodic or cathodic contributions can be completely neglected. A spreadsheet program was used to perform iterative calculations until the updated values of $\eta_{a,n+1}$ no longer changed and the solution could be considered converged. A similar iterative method was used to determine the cathodic overpotential η_c, used in

$$i = i_o (\exp(b_{c,a}\,\eta_c) - \exp(-b_{c,c}\,\eta_c)) \tag{14}$$

The Ohmic resistance of the electrolyte used in Eq. (6) can be expressed as

$$R_c = \frac{\rho_e A_c}{d} \tag{15}$$

where ρ_e is the electrolyte resistivity, A_c represents the cross-sectional area of the cell, which corresponds to the nominal area of both the anode and cathode, and d represents the distance between the electrodes.

The parameters used for the electrochemical model are given in Table 1. The electrolyte resistivity was obtained from independent impedance spectroscopy measurements and the kinetic parameters were obtained from Conway (1969). The simulation results were not strongly affected by the kinetic terms, because the dominant term was the electrolyte or Ohmic resistance.

The solution of Eqs. (6), (7), (14) and (15) provides a relationship between cell potential and current. Equation (4) provides the amount of water removed for application of an electric field over a specified period of time. The model was used to simulate the data presented in Fig. 7, and the results are presented as open circles. The corresponding numerical values are presented in Table 2. These value have good agreement with the experimental values. The agreement of the model with the experimental data suggests that the constitutive relationship given as Eq. (4) can be used in combination with electrochemical relationships to predict energy requirements. This agreement also validates the use of the constitutive relationship to characterize the bench-top experiment.

The calculated energy requirement for two applied electric fields is presented in Fig. 8 as a function of elapsed time. As indicated by Eq. (4), an upper limit was found for the change in solids content at a given electric field. The time to achieve a given fraction b of this upper limit is a function of electric field and is given by

$$t_b = \frac{\Delta w_{c,max}}{0.77E}\left(\frac{b^5}{1-b^5}\right)^{1/5} \tag{16}$$

Table 2 — Results of calculations used to model the energy requirements presented in Fig. 7.

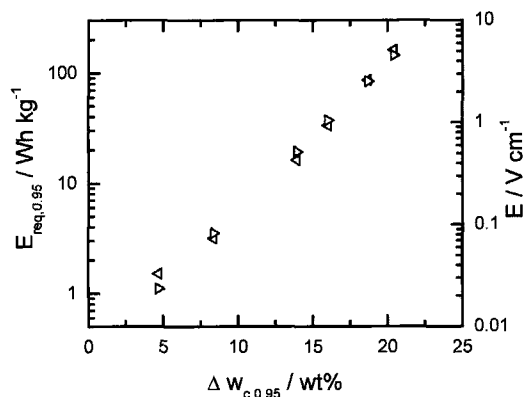| E, V/cm	$V_{cell}I$, W	Δm_w, kg	t / h	E_{req}, Wh/kg
0.08	0.01	0.34	60	1.7
0.52	0.24	0.34	9	6.4
1.05	0.95	0.54	9	15.7
2.54	5.34	0.79	9	60.6
4.54	16.9	0.87	9	174.8

Figure 9 — Required energy and associated electric field at which 95% of the maximum increase in solids content is achieved as a function of change in solids content. The apex of the symbols points toward the respective axis.

Figure 10 — Calculated value of terminal time, at which 95% of the maximum water removal is achieved, as a function of applied electric field. The symbols represent the operating time for the experiments reported in Fig. 7.

The time required to achieve 95% of the maximum change in solids content is indicated in Fig. 8 as a terminal time $t_{0.95}$. For $t > t_{0.95}$, the application of electric field increases the numerator in Eq. (5), but has no impact on the denominator.

The energy required to achieve 95% of the maximum increase in solids content is presented in Fig. 9 as a function of corresponding change in solids content. The corresponding electric field is also presented in Fig. 9. The apex of the symbols points toward the respective axis. The energy requirement, and the corresponding electric field, increase roughly exponentially with the increased change in solids content.

The terminal time is compared in Fig. 10 to the operating time for the experiments reported in Fig. 7. The corresponding energy requirement, shown as the solid line in Fig. 7, shows a boundary for the effective application of electrical current. Application of an electric field for time greater than $t_{0.95}$ will increase the value of E_{req} without increasing the amount of water removed.

Conclusions

The benchtop experiments showed that an electric field can enhance separation of water from phosphatic clay suspensions from a central Florida mine. A proof-of-concept bench-top experiment, performed at a cell potential of 80 V (or 4 V/cm), showed that in nine hours the solids content approached 35 wt%. A series of experiments were conducted to show that, at short operating times, the increase in solids content was proportional to the product of the electric field and the time over which the field was applied. A maximum solids content was reached at longer operation times. This maximum was a strong function of the electric field. The time required to achieve this limiting value was also a function of the field. The energy requirement for removal of water ranged from 1.25 to 175 Wh/kg water removed as a function of the electric field.

A constitutive relationship was established that relates the increase in solids content to operating time and the applied electric field. Such relationships are required for economic evaluation of electrokinetic dewatering operations (McKinney and Orazem, 2010). A mathematical model was developed which provided good agreement with the experimental values and validated the constitutive relationship.
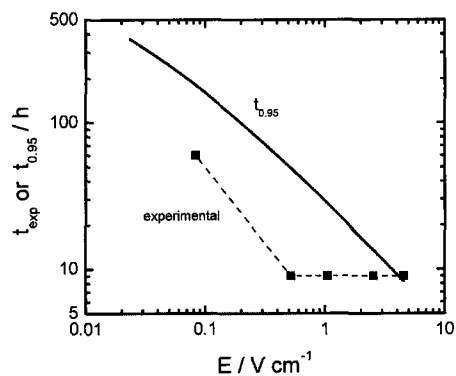
Work is needed to explore how the relationship, developed for a 9-11 wt% initial solids content, would need to be modified for suspensions with smaller values of initial solids content. It is anticipated that suspensions with higher values of initial solids content could be treated as starting at a point $t > 0$ along the solids content – time trajectories presented in Fig. 5.

Acknowledgments

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