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Electrokinetic dewatering and thickening. II. Thickening of ball clay

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The electrokinetic thickening of a 20% slurry of ball clay over a range of pH values has been studied. By employing a cell utilizing a parallel plate configuration, together with a scraper and collector system to remove the electrophoretically thickened clay, a continuous thickening process has been devised.

In addition to the electrophoretic anodic deposition process, water is simultaneously electro-osmotically ‘pumped’ from the region of the cathode, the catholyte containing less than 0.3% solid. By employing this integrated design the cell can be operated with a steady-state clay concentration of about 15% from a 20% feed. At this operating concentration a thickened clay of 60–70% is obtained for energy consumption of 170 kW h per dry tonne of clay.

1. Introduction

The previous paper [1] reviewed the background to electrokinetics. Part II of the series continues the applications of electrokinetics with particular reference to electrophoretic separation. The separation of small particles (< 5 μm) from aqueous colloid suspensions can prove very difficult to achieve by normal filtration technology and in these cases thermal drying has to be applied. It was for this reason that a study of the dewatering of a typical ball clay was undertaken.

Ball clay covers a very wide range of compositions [2] and is obtained in two distinct areas of Britain, namely Devon and Dorset [3]. In this study a Dorset ball clay was examined. The approximate composition of the clay was 52% kaolin and 48% mica, with a particle size distribution of 90% less than 5 μm, the majority less than 0.15 μm and only 2% above 53 μm. In addition to the very small particle size the presence of an organic coating (humic acid), also a feature of ball clay, improves the plastic properties of otherwise relatively coarse kaolinite fraction.

Normally, ball clay requires no treatment other than drying and is of satisfactory brightness in the majority of cases. However, occasions arise when clay is not of acceptable brightness, containing contaminants which cause discolouration, e.g. iron oxides. In the case of ball clay, which is used extensively in whiteware products, colouration is unacceptable. Chemical bleaching with, for instance, dithionite (sodium hydrosulphite) can be applied, but unless the impurity levels are low the large chemical additions necessary to ‘bleach’ the impurity may result in increases in slurry viscosity. An alternative method for removing iron is to use high-grade magnetic separation.

In order to facilitate this approach the clay at 82% solids as quarried from the seam is blunged down with water and a deflocculant added to produce a 25% slurry. This slurry is then passed through the magnetic separator loop where the iron contaminant is removed and the clay process stream leaves the separator loop at 20%. Having carried out this beneficiation step it is necessary to ‘dry’ the clay. Ball clay is a material which cannot be dried by mechanical methods due to the small particle size and therefore the only conventional technique has been to dry the product thermally.

However, Von Schwerin [4] had demonstrated that using a drum anode fabricated from lead it was possible to deposit clay electrophoretically onto the rotating anode and to remove the

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product from the anode drum with a fixed doctor blade. A detailed description of the plant and its operation has been given by Hind [5]. Other workers, e.g. [6–10], have also examined the dewatering of clay suspensions from a practical standpoint.

It is obvious from the above that the electrophoretic process dries the clay by concentrating the clay at the anode so that the remaining electrolyte (slip) becomes progressively more dilute. Eventually a point is reached where the slip becomes so dilute that is is uneconomic to continue the process. At this stage a slip containing, say, 5% solids must be discharged and may create an effluent problem. In order to avoid this it is logical to couple the electro-osmotic and electrophoretic processes so that solids in the interelectrode region can be maintained at a constant concentration [11]. Similar lines of reasoning were disclosed independently by Kunkle *et al.* [12]. It appears that many workers have not appreciated the role electro-osmosis can play in an integrated process and continue to use 'classical' techniques for removing water from the system, e.g. ultrafiltration. It will be shown in this and subsequent discussions that electro-osmosis is the main driving force in the water removal process.

Earlier electrophoretic devices have in general employed rotating drum anodes. With the exception of Kunkle's filter assembly they have not coupled the electro-osmotic and electrophoretic processes together. It was with a view to producing a continuous integrated system for dewatering that this work was commenced.

