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**ELECTROKINETICS OF SAMPLES TREATED BY
ELECTROCOAGULATION METHODS - PART 1.
CONCENTRATED DISPERSIONS OF CLAY PARTICLES**

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Electrokinetics of samples treated by electrocoagulation methods - Part 1. Concentrated dispersions of clay particles/ C.W. Angle and J.C. Donini. -- (CANMET Report, Natural Resources Canada, 1992), 19 pages.

An attempt was made to determine the actual mechanism of operation by studying the electrokinetics of highly concentrated model clay, and process clay suspensions, both before and after electrocoagulation. Both electrokinetic sonic amplitude and microelectrophoresis techniques were used for measuring the charge on treated and untreated dispersions, together with controls. Scanning electron microscopy was used to determine whether aluminum ions were released onto latex and process clays. Some insight into the actual mode of operation was achieved by qualitative experimental observations, electrokinetic data, and analysis of aluminum-coated particles.

Résumé is missing.

ELECTROKINETICS OF SAMPLES TREATED BY
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CLAY PARTICLES

by

C.W. Angle* and J.C. Donini*

ABSTRACT

Electrocoagulation has been used for water treatment without a complete knowledge of the actual mechanism of operation. Process upsets occurring daily in a water treatment operation made it imperative to understand the actual mechanism of operation. The contending mechanisms proposed in the earlier literature were charge neutralization and dipole-dipole interaction explanation. In this study, an attempt was made to determine the actual mechanism of operation by studying the electrokinetics of highly concentrated model clay, and process clay suspensions, both before and after electrocoagulation. Both electrokinetic sonic amplitude and microelectrophoresis techniques were used for measuring the charge on treated and untreated dispersions, together with controls. Scanning electron microscopy was used to determine whether aluminum ions were released onto latex and process clays.

Some insight into the actual mode of operation was achieved by qualitative experimental observations, electrokinetic data, and analysis of aluminum-coated particles. In order to obtain further confirmation of a charge neutralization mechanism, studies dilute dispersions are proposed whereby the 'kinetics' of the interactions are accounted for.

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INTRODUCTION

The following study was designed to investigate the destabilizing mechanism(s) involved in the treatment of solids derived from a processing operation in which electrocoagulation was the major treatment method for plant effluent water. The water treatment plant was experiencing difficulties because of daily fluctuations in its electrocoagulation process efficiency. The question was whether the suspension destabilization occurred through charge neutralization by the Al^{3+} generated at the aluminum electrodes, leading to double-layer compression according to the Schulze-Hardy relationship (1), or the Al^{3+} forming hydroxide complexes that flocculate the particulates by the "sweep-cloud"-type gelation mechanism which entraps the particles and settles them into large flocs (6,8). Coagulation (physicochemical destabilization of colloidal systems) and flocculation (the aggregation of particles) are important in many water treatment processes (8) and were used by ancient Egyptians and Greeks who utilized mineral alum salt for its clarifying properties. Although the electrocoagulation effect has been known for some time its mode of operation has been the subject of argument (10). A dipole-dipole mechanism has been proposed based on the assumption that coagulation occurs due to the attractive interaction of the dipoles induced by externally imposed electric fields, as opposed to a charge neutralization mechanism (10).

In order to determine the mechanism by which the electrocoagulation process operates we studied the electrokinetic sonic amplitudes (ESA) of treated and untreated concentrated suspended particles (near-plant conditions), using a small-scale process. Detailed studies were carried out using microelectrophoresis of the diluted treated and untreated samples. The following study describes the measurements of the concentrated plant clay mixture using ESA for the high volume fraction of solids. Later, we present microelectrophoretic mobility distributions of electrocoagulated and control solids which were allowed to settle in a measuring cylinder for 12 h to permit a more detailed look at the particle population surface charges. Several vertical zones in the cylinder were compared with samples treated with conventional alum (aluminum sulphate).

