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ELECTROPHORETIC SEPARATION OF AN INORGANIC AMORPHOUS MATERIAL FROM THE LESS THAN 0.2μm FRACTION OF A SOIL CLAY MIXTURE[1]

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Abstract

An inorganic amorphous material was separated from a soil clay mixture by use of an electrophoretic continuous-particle separator. The clay suspension was introduced into the electrophoretic cell at a rate of 0.1 ml per minute using 0.0005 *M* Na_2CO_3 at a pH of 5.5 as the suspension media. The potential gradient across the cell was 32 V/cm. The clay separated into four major bands which were collected and analyzed by X-ray diffraction, differential thermal analysis, and chemical analysis. One of the fractions collected showed only a small amount of crystalline structure as determined by X-ray diffraction and differential thermal analysis.

Introduction

It is often desirable to study the mineralogical, chemical, and physical characteristics of the individual clay minerals in soil clay mixtures. Studies of this type have been complicated due to a lack of a good method for quantitative separation of the various clay mineral components. Among particle separation techniques that have been reported are density gradient centrifugation (Anderson, 1963), countercurrent distribution techniques (Albertsson, 1960), and electrophoretic techniques (Bergseth, 1961; Beavers and Larson, 1953; McNeal and Young, 1963). It appears that electrophoresis shows the most promise for making quantitative separations. The cells used by these investigators are not adaptable to the fractionation and collection of large quantities of particulate matter necessary for clay research. Recently Park and Lewis (1969) used an electrophoretic cell similar in design to the one devised by Strickler, Kaplan, and Vigh (1966) to perform a separation of a mixture of pure clays. The cell overcomes the mechanical difficulties encountered in existing cells for electrophoresis, in that electrophoresis and fractionation are accomplished in a free-flowing film of solution. The advantages of using a cell of this type are that the clay is not absorbed on a supporting media and that continuous fractionation can be accomplished.

The purpose of the investigation reported herein was to determine the

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applicability of a continuous-particle electrophoretic cell for the separation of an inorganic amorphous material from the clay fraction of a soil shown to contain large amounts of amorphous material.

Cell Design and Operation

The basic design and operation of the cell is as follows: the cell is made up of basically three different parts, the two electrode chamber assemblies and the center curtain assembly (Figure 1). The center portion of the cell consists of two glass plates each having dimensions of 2.5 cm×1.25 cm×30 cm. The plates are separated at the top and bottom by a rubber gasket to insure a watertight seal, and also to serve as a spacer between the two plates, the thickness being 3 mm.

Directly below the curtain inlet port is located a rotatable capillary tube with an inside diameter at the opening of 0.5 mm through which the sample suspension is introduced into the cell. At the bottom portion of the curtain assembly is located another rotatable capillary tube which serves as the sample pickup tube.

The electrode chamber assemblies are made of lucite having outside dimensions of 2.5 cm×2.5 cm×30 cm. Each of the assemblies has two channels, one next to the curtain assembly having the dimensions of 0.8 cm×0.5 cm×25 cm, connected to another channel by a series of aperatures of 1.6 mm diameter spaced four per 2.5 cm. This channel has the dimensions of 0.8 cm×0.8 cm×25 cm, which houses the 1.63 mm diameter platinum electrodes.

Semipermeable cellophane membranes separate the electrode assemblies from the curtain assembly, which serves to maintain electrical conductivity through the cell and to separate the electrolyte flow characteristics of the electrode assemblies and the cell curtain.

During operation electrolyte solution enters the electrode rinse inlet located in the intermost channels (Figure 1). The solution then flows upward with a greater velocity in the channel adjacent to the electrode channel. This arrangement is important in that it prevents a buildup of electrolysis products next to the semipermeable membrane, which otherwise would cause erratic operation of the cell.