2. Experimental details

2.1. *The cell*

It is well recognized that if any new technology is to be accepted, the overall design must lend itself to automatic operation and to low maintenance costs. Confronted with these constraints it was obvious that a radical change in design concept is needed. Drum anodes, although used by previous workers, have the disadvantage that high fabrication costs are incurred and, in the event of an anode or cathode failure, the strip-down procedure is complex and costly. The requirement, therefore, is for readily available and easily replaceable electrodes; plate electrodes are the obvious choice. Once the electrodeposited clay has formed on the anode it should be removed without interruption of the deposition process. The use of a chain-driven scraper system seemed a logical method for removing the clay deposit as such systems are in common use in many industrial unit processes. Plate electrodes lend themselves to a simple cell geometry with the electrodes mounted vertically and readily removable. The use of a vertical configuration also resulted in a minimum floor area requirement, an important point when scale-up was considered.

2.2. *Cell structure*

A section through the cell is shown in Fig. 1. The main cell structure was fabricated from PVC with the anode forming one side of the cell. The cathode was mounted in the centre of the cell and was separated from the clay slip by a filter cloth spaced off from the cathode by 1–1.5 mm.

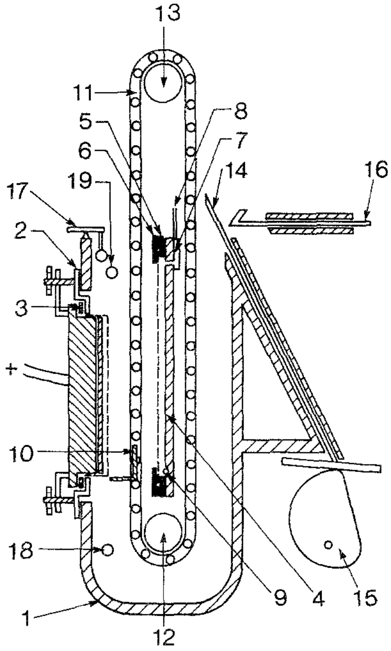

Fig. 1. Schematic section through clay thickening cell. 1, Main cell structure; 2, anode frame; 3, silicone rubber gasket; 4, cathode stainless steel plate; 5, PVC mask; 6, PVC mask; 7, cathode weir; 8, gas outlets; 9, cathode plate holes; 10, scrapers; 11, stainless steel drive chains; 12, idler sprockets; 13, drive sprockets; 14, inclined slide; 15, cam; 16, horizontal slide; 17, float switch; 18, cell inlet; 19, cell outlet.

During operation, electro-osmotically 'pumped' water passed from the front face of the cathode to a weir mounted on the back of the cathode where it passed out through two slots in the top portion of the stainless steel plate.

To remove any solids that built up within the cathode structure during extended running of the cell, holes were provided in the bottom of the plate so that solids could be pumped out if necessary.

2.3. *Clay recovery*

The thickened clay was removed from the anode by L-shaped scrapers attached between two stainless steel chains, cathodically protected to prevent corrosion. A 'Zero Max' variable speed drive was used to drive the chains via the drive sprocket. Four scrapers were used to remove thickened clay. Each was designed with the front edge of the horizontal surface set progressively closer to the anode face; the first scraper was set furthest from the anode. The scrapers were fabricated from stainless steel coated with an epoxy resin. The use of multiple scrapers reduced the loading on individual scrapers so that a smaller drive motor could be used.

The clay was removed from the L-shaped scrapers by a combination of both an inclined and a horizontal slide which engaged with the scraper; the synchronizing of the removal process was achieved using a cam driven off the drive sprocket.

As work extended to feed materials other than clay, alternative methods were devised. The electrodes, however, always remained in the cell. This is in contrast to the D'Orr Oliver Electrofilter [8–10] which uses a complex anode structure involving the application of a vacuum to prevent the anode membrane rupturing during the anodic product removal procedure which is carried out after the anode is lifted out of the cell.