EXPERIMENTAL

INSTRUMENTATION AND APPARATUS

The electrocoagulation apparatus consisted of four components: a frequency wave generator, a voltmeter/ammeter, a power supply, and a cell which held the parallel, rectangular, flat aluminum electrodes vertically. The current generator was a Kepco bipolar power supply/amplifier, the function generator was from Hokuto Denko Ltd. (model HB-105) to generate alternating current of the required frequency and waveform. A Keithly 196 System digital multimeter was used to monitor the voltage and current. The rectangular electrocoagulation cell was made of plexiglass and had inner dimensions of 2 cm x 2.5 cm x 70 cm. The two aluminum electrodes (2 cm x 70 cm x 0.1 cm) ran along the sides of the cell, parallel to each other, 2.5 cm apart.

Electrokinetic sonic amplitude (ESA) measurements were made according to the methods described in (2), using the Matec MBS- 800 (ESA) / ultrasonic vibration potential (UVP) instrument with the SP-80 probe. Conductivity, pH, and temperature readings were simultaneously.

Microelectrophoretic mobility distributions (EMDS) were determined on the PEN KEM System 3000 automatic electrokinetic analyzer according to methods described elsewhere (3,4).

Elemental analysis of the treated suspensions was done using a Hitachi X-650 scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (Tracor 30 mm³ Si(Li) detector).

MATERIALS AND METHODS

Samples consisted of clay obtained from Luscar Sterco: (a) 4.73 wt% at pH 8.7, and (b) 4.5 wt% at pH 6.7. These samples were prepared by suspending the dry clay in deionized water and stirring overnight to equilibrate, then decanting to select the finer suspended particulates. The specific conductivity was 1408 uS/cm² at pH = 6.7 and 447 uS/cm² at pH 8.7. The pH was adjusted from 8.7 (natural plant condition) to 6.7 using HCl.

Latex standard in 0.01M KCl at pH 5.7 which was normally used for microelectrophoretic calibrations, was used as a control test sample. A 1.6-wt% (volume fraction

of 0.061) of montmorillonite (Fisher brand) was also used as a test sample after equilibration in deionized water at pH 8.7. ACS-grade NaCl and KCl were used where required to adjust ionic strength. pH measurements were made with a glass/calomel combination electrode, after calibration at three points with phosphate buffers of pH 4.0, 7.0, and 10.0.

Before electrocoagulation, baseline readings of ESA, high-frequency conductivity, pH, and temperature of the suspension were measured in the Matec cell. Then, 300 mL of the suspension was placed in the electrocoagulation cell, and an alternating square-wave current at 0.1 Hz and 300mA was applied for 5 min. The sample was removed from the cell and the above parameters were again measured. This process was repeated on the same 300mL suspension. A control run using electrolyte alone (0.01M KCl at pH 7.5, 300 mA, for 5 min) was made to determine background ESA values and to note the effect of any soluble byproducts of the process. Basic pH was used to simulate plant operation conditions.

The sensitivity of the method of detection, as well as the effects of the chemistry of alum (aluminum sulphate) on the solids were investigated by measuring the above parameters before and after dosing the clay suspensions, at basic pH, with incremental amounts of alum.

Microelectrophoretic mobility distributions of control and electrocoagulated solids were conducted in parallel, after the suspensions had been mixed in 100 mL measuring cylinders and allowed to settle overnight. The top 15-mL fractions were removed and analyzed electrophoretically. The alum-dosed samples were also measured electrophoretically.

To confirm that aluminum was being produced during the electrocoagulation process, the latex sample and the process clays were examined by SEM.

RESULTS AND DISCUSSION

The passing of 300 mA of current through 0.01M KCl at pH 7.5 for 5 min produced a white gelatinous precipitate after the treated electrolyte was allowed to sit for awhile. This gelatinous white precipitate was believed to be $Al(OH)_3$, because of its low solubility product of 2×10^{-32} , at basic pH (5,8,9).