Solution is also introduced into the curtain inlet located at the top of the curtain at the apex of the rubber gasket. The solution flow conforms to the shape of the gasket radiating out from the apex. The capillary can thus be placed at any angle and the solution flow would be parallel to the capillary preventing turbulance from forming at the top of the cell. The solution then flows down between the plates in a laminar parallel manner giving a free-flowing film as a supporting medium for electrophoresis. The suspension is introduced continuously via the sample inlet tube at the upper portion of the curtain assembly and is carried downward with the free-flowing film.

When a potential is applied across the cell, the sample suspension separates into a series of bands radiating outward and carried downward by the moving solution in the curtain assembly. In order to collect a given band, the fractionating capillary is rotated to intercept the desired band. This material is then drawn out of the cell by adjusting the flow through the fraction collector to correspond to the downward flow of the desired band. The assembled cell used for the work reported herein is shown in Figure 2.

Methods and Materials

The soil clay used in this investigation was from the B21 horizon of the Sebree soil series found in southwestern Idaho. The soil was chosen because work reported by Lewis (1962) indicated the soil was high in an inorganic amorphous material.

The soil was air dried, ground, and passed through a 2 mm screen. The pre-treatment of

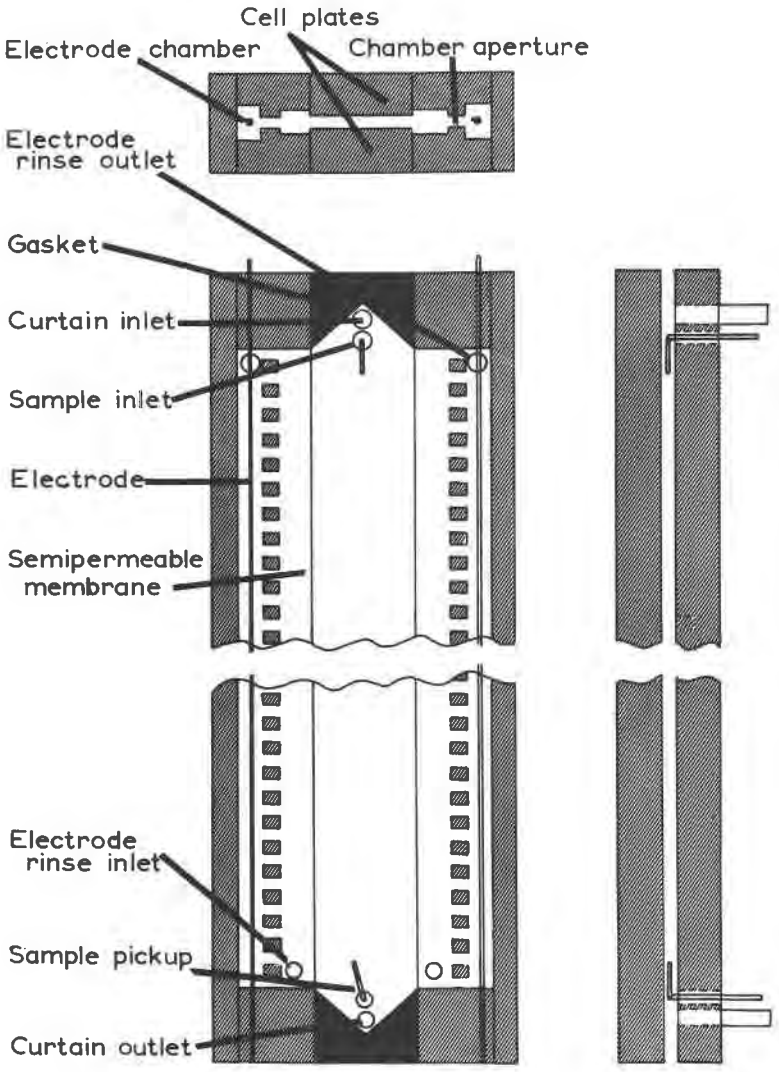

FIG. 1. Electrophoresis cell design.

the soil samples was according to Kunze (1965) for the removal of soluble salts, carbonates, organic matter, and free iron oxides.

The soil samples were washed three times with 2 percent Na_2CO_3, the supernatant being discarded after each wash. Distilled water was then added to the soil and the less than 0.2 μ fraction separated by centrifugation.

