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Semi-Continuous Electrokinetic Dewatering of Phosphatic Clay Suspensions

Rui Kong, Mark E. Orazem*

Department of Chemical Engineering, University of Florida, Gainesville, FL, 32611, USA

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ABSTRACT

A semi-continuous electrokinetic dewatering process, representing an intermediate step in development of a technology for continuous electrokinetic dewatering of phosphatic clay suspensions, was designed and evaluated through measurement of supernatant turbidity, pH, and changes in solids content. The influence of feed flow rate, electric field, and electrode separation was evaluated. The results showed that low-turbidity water can be separated from a clay solids suspension by a combination of electrokinetic dewatering and free settling. This work also suggests that separation can be enhanced at larger electric fields and that optimized separation may be achieved at a residence time of 11 h for this specific configuration. The energy requirement for this operation was shown to be consistent with previously published results for batch operation. The results provide guidance for the on-going development of a device for fully-continuous electrokinetic dewatering of phosphatic clay suspensions.

1. Introduction

Phosphate-deposits, containing carbonate-fluorapatite (francolite), quartz, dolomite, and clay minerals [1] are the primary source of phosphoric acid, which is an intermediate in production of phosphate fertilizers. Phosphate ores are mined in seven locations in Florida that represented 65% of domestic production in 2011 [2]. The phosphate mining operation in Florida is a strip-mining process. Draglines are used to remove the 15–50 feet (4–15 m) of top layer of earth (referred to as overburden) to expose the desired matrix layer that has a thickness extending 10–20 feet (3–6 m). The phosphate matrix is comprised of roughly equal mass fractions of phosphate ore, sand, and clay [3]. During the beneficiation process, phosphate rock is separated from sand and clay, and sent to processing plant to produce a final phosphate product. Sand is returned to fill mine pits for land reclamation. The phosphatic clay suspension, which has an initial solids content of 2–3 wt%, is pumped to large retention ponds and allowed to settle. The phosphatic clay suspensions represent a major waste product of the Florida phosphate mining industry [4], which raises environmental concerns for phosphate mining companies. Under gravity, the clay settling and consolidation process requires decades to reach a solids content of 20–25 wt% for which reclamation becomes possible. These clay settling areas currently cover an area of over 100,000 acres in Florida, which is approximately 30% of the mined land [5].

Numerous methods have been attempted in the search for a better clay dewatering process. Major methods include flocculation and mechanical dewatering. Addition of polymer Flocculants [6–8] is most widely used in the mining industry to achieve a 10 wt% solids content starting from 3 wt%. Flocculants such as polyethylene oxide and polyacrylamide are added to the suspension to induce the small clay particles to coagulate, thus forming larger clusters that can settle more easily. Another common method is to employ mechanical dewatering such as filtration/compression [9,10] and centrifugation [10,11] to facilitate dewatering. It is not easy to achieve sufficient low water content with this method as only free water can be removed with mechanical force. Therefore, the mechanical method is often combined with other methods to achieve better separation [12,13].

Electrokinetic concepts have been widely used in the field of soil and water treatment. Electokinetic remediation was used to extract heavy metal such as Zn, Ni [14], copper, chromium, and arsenic [15] from contaminated soil. It was also used to enhance the delivering of bioremediation additives for remediation of low-permeability clay contaminated by chlorinated solvents [16]. Johnson and Davis conducted electrophoretic clarification on colloidal suspensions of coal-washing effluent [17]. They studied the electrokinetic clarification of effluent from a coal-washing facility. They designed the apparatus which is capable of running either batch or

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* Corresponding author.
E-mail address: meo@che.ufl.edu (M.E. Orazem).

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semi-continuous operation [18]. They also developed the mathematical analysis on the motion of charged particle in suspension and the conductivity of the suspension, using the Navier-Stokes equation and solved with finite-difference method [19].

The exploration of clay dewatering by electrokinetic phenomena began in the 1940s [20]. Shang used a bench-top electrokinetic cell to evaluate the electrokinetic dewatering of three natural clay slurries [21]. Electrokinetic dewatering relies on the negative surface charge of clay particle that causes it to move in the presence of an electric field. The process includes electrophoresis and electro-osmosis, representing the movement of particles and the flow of water in porous media, respectively. The electrokinetic process is influenced by both internal and external factors. The internal factors are associated with materials properties such as grain size, mineral type, salinity, pH, and hydraulic permeability. The external factors are operation parameters including current density, electrode materials, and electrode configuration [22]. Thus, proper design could improve the electrokinetic dewatering efficiency by optimizing the operation parameters.

Various designs have been attempted to optimize the process by modifying the external factors, such as rotating anode [23], electrokinetic belt filter press [12,24,25], electrokinetic bag [26], and in-situ electrokinetic consolidation [27]. Despite these attempts, process equipment based on electrokinetics have not made the transition from lab scale prototype to on-site industrial application due, in part, to the high energy requirement which makes it economically unfeasible.