2.4. *Electrolyte feed*

Electrolyte was fed into the cell only when the level fell below a preset value sensed by a float switch. The float switch was used to actuate a solenoid valve on the inlet to the cell, slip being pumped via this valve into the cell from a continuously pumped loop. In order to achieve good heat and mass transfer in the interelectrode gap, internal circulation across the anode face was provided. Circulation of the electrolyte also allowed the slip to be passed through a thermostatically controlled heat exchanger so that a constant temperature could be maintained in the cell.

2.5. *Cathode cloth*

The use of a cloth to prevent mixing of the solid-rich electrolyte with the solid-depleted catholyte was examined. It might be expected that submicron particles of clay would readily pass through the cloth. However, if a verticlly orientated cathode configuration and a weir take-off point located just below the level of the clay are used, the cloth blinds sufficiently after about 5 min to prevent further filtration.

Nevertheless, on application of a d.c., field water together with a small amount of suspended solid, was electro-osmotically 'pumped' through the cloth. The clay particles presumably bridge the holes and essentially allow only water (plus dissolved salts) to be transported through the clay matrix. Early work with different cloths demonstrated that the material, e.g. polyester or polyamide, was unimportant; this implied that the clay was, in effect, coating the cloth and therefore providing the condition for electro-osmotic flow to occur. That this was so was demonstrated in separate experiments to determine the streaming potential [13, 14]. It was observed that only a small potential difference ($\sim 2\,\mathrm{mV}$) was developed across the cloth in the absence of clay; this represents a zeta potential of $\ll 1\,\mathrm{mV}$ which is extremely small.

2.6. *Instrumentation*

The power supply used in this work was a Roband Varex 60-5 Twin unit operated in the constant current mode. A HiTek Integrator was used to monitor the number of volt seconds during the course of the experiments.

A process timer designed in these laboratories was used to control the clay removal cycle. The timer was reset at the end of each cutting cycle by a microswitch activated by a lever attached to the third scraper. A typical thickening cycle consisted of a 15 min period during which clay was thickening on the anode followed by the scraping cycle. At the end of a further 15 min the cutting cycle was repeated.

Conductivity measurements were made with a Marconi Universal Bridge using a previously standardized conductivity cell of the flow-through type. The cell was located in the circulation loop of the thickening cell. Measurements of pH were made using a Pye Unicam pH Meter and EIL pH electrode.

Solids levels in this work were determined from specific gravity measurements

3. Results

3.1. *Anode materials*

The early experiments were carried out with anodes that corroded in the slip during the electrophoretic thickening process. The following electrode materials were examined: iron, nickel, stainless steel, carbon, aluminium, lead and platinized titanium.

The iron and nickel electrodes corroded to form black oxides which subsequently contaminated the clay making the dried clay unacceptable. Stainless steel corroded releasing chromium as the yellow oxide. Lead, on the other hand, did not cause discolouration of the clay; however, lead dioxide, (the product of lead oxidation) was occasionally shed from the anode and black lead dioxide was noted in the clay product. The natural level of lead in the virgin clay was found to be between 15 and 25 p.p.m. This increased in the electrophoretically thickened clay to 50–70 p.p.m. and occasionally levels of up to 300 p.p.m. were noted when lead dioxide became occluded in the thickened clay.

Carbon was successful in thickening the clay but contaminated it with black particles. Aluminium, as expected, formed a resistive alumina film. With platinized titanium, when used in the thickening cell with a thin layer of clay maintained on the anode, deposition was successfully achieved. The dryness of the clay obtained on lead and platinized titanium was virtually the same. In view of the impending legislation forbidding the use of lead in ceramic products, platinized titanium was chosen as the most suitable anode material. The results presented below are those obtained using a platinized titanium anode.

3.2. *Electrolyte conductivity*

The conductivity of the clay slip varied from 4×10^{-4} to $9 \times 10^{-4} \Omega^{-1} \mathrm{cm}^{-1}$ over the range of samples studied. Fig. 2 shows the effect of temperature at two pH values constant slip concentration on the conductivity. The graph shows that on increasing the pH from 8.14 to 9.6 a 16% increase in the conductivity is to be obtained.