The montmorillonite samples at pH 9.73, which were also electrochemically treated at 300 mA for 5 min intervals, showed generally higher specific conductivity and pH (10.7) after the current had been passed. Lumpy gelatinous coagulates coated the electrodes, and a slightly less negative ESA (-0.180 mPa/V to -0.177 mPa/V) was measured, but not significantly so.

These observations suggested that little double-layer compression effects over the potential-determining ion (OH^-) effect occurred, but the texture of the electrochemically treated material appeared different from that of the original particulates. The presence of the gelled montmorillonite mixture also suggests that the mechanism involved rapid formation of the hydroxide complexes producing sweep-zone "enmeshed cloud"-type flocculation of particulates (6,8,9). However, the adding of the gelled material (the treated 0.01M KCl) into montmorillonite control (untreated solids) did not produce the same effect. This indicated that "time" of formation as well as "kinetics" formation and entrapment are crucial. The electrokinetic readings indicated little change in charge showing that exposed surfaces were still negative; this may signify that surfaces measured in this pH region are polymeric like those of sweep-zone flocculation (68).

Process clays (4.7 wt% at pH 8.7) treated for a total time of 40 min at 300 mA produced electrocoagulated material. However, after an initial rise in pH and conductivity at small coulombic dosage, a drop of pH to 8.2 and conductivity to close to its initial value indicated the removal of free OH^- ions from solution. ESA values (Table 1) suggest a slightly increased electronegativity; however, since temperature also increased, the significance of this effect became questionable as viscosity is directly dependent on temperature. Although increased negative charge with increased pH (hydroxide ions) is typical of clay surfaces, it was apparent at this point that Al^{3+} ion effect was being observed by this method under the experimental conditions chosen.

Data for a nearly neutral "process clay" suspension (pH 6.7, 4.5 wt%), treated for 5 min at 300 mA intervals (for a total of 4 times) are shown in Table 2, where the ESA, the results are given together with other experimental parameters, such as pH, temperature, high-frequency conductivity, dynamic electrophoretic mobility (proportional to ESA), and the coulombic dosage. The results of two runs are presented. The effects of addition of HCL to the electrocoagulated material can also be seen. The slight increase in pH and decreased conductivity

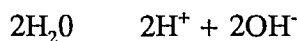
were consistent with previous observations. However, slight decreases in ESA values suggest that charge neutralization was occurring, although pH was increasing and OH⁻ ion effect may not be significant. The initial pH of the suspension is crucial in the chemistry of aluminum and hence its interaction with the solids (8).

Addition of HCl to decrease the pH of above suspension produced a decrease in the ESA values. This decrease confirmed that the effects observed were the result of a combination of potential-determining ion (H⁺) and double-layer compression of the solids, since specific conductivity increased. Differentiating between the effects of H⁺ and ionic strength on the solids cannot be made at this stage. The H⁺ ions are expected to affect the Al-ion chemistry (6).

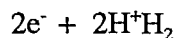
The absence of large changes in charged particles as detected by ESA values strongly suggests that a more complicated phenomenon occurred, that the method of detection of charge neutralization may not be sensitive to the small changes induced at high solids concentrations, or that the changes were indeed insignificant.

The standard latex samples which were electrocoagulated for 5 min at 300 mA produced a white gelatinous coagulated material. This was removed and analyzed by x-ray, together with treated and untreated Luscar clays; the results are shown in Fig. 1 and 2. Figure 1 shows that the latex exhibited Al on its surface whereas the Al on the treated clays was indistinguishable from the control sample (Fig. 2). In addition, the sharp rise in pH of the latex suspension (with no buffering capacity, pH 5.7 to 8.2) strongly indicated that OH⁻ ions were being released during the electrochemical treatment.

In solution:



During electrocoagulation:



This rise in pH was accompanied by increased negative charge of the latex as expected. Since specific conductivity was constant, it followed that any conductive OH⁻ ions released with Al³⁺ ions at this pH adhered to the latex surface in a form of an aluminum hydroxo- complex (8).