The less than 0.2 μ clay was dialyzed against 0.0005 M Na_2CO_3 to achieve the same concentration of Na_2CO_3 solution in the suspension as that in the electrophoretic solution.

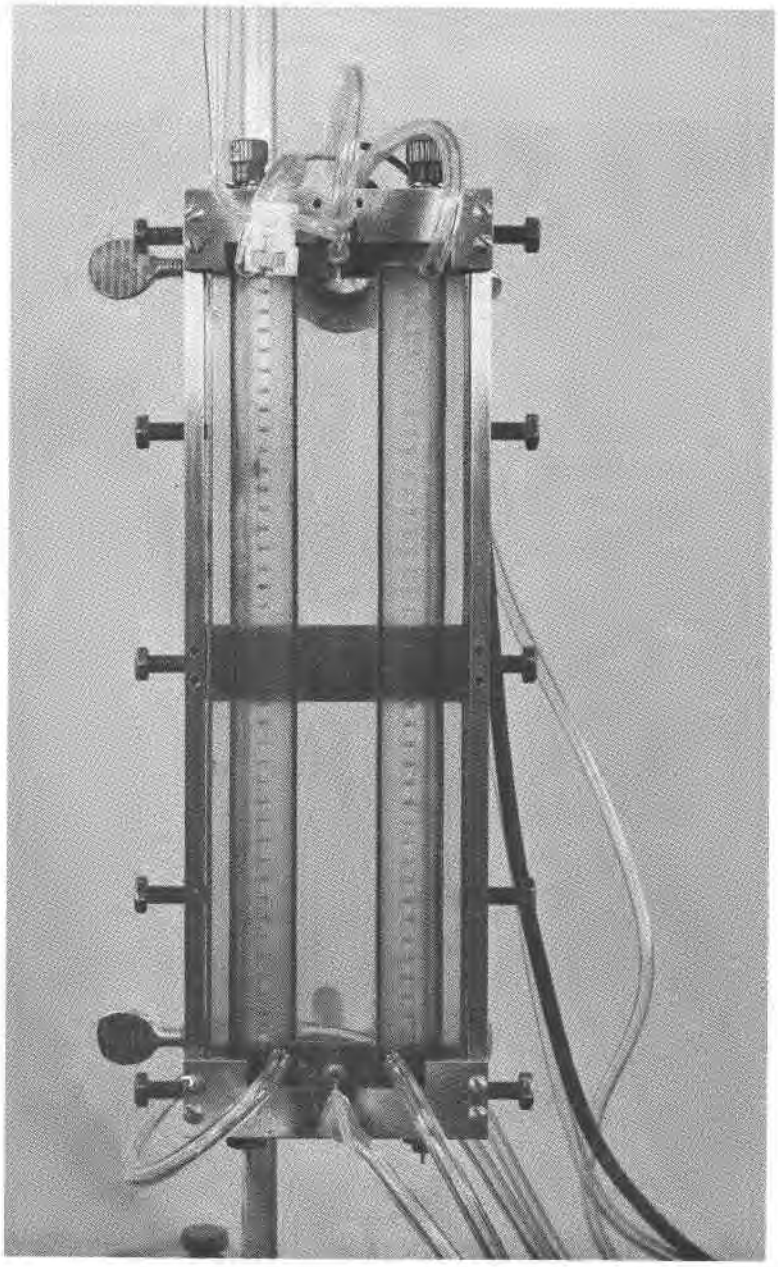

FIG. 2. Electrophoresis cell assembly.

A small amount of NaCl was added to the suspension in the dialysis bag to determine when the suspension was in equilibrium with the 0.0005 *M* Na_2CO_3. The dialyzate was changed periodically and tested for the presence of Cl^-. It was assumed that the suspension was in equilibrium with the electrolyte solution when there was a negative test for Cl^-. The concentration of the clay suspension was adjusted to 0.0023 g/ml using additional amounts of 0.0005 *M* Na_2CO_3 solution.