3.3. *Data obtained for the electro-osmotic and electrophoretic processes*

The electro-osmotic data is expressed in terms of the number of Wh ml^{-1}, i.e. the energy required to 'pump' 1 ml of water. Obviously the lower the Wh ml^{-1} value the more efficient is the dewatering process.

The electrophoretic data is split into three sets: (i) the wet mass of solid recovered, (ii) the dry mass of solid recovered, and (iii) the number of Wh kg^{-1} of dry solid recovered. In these experiments both constant voltage and constant current control were investigated. Although the results were not significantly different, constant current operation was used routinely. By using constant current and a fixed deposition period a constant charge was passed so that the mass of solid deposited in each cycle could readily be compared.

In addition to the above data, measurements

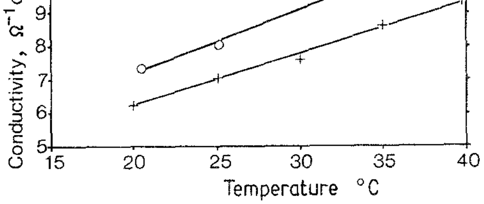

Fig. 2. Conductivity of ball clay as a function of temperature at pH 8.14 (O) and pH 9.90 (+).

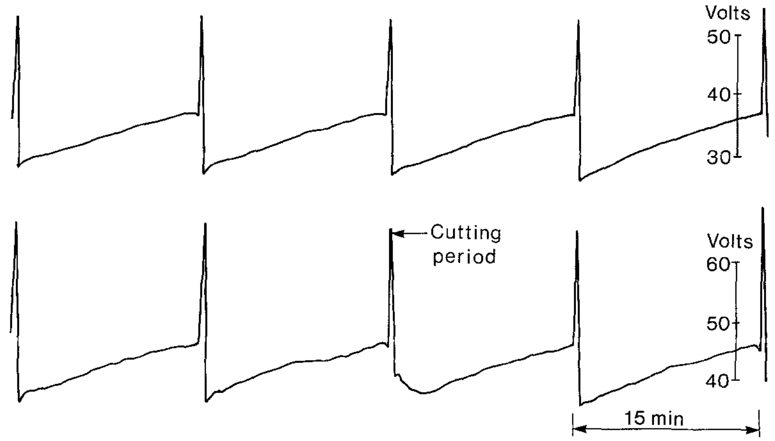

Fig. 3. Voltage–time plot at two current densities.

of pH, specific gravity and conductivity were made. The feed slip in these experiments was maintained constant at 20% solids.

During the thickening cycle it was observed that at constant current the voltage progressively fell with time. A typical voltage–time trace is shown in Fig. 3. The solids electrodeposited at the anode were in the range 50–60% and typical results are shown in Table 1.

3.4. *Effect of current density on the process efficiency*

The deposition and dewatering processes were studied over a range of current densities for a fixed deposition time; results are summarized in Table 1, and the relationship between the number of Wh kg^{-1} of dry clay and current is expressed graphically in Fig. 4. It should be noted that with increasing current density, the efficiency of the deposition process decreases. This observation is discussed further in Section 4.

3.5. *Effect of pH*

The pH was observed to affect both the deposition and dewatering processes. Increasing pH favoured the formation of a drier product but was accompanied by a reduction in the dewatering efficiency. The pH range studied was 7.2–9.2 and typical results are given in Table 2. These determinations refer to batch beaker experiments and were carried out by varying the pH by the addition of sodium hydroxide, with the level of solids maintained constant. These results were further confirmed for the integrated system as shown for pH 7.5 and 8.2 in Table 3. It should also be noted that the dry weight of solid is also reduced.