The sensitivity of the method of detection as well as the effects of the chemistry of alum on the solids were further investigated by measuring ESA values on these clays by dosing with aluminum sulphate (alum) starting at basic pH (Table 3). The sample exhibited increased negative ESA and decreased pH, and it was flocculated as expected. Retitration back to the basic region, which should induce precipitation of $\text{Al}(\text{OH})_3$, produced no changes in ESA, however. This treatment produced increased conductance and further clarification of water as expected.

The lack of large changes in ESA strongly suggests that some of the following may hold:

- 1) The method of detection was not sensitive to electrokinetic changes.
- 2) The sample of clay was producing an Al-hydroxo-complex for which H^+/OH^- was not especially potential determining.
- 3) The Al^{3+} was complexed to the OH^- producing a gelled surface, which was negative in charge.
- 4) There was too large a clay concentration and too small a dosage of Al^{3+} ; thus the major population of particulates was entrapped in the gel layer with no access to free Al^{3+} ions.
- 5) AlO_2^- , $\text{Al}(\text{OH})_4^-$ were predominant species in complexes.
- 6) The polymeric aluminum hydroxo species were adsorbed to the particle surfaces.

MICROELECTROPHORESIS OF SEDIMENT LAYERS

Electrophoretic mobility distribution spectra of the electrocoagulated and controlled luscar clay in the sedimented layers which were conducted in parallel and were mixed in 100 ml measuring cylinders and allowed settle overnight, are shown in Figures 3 and 4. The top 15 ml fractions show little difference between the two particulate populations were observed as shown in Fig. 3 and 4, spectra #25 to #35, with one general exception. The electrocoagulated samples produced a narrower distribution of negatively charged particulates, but the untreated samples displayed a slightly more negative average EM closer to the consolidation zone (spectra #31 vs #32, #35 vs #33, Fig. 3 and 4). This suggested that electrocoagulation produced more

uniformly charged particulate surfaces, confirming the observations resulting from the SEM data, in Fig. 2 and 3.

The general increase in pH during the electrochemical process, with small change in negative charge, together with the observation of coagulated gelatinous solids closer to the electrodes, suggests that the electrocoagulation process may be governed by several factors: (1) kinetics of formation of Al^{3+} , (2) diffusion of Al^{3+} in concentrated dispersions limiting accessibility to all solids particulates, (3) the higher pH and low K_{sp} (2×10^{-32}) inducing the rapid formation of aluminum hydroxide species prevents and thus preventing Al^{3+} ions from remaining free to access all solids particulates.

CONCLUSIONS

- (1) The electrochemical treatment of highly concentrated solids is limited by the availability of free Al^{3+} ions which are quickly removed to form $Al(OH)_3$ and complexes at high pH, typical of normal plant operations. Larger numbers of particulates may act as nuclei for rapid precipitation, and influence the sweep-zone mechanism.
- (2) The collection of the coagulate near the electrodes suggests that diffusion of Al^{3+} ions to the solids surfaces is limited at high solids concentration; more stirring and/or the use of a rotating electrode system to increase the mass flux at the electrode surface may increase efficiency.
- (3) Al^{3+} ions produced and adsorbed on the surfaces, occur in quantities that cannot be detected on these clays or aluminosilicates by x-rays, but they are detectable in latex.
- (4) The method of detection (ESA) of changes on charged particles is not sensitive to small changes in a bulk suspension. A large negatively charged population governed the average results.
- (5) The presence of large gelled coagulates during the electrocoagulation process, is contrasted with the evidence of hydroxide precipitates in standard KCl controls, which when added to the untreated clay samples could not produce the identical effect of sweep-

zone cloud type flocculation. This observation strongly suggests that the "kinetics" of reaction are crucial and that unhindered diffusion is important for this charge neutralization mechanism to hold.

