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ELECTROCHEMICAL ALTERATION OF CLAY SOILS*

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Abstract—The composition and physical properties of three clay soils were altered by introducing aluminum under an electro-chemical gradient in order to evaluate the role of pH in controlling changes in soil composition and the feasibility of pH buffering during electrochemical treatment.

Both X-ray diffraction and selective chemical extraction methods were used to determine the distribution and mode of occurrence of aluminum in the treated samples. Aluminum was detected in the treated samples in both exchangeable form and as a hydroxy-aluminum interlayer. Aluminum oxide minerals such as gibbsite were not detected in any of the treated samples. Mineralization by aluminum ions was speeded and intensified in bentonite soils by buffering the catholyte with carbon dioxide.

Plasticity of bentonite soil samples from South Dakota was reduced markedly by electrochemical treatment, whereas the plasticity of an illite soil from Illinois and an illite-montmorillonite soil from Mississippi were relatively unaffected. Nearly all treated samples exhibited some degree of electrochemical induration or mineralization. Induration was most pronounced in bentonite soil samples with high water contents and alkaline pH largely because of hydroxy-aluminum interlayering in the clay. On the other hand interlayering was negligible in illite soil samples with low pH; the main effect of electrochemical treatment in this case was the addition of aluminum in exchange sites.

INTRODUCTION

WHEN two electrodes are inserted in wet ground and a direct current passed between them, a flow of water will occur from one electrode to the other. This is the phenomenon of electro-osmosis which has been used successfully by civil engineers to dewater and stabilize soft ground (Casagrande, 1953; Adamson *et al.*, 1966).

Certain electrochemical effects invariably accompany electro-osmosis, particularly if iron or aluminum electrodes are employed, and if sustained high-density currents are used with no provision for control of pH. These conditions are typical of most electro-osmotic field installations. It is not clear at present what the nature of these electrochemical effects is nor is it clear in what manner or to what extent they contribute to stabilization during so-called electro-osmotic treatments of clay soils. Possible effects include ion exchange, alteration of constituent minerals, and the introduction of new mineral phases from the electrodes.

The main purpose of this investigation was to determine experimentally the changes in composition and mineralogy of selected clay soils subjected to a specific type of electrolytic or electrochemical treatment and to correlate this information with changes in physical properties of the soils. Objectives of the study were to determine the distribution and mode of occurrence of aluminum which was electrochemically introduced into the soil and to examine the role of pH in controlling the rate and extent of electrochemical alteration. This paper describes primarily the nature and extent of compositional changes resulting from electrochemical treatment of clay soils