When the pH is increased by changing the slip this is accompanied by a rapid rise in the number of Wh ml^{-1} removed. This data is tabulated in Table 4. Accompanying the increase in the number of Wh ml^{-1} is a decreasing slip concentration which becomes more pronounced as

Table 1. Deposition of ball clay as a function of current density deposition time fixed at 15 min, at a 20% slip feed, a pH of clay of 7.9, and a temperature of 32° C

Current density (mA cm^{-2})	*No. of passes*	*Mean mass of wet solids (g)*	*Mean mass of dry solids (g)*	*Percentage Solids*	*Mean Wh kg^{-1}*	*Mean Wh ml^{-1}*	*Steady state cell concentration (% solids)*
9.7	11	324	186	57.5	77	0.0215	17.60
12.9	7	377	226	60.0	103	0.0262	16.25
16.0	8	467	285	61.0	122	0.0330	16.25
19.3	4	543	324	60.0	126	0.0363	15.60
22.6	3	676	363	54.0	117	0.0365	16.00

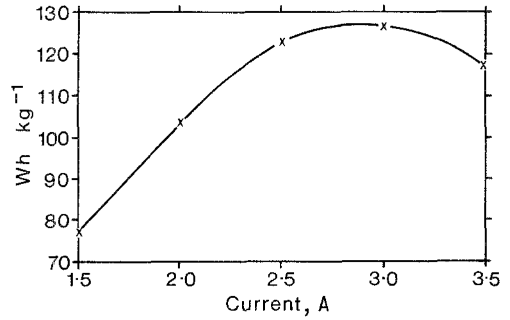

Fig. 4. Plot of number of Wh kg^{-1} of clay versus the applied current.

Table 2. Deposition of clay as a function of pH at a current density of 9 mA cm^{-2}, and a 20% slip feed

pH	*Wet mass of clay (g)*	*Dry mass of clay*	
		(g)	*(% solids)*
7.2	9.55 (clay very wet solids fell off electrode)	3.00	31
8.3	9.28	3.51	38
9.2	6.87	3.03	44

the cathodic dewatering process becomes less effective.

3.6. *Role of temperature on the thickening process*

The effect of temperature on the overall process was investigated. The results are summarized in Table 6, the most striking feature to note being the decrease of 18% in the number of Wh ml^{-1} as the temperature is increased from 20 to 36° C. Only a small increase in the electrophoretic efficiency was recorded despite a 23% decrease in the voltage over the temperature range 20–36° C at constant current.

Table 4. Effect of changing the pH of the slip feed on the electro-osmotic process, at a current density of 19.35 mA cm^{-2}

Time (min)	*Wh ml^{-1}*	*pH feed slip*
0	–	8.1
60	0.0553	8.1
120	0.0570	8.1
180	0.0700	8.1
240	0.0717	8.1
300	0.0697	8.1
310	0.0719	10.6 feed change
370	0.0843	10.6 feed change
416	0.1250	10.6 feed change

4. Discussion

The electrokinetic thickening process involves the movement of the solid clay particles to the anode and water to the cathode. Since the charge on the particle and the double layer govern the overall processes, factors which affect the double layer charge will affect the dryness and the weight of clay produced.

4.1. *The role of clay precoat*

Initial results on the thickening of ball clay with corroding anodes suggested that specific adsorption of the cation, e.g. lead, was necessary to effect the thickening process. This was confirmed by detailed calculations of the flocculation concentration predicted by the Schulze–Hardy rule [15, 16] for a divalent ion, e.g. lead.

From the concentration of lead in the clay (50–70 p.p.m.) an equivalent concentration of the lead ion concentration associated with the clay suspension was obtained. This value was found to be equivalent to about 0.7 mM, which is close to the flocculation concentration predicted by the Schulze–Hardy rule for a divalent ion, namely 0.52 mM. The lead ions are provided by the anodic reactions.