The electrophoretic separation procedure requires an electrolyte which gives good dispersion of the particles. It also requires the concentration of this electrolyte which results in the greatest difference in mobility between mineral species. The greatest difference in mobilities was obtained with 0.0005 *M* Na_2CO_3 at a pH of 5.5. The combination will yield a 0.0009 *M* NaCl/0.00003 *M* $NaHCO_3$ solution very weakly buffered by exchange of CO_2 with the atmosphere. A more strongly buffered solution, or one having a higher ionic strength, tended to decrease the difference in mobility between the different mineral species in the clay.

The clay suspension was introduced into the electrophoretic cell at a rate of 0.1 ml per minute using 0.0005 *M* Na_2CO_3 at a pH of 5.5 as the suspension media. The curtain flow rate was 7 ml/min with an electrode chamber flow rate of 80 ml/min. The potential gradient across the cell was 32 V/cm.

The electrophoretic fractions were flocculated with a saturated solution of sodium chloride and the solids collected by centrifugation. The solids were washed with ethyl alcohol until a negative test for chloride ion was attained. The solids were dried at 100°C.

Samples containing 50 mg of sodium saturated electrophoretic fractions, total clay prior to electrophoresis and glycolated total clay were analyzed by X-ray diffraction. The diffraction patterns of the samples were obtained using a General Electric model XRD-5 with a copper target X-ray tube.

The differential thermal analysis data were determined by the Sadtler Research Laboratory using a DuPont model 900 Differential Thermal Analyzer. The instrument parameters were as follows: The sample size was 15 mg, dried at 100°C; reference material, αAl_2O_3; heating rate, 10°C/min; atmosphere N_2 at 760 mm, Δ T scale 0.5°C/inch; thermocouples, chromelalumel. The samples were scanned from ambient to 860°C.

The amount of amorphous alumino silicates present in the less than 0.2 micron clay fraction before electrophoresis was determined by the partial dissolution treatment described by Hashimoto and Jackson (1958).

Before the elemental analysis, samples of each of the solid materials were dried at 100°C, then decomposed with the Na_2CO_3 fusion procedure according to Jackson (1964).

The aluminum was determined by the aluminon procedure according to Chenery (1948) with thioglycollic acid used as an inhibitor for iron present in the solution. The iron was determined by the KSCN method of Jackson (1964) and the silicon was determined by the molybdate method according to Jackson (1964).

Results and Discussion

The X-ray diffractogram of the glycolated total clay prior to electrophoresis (Figure 3F) shows a montmorillonite peak at 17.7 Å, illite at 10.0 Å, and the sodium saturated clay (Figure 3E) shows the montmorillonite peak at 13.5 Å, and the illite peak at 10.0 Å. The X-ray diffraction data were used for a qualitative analysis of the material before electrophoretic separation; however, the primary use was to determine if separation was accomplished during electrophoresis.