- (6) A very small reduction in charge of the consolidated clay population was detected by microelectrophoresis. However, the decrease in pH of the treated samples would account for this small decrease. Negative particulates are indicative of a complex mixture of aluminosilicate hydroxo-complexes.

RECOMMENDATION

- (1) Further investigations are recommended using a standard silica and microelectrophoretic methods for dilute systems, where time is considered as a critical factor together with the continuous medium chosen.

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Table 1 - Electrokinetic data on 4.73%, pH 8.7 process clays suspension before and after electrocoagulation

ESA mPa.m/V	Dyn Mob $\text{m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	pH	Cond. Sem^{-2}	Temp. $^{\circ}\text{C}$	Coul.
.092 $\pm .001$	-2.32E-09	8.7	447	23.1	---
.105 $\pm .001$	-2.63E-09	8.92	447	27.9	180
.104 $\pm .001$	-2.60E-09	8.83	446	24.7	180
.104 $\pm .001$	-2.60E-09	8.51	429	27.3	270
.105 $\pm .001$	-2.63E-09	8.27	427	27.2	360
.106 $\pm .001$	-2.66E-09	8.18	433	27.2	450
.109	-2.73E-09	8.14	443	27.8	630

Table 2 - Electrokinetic data for process clay solids in suspension 4.5 wt% at pH 6.7 before and after electrocoagulation.

Sample Run	HCl	Amt HCl (μL)	ESA mPa m/u	Dyna Mob. $m^2 \cdot V^{-1} \cdot s^{-1}$	Phase Deg.	pH	Cond. Scm^{-2}	Temp. °C	Coul.
First	None	0	-.124	-3.16	-1.9	6.68	1408	23.1	0
First	None	0	-.121	-3.08	-2.5	6.64	1373	23.7	90
First	None	0	-.116	-2.95	-1.5	6.81	1371	24.2	270
First	None	0	-.113	-2.88	-2.7	6.94	1339	24.4	450
Second	None	0	-.123	-3.13	-1.7	6.77	1396	23.3	0
Second	None	0	-.118	-3.01	-2.5	6.78	1349	24.3	90
Second	None	0	-.113	-2.87	-1.8	7.03	1359	26	450
Second	None	0	-.109	-2.77	2.1	7.29	1360	26.3	810
Second	None	0	-.115	-2.91	2.7	7.38	1361	27.5	1350
Second	Added	50	-.114	-2.91	8.7	7.12	1439	27.1	1350
Second	Added	100	-.113	-2.86	11.8	6.81	1511	26.9	1350
Second	Added	150	-.109	-2.77	13.7	6.47	1585	26.7	1350
Second	Added	250	-.1	-2.54	14.2	5.83	1720	26.5	1350
Second	Added	350	.09	-2.28	11.8	5.24	1872	26.3	1350
Second	Added	450	-.085	-2.15	9.7	4.94	2027	26.3	1350

Table 3 - Effects of aluminum sulphate (alum) on 4.73 wt%, pH 8.7 process clay suspension diluted to 250 mL from

Alum μL (47.5 wt%)	ESA mPa.m/V	Dyn Mob $\text{m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$.	pH	Cond. S/cm ²	Temp.
0	-.101	-5.07E-10	8.52	499	23.6
50 μl	-.115	-2.87E-09	7.16	706	23.6
100 μl	-.121	-3.03E-09	6.6	847	23.6
150	-.123	-3.09E-09	6.23	971	23.5
250	-.124	-3.10E-09	5.87	1081	23.5
500	-.126	-3.15E-09	5.10	1403	23.5
700	-.131	-3.27E-09	4.68	1858	23.5
1700	-.119	-2.98E-09	3.97	3407	23.6
2700	-.121	-3.04E-09	3.74	4735	23.6
3700	-.129	-3.23E-09	3.65	5628	23.6