Table 3. Effect of pH on the electrokinetic processes at an applied current density of 12.8 mA cm^{-2}, and a 20% slip feed

Feed pH	*Cell pH*	*Wet mass of solid (g)*	*Dry mass of solid (g)*	*Percentage solids*	*Wh kg^{-1}*	*Wh ml^{-1}*
7.5	10.5	378	226	60	104	0.0262
8.2	11	226	153	68	142	0.057

However, this is not the complete situation since it was found that if a thin deposit of clay was maintained on the anode in the case of inert electrodes, which formed no corrosion products*, the clay would be successfully thickened up to 60–70% solids. The thin clay deposit, which is termed the 'precoat', was formed by progressively extending the thickening period from a continuous scraping sequence up to a 15 min thickening period over the course of an hour. If the precoat was removed, the clay produced in the following three or four thickening cycles produced a deposit lower in solids. Once the precoat had reformed, the 'dry' product was obtained. The role of the precoat must be two-fold: in the first instance it must allow a layer of clay to form which then acts as a matrix on which further deposition can occur and, secondly, it must act as a barrier to the proton formed by the accompanying anodic faradaic reaction, the decomposition of water. The clay was found to be acidic with a pH between 3 and 4, so that in effect the clay has 'trapped' the proton. The loss of the anodic precoat was prevented by using an open mesh cloth, 0.37 mm thick, placed over the face of the anode.

Product testing of the electrophoretically deposited clay demonstrated that the acidity within the clay did not adversely affect its properties. Any pH adjustment that was required could in fact be achieved during the preparation of the slip (e.g. addition of lime) prior to final drying or slip casting.

The deposition process can be considered a two-step process: (i) electrophoretic migration and (ii) deposition. Coughanour and Utter [17] used an optical microscope technique to study the electrophoretic migration velocity of kaolinite, μ_c, and found that the experimentally measured velocity ranged from 4×10^{-4} to 8×10^{-4} cm s^{-1}.

From the expression

$$\mu_c = \frac{\varepsilon \zeta \vec{F}}{4\pi\eta} \tag{1}$$

where ζ is the zeta potential (V), η is the viscosity assumed to be that of water (i.e. 0.01 poise), ε is the dielectric constant (= 80), and $\vec{F}$ is the applied field (V cm^{-1}), expressed in c.g.s. electrostatic units, a value of 40–80 mV was obtained for the zeta potential.

This compares with a calculated value of 35 mV for ball clay from the electro-osmotic data obtained in this study. Considering the higher concentration used in this work (20% compared with 0.01% solids in Utter's work) and the difference in the surface charge distribution, the zeta potentials are in reasonable agreement.

If the mobility of the clay particles, μ_c, are compared with that of the proton, $\mu_{H+} = 4 \times 10^{-3}$ cm s^{-1} [16], it is noted that μ_c is an order of magnitude smaller than μ_{H+} so that as the clay electrophoretically deposits the proton migrates in the field and becomes 'trapped' in the growing clay layer. Close to the anode a low pH is observed which increases as the distance from the anode increases. Product dryness is observed to increase with increasing pH, and the mass of wet clay decreases. This can be explained in terms of a fall in the zeta potential as the pH increases. This explanation is supported by ion exchange studies of Mattson [18] and Holdridge [2] on electrodialysed clay, in which they observed that as alkali additions were made to the neutral clay suspension the zeta potential increased very sharply with small alkali additions and then exhibited a progressive fall in zeta potential as further additions were made. The deposition of a drier solid as pH increases reflects the effect on the proton on the flocculation process. It has been suggested that the proton exchanges with sodium, aluminium or potassium and suppresses ionization of ball clay and therefore the interparticle electrical repulsions are smaller than in the case of a sodium clay so that a higher packing density is realized.

4.2. *Effect of current density*

The electrophoretic process was studied over a range of current densities for a constant deposition time of 15 min. Referring to Table 1 it can be seen that the number of Wh kg^{-1} increases with current density up to about 16 mA cm^{-2}

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* The level of platinum in the electrodeposited clay was below the detection level of X-ray fluorescence and plasma emission techniques, i.e. 0.7 and 0.2 p.p.m. respectively, and so the involvement of a metal ion species need not be considered in this instance.