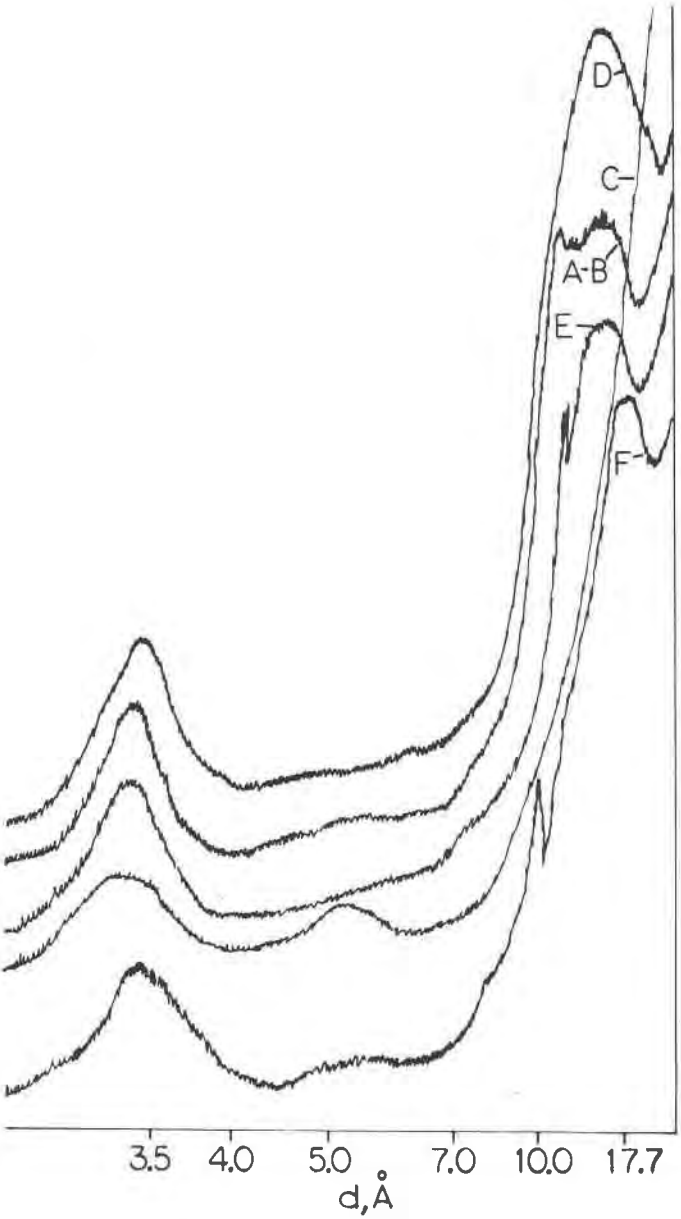

FIG. 3. The X-ray diffractograms of the sodium saturated and glycolated total clay prior to electrophoresis and the sodium saturated electrophoretic separates.

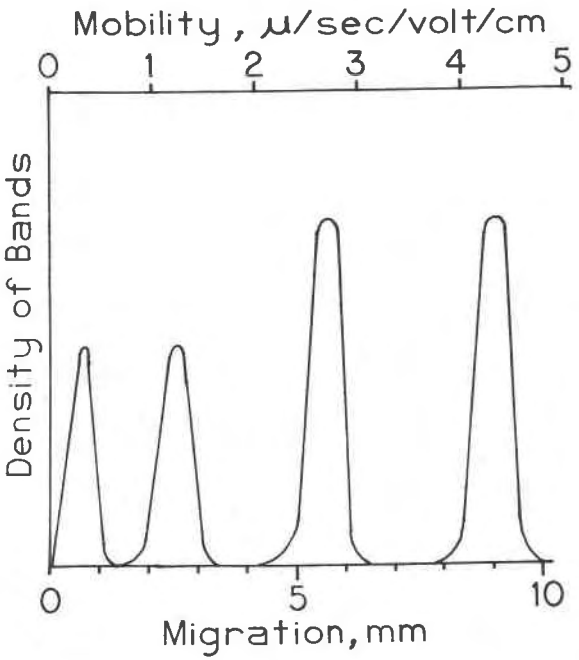

FIG. 4. The resolution, migration, mobility, and band widths of the soil clay during electrophoresis.

Four well-defined bands were obtained by passing the less than 0.2 μ clay through the electrophoresis apparatus. The band width, amount of migration, mobility, and the relative intensity of the bands are shown diagrammatically (Figure 4). Samples of band C, band D, and a mixture of bands A–B were collected. Bands A and B were too close together to fractionate without difficulty.

A combination of techniques was used to identify the nature of the materials separated and to see if an inorganic amorphous material was one of the fractions. The techniques used for evidence of separation were X-ray diffraction, differential thermal analysis, and chemical analysis.

X-ray diffractograms of the sodium saturated electrophoretic bands (Figure 3 A–B, C, D) indicated that the combination of bands A and B is illite and montmorillonite. Band D shows only montmorillonite. The montmorillonite exhibits two different mobilities illustrating the variation of mobilities existing in montmorillonite. In previous work it was found that montmorillonite from other sources and also Wyoming bentonite gave several different electrophoretic bands. Collection of several of these bands yielded similar or very similar X-ray diffraction patterns.