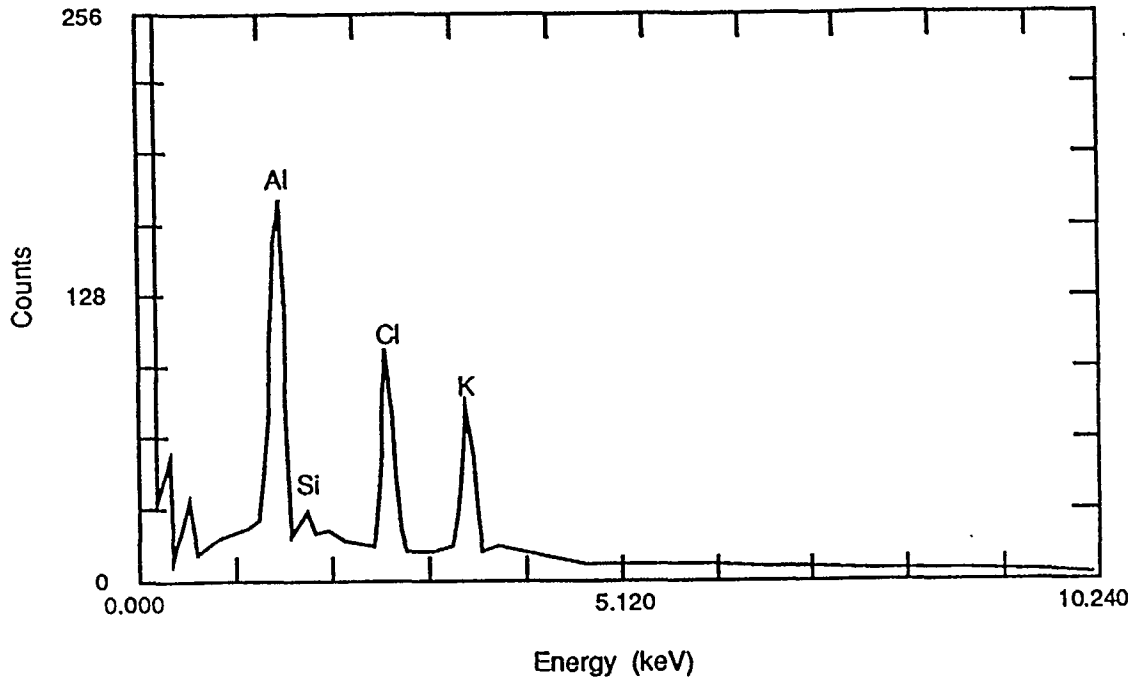


Fig. 1 - Elemental profile from SEM analysis of electrocoagulated latex

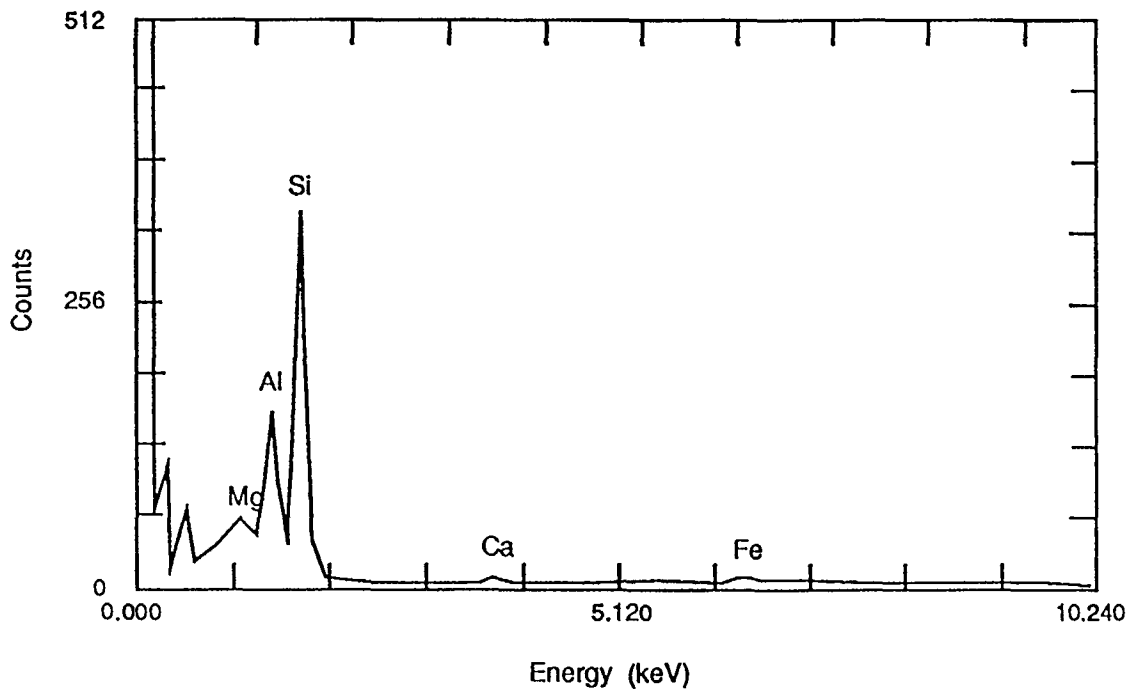


Fig. 2 - Elemental profile from SEM analysis of electrocoagulated Luscar solids