Table 5. Deposition of clay at constant charge (1.45×10^{-4} C) for varying current densities

Current density ($mA\,cm^{-2}$)	Deposition time	Wet mass of solid (g)	Dry mass of solid (g)	Percentage solids	$Wh\,kg^{-1}$	$Wh\,ml^{-1}$
12.9	18 min 45 s	497	281	59	109	0.0310
16.1	15 min	470	283	60	118	0.0322
19.3	12 min 30 s	467	283	61	164	0.0454

and then exhibits a decrease in the power required to produce 1 kg of clay. This increase in efficiency of the deposition process is attributed to the falling voltage which occurs as a result of the growing clay front; obviously at the higher current the interelectrode gap decreases more rapidly than at the lower current densities so giving an apparently increasing efficiency. Mass transfer limitations do not occur. This can be inferred from Table 5 which demonstrates that the dry weight of clay deposited is directly proportional to the charge passed.

It is calculated that for each Faraday passed, 12.6 kg of clay are electrophoretically deposited and 1430 moles of water are electro-osmotically transported. The catholyte produced is very low in solids, containing less than 0.3%. Values below 0.1% were regularly obtained and it was observed that the solids settle over a 1–2 h period leaving a clear alkaline catholyte (of pH 12) which could be recycled.

It is appropriate at this point to compare the results reported by Freeman [8] for 'vacuum enhanced filtration' with those obtained in this work using field-assisted filtration. Although it is not possible to make absolute comparisons, the fact that the masses of product electrophoretically deposited in each case are similar (which implies the zeta potentials on the particles are similar) does allow comparisons to be made. In both studies the applied current densities were in the same range (8–18 mA cm^2), and recalculating Freeman's data it is noted that the value for the Wh ml^{-1} of water removed falls into the range 0.02–0.125 Wh ml^{-1} which compares with the value 0.0215–0.0365 Wh ml^{-1} in this work. This strongly suggests that vacuum-augmented filtration is unnecessary for the successful operation of the process.

4.3. *Effect of temperature*

It was found necessary to pass the internally circulating slip through a heat exchanger in order to maintain a constant cell temperature. The ohmic drop in the cell obviously results in a waste of energy and gives rise to heating effects. This does have a positive benefit on the process, however, since at constant current the voltage falls with increasing temperature. Examination of constant charge deposition at two temperatures, 20 and 36° C, showed a 7% improvement in both weight of clay and power consumption at the higher temperature which implies that temperature does not have a profound effect (over the range studied) on the electrophoretic process. The converse is true in the case of the electro-osmotic process where, under constant current control, the number of Wh ml^{-1} decreased as the applied voltage fell; this can be implied from Table 5. The scant literature on temperature effects suggest that a maximum in

Table 6. Effect of temperature on the electrokinetic processes at an applied current density, of 9.6 $mA\,cm^{-2}$ and a deposition time of 15 min

Temperature (° C)	Wet mass of solid (g)	Dry mass of solid (g)	Percentage solids	$Wh\,kg^{-1}$	$Wh\,ml^{-1}$
20	325	196	60	93	0.0288
28	289	176	60	88	0.0266
36	283	167	59	87	0.0235

the dewatering efficiency occurs at about36° C. Temperatures above 36° C were not examined as it was observed that the slip became unstable and agglomeration began to occur above 35° C. In practice the thickening cell was operated between 30 and 36° C.

5. Conclusions

It has been shown that electrokinetic dewatering is a viable process. It can be operated either continuously or intermittently with no deterioration in performance and is capable of producing solids in the range 60–70% from a clay feed of 20%. The catholyte contains a low level of solids (< 0.3%) and is suitable for the blunging of fresh clay. Integration of the anode and cathode processes allows the cell to operate at a 16% steady state concentration from a 20% slip feed.

The cell produces 92 kg of dry clay per m^2 of anode per hour. This is achieved with high efficiency, 1 Faraday producing 12.6 kg of dry clay. For a typical set of data 170 kWh yielded 1 tonne of dry clay.

The variables that influence the thickening process are pH, ionic strength and ultimately the anode precoat. The pH of the feed clay can be controlled during the benefication process so enabling the dewatering process to be optimized for the production of high solids and a steady state concentration of clay within the dewatering cell.

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