Previous lab-scale batch experiments described by McKinney and Orazem [28] demonstrated the effects of electrokinetic dewatering. Under the electric field, the feed suspension could be separated into a water-rich phase and a solids-rich phase. A constitutive relationship was identified that related the increase of the solids content of the solids-rich phase to elapsed time and applied electric field. The solids content increased with an increasing operation time and electric field in a short period, and only depended on electric field at longer times. An economic analysis, performed using boundary-element calculations and using the constitutive relationship, showed that energy consumption for batch dewatering of a clay-settling impoundment with a one square mile Clay Settling Areas (CSAs) would be in a reasonable range, but the power consumption was too high [29].

The objective of this work was to explore the potential of semi-continuous operation as a means to effect separation at a low power consumption while maintaining a low energy consumption. The semi-continuous design is envisioned as a precursor for design of a fully-continuous electrokinetic separator.

2. Experimental

The semi-continuous prototype described in the present work represents an intermediate step in a series of prototypes for electrokinetic dewatering of phosphatic clay suspensions. It serves as a transition between batch experiments and fully-continuous experiments. By helping to explore the ability of electrokinetic technology to continuously remove water, the semi-continuous prototype is expected to facilitate the design of a fully-continuous prototype. The experimental system allowed semi-continuous operation into which a dilute particulate suspension was continuously fed and supernatant liquid was continuously removed. The thickened solids accumulated in the bottom of the tank.

2.1. Cell Design

A schematic representation of the deep-tank semi-continuous electrokinetic separator is presented in Fig. 1. A plastic storage box with the dimensions of 88.9 cm × 42.5 cm × 32.7 cm was used as the container. Two mesh plate electrodes were suspended in the tank at an adjustable height. Both cathode and anode were made of titanium with an iridium oxide coating (Water Star Inc.). These electrodes had minimal surface overpotential for hydrogen evolution and oxygen evolution reactions, respectively, thus maximizing the ohmic potential drop. The use of suspended electrodes served to provide more space under the anode. This space functioned as a reservoir for solids-rich suspensions, thereby expanding the pseudo-steady-state period. The dilute feed suspensions were pumped into one end of the tank at a controlled flow rate. The fine particles moved downward under the influence of the electric field, forming a cake on the anode. When particles passed through the anode, they settled and accumulated at the tank bottom by gravity, creating a solids-rich suspension. The supernatant water, with low solids content, was removed by gravity flow through a sharp-edged weir at the other end of the tank. Once the capacity of the tank to store accumulated solids was exceeded, the pseudo-steady-state operation was concluded, and the experiment was terminated.

2.2. Feed Suspensions

The tank was filled with suspensions provided by the Mosaic Fertilizer, LLC, from their Four Corners Phosphate Mine. These were pretreated by flocculant addition and then allowed to reach an solids content of around 10 wt%. The particle distribution analysis demonstrates that 90% of the particles had a diameter of less than 60 microns and about 65% had a diameter of less than 2 microns. The overall zeta potential of the untreated suspension was −20.1 mV. The suspended solids consisted of approximately equal mass fractions of silica, residual phosphate ore, and clay [28,30].

2.3. Experimentation Protocol

The tank, with suspended anode and cathode, was initially filled with feed solution. At $t = 0$, the pump delivering the feed was started and the electrical potential was applied under potentiostatic conditions. To avoid unattended operation, the pump and application of electrical power were discontinued overnight and resumed in the following morning. In previous work, McKinney and Orazem [28] demonstrated that intermittent operation did not adversely influence the observed trends in batch experiments. The present results show that, for semi-continuous operation, trends were unaffected by the intermittent operation.

Supernatant water samples were collected throughout the electrokinetic separation process at 30-minute intervals. Turbidity and pH measurements were conducted on the supernatant water immediately after collection and after 24 hours of in-cell free settling. For samples with turbidity values in excess of 1000 NTU, the original sample was diluted, and the recorded turbidity value was calculated from the product of the reading value and the dilution ratio.

After the completion of the experiment, water was removed from the volume above the anode, and phosphatic clay samples were collected. A plastic cylinder of 28 cm in length and 2.6 cm in diameter was used to collect samples. The upper opening was covered after the cylinder was inserted straight into the clay such that, due to air pressure, the clay sample remained in cylinder when it was pulled out of the tank. As electrodes covered nearly the entire surface area of the tank, sampling locations were selected at an approximately 15 cm interval.

The solids content was calculated by measuring mass loss by evaporation. An empty 250 ml beaker was weighed, represented by w_1. Then the clay sample was transferred to beaker, weighed as w_2. The beaker with wet clay was then put into the oven to dry.