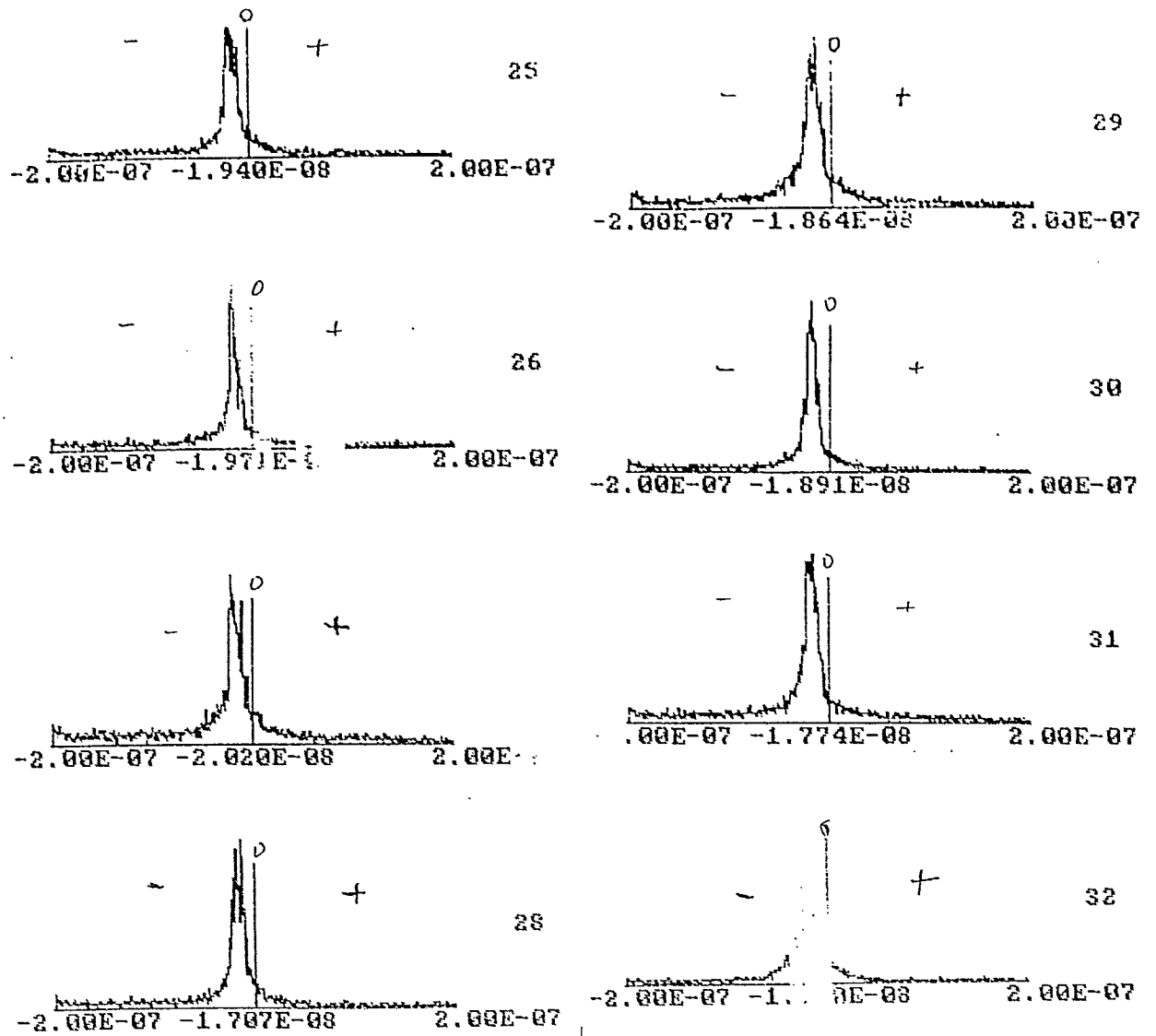


Fig. 3 - Electrophoretic mobility distribution spectra of sedimented process clays before and after electrocoagulation.

(25) before, 1st 10 mL

(27) before, 2nd 15 mL

(29) before, 3rd 15 mL

(31) before, 4th 15 mL

(26) after, 1st 10 mL