The reason is not understood; however, it is suspected the differences in mobility could be due to variations in ionic substitutions in the tetrahedral and or the octahedral layers.

Band C shows very little crystalline structure (Figure 3 C) with the exception of diffraction maximums at about 3.5 Å and 5 Å indicating a more ordered structure than glass. White (1953) found similar results on

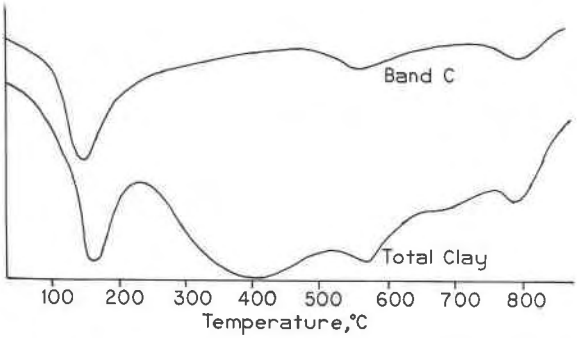

FIG. 5. Differential thermal analysis thermograms of the total clay and the amorphous fraction (band C).

allophane samples where diffraction bands were observed at 3.5 to 3.0 Å, 2.26–2.08 Å, 1.45 to 1.27 Å, and 1.22–1.12 Å.

The evidence of separation of the amorphous material by electrophoresis was further substantiated by differential thermal analysis on the less than 0.2 μ total clay and the amorphous material (band C). The DTA thermogram of the total clay prior to electrophoresis (Figure 5), showed an endotherm at 160°C, which is likely due to the desorption of water. Endotherms also are exhibited at 410°C, 560°C, 755°C. It is suggested that the endotherm of the total clay occurring at 560°C is due to the dehydration of illite and the endotherm at 755°C is due to the decomposition of montmorillonite. The endotherm at 410°C is of indefinite interpretation.

The thermogram of the amorphous material shows an intense endotherm at 140°C and slight endotherms at 560°C and 755°C. The endothermic reaction occurring at 140°C is likely due to the desorption of water and the slight endothermic reactions at 560°C and 755°C are possibly due to residual traces of illite and montmorillonite that were not removed by electrophoresis. The possible presence of the montmorillonite and illite in the amorphous fraction could be due to contamination during fractionation or a small percentage of the crystalline material could be coated with the amorphous material masking the characteristic

mobility of the crystalline material, thus preventing electrophoretic separation.

The thermogram of the amorphous material is very similar to those obtained by White (1953) from allophanes collected from Lawrence County, Indiana, which show intense endothermic reactions at 150°C–200°C and slight endotherms at 500°C.

TABLE 1. CHEMICAL ANALYSIS OF CLAY MATERIALS

	% Fe	% Al	% Si	% Loss due to dissolution
Total clay	4.94	8.73	24.2	34.4
Clay after dissolution	1.75	9.1	24.9	
Amorphous material	3.36	6.58	15.30	
Dissolution extract[a]	1.43	2.36	5.2	
Adjusted dissolution extract[b]	4.16	6.90	15.0	

[a] Percentage calculated in terms of weight of total clay prior to dissolution.

[b] Percentage calculated in terms of weight of dissolved material; or where % element in question $= \frac{\%\ \textit{element in dissolution extract} \times 100}{34.4}$.

The chemical analysis of the amorphous material, total clay, and the dissolution residue (Table 1) shows that the total clay and dissolution residue are somewhat higher in aluminum and silicon than the amorphous material. The analysis of the adjusted dissolution extract was compared with the analysis of the amorphous fraction (Table 1). The results compare favorably, which indicates the material separated electrophoretically is nearly a pure inorganic amorphous material.

This investigation shows that under carefully controlled conditions an electrophoretic continuous particle separator can be adapted to a soil clay separation. It appears that a cell of this type will enable the investigator to separate some of the various mineral species occurring in a soil clay.

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