(28) after, 2nd 15 mL

(30) after, 3rd 15 mL

(32) after, 4th 15 mL

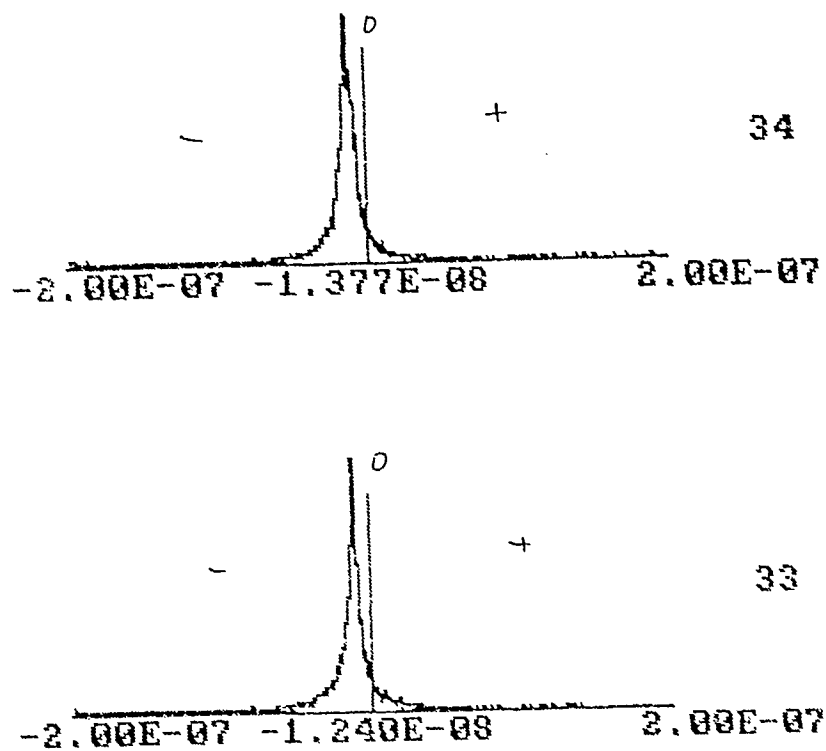


Fig. 4 - Electrophoretic mobility distribution spectra of whole-process sedimented clays before and after electrocoagulation
(33) after (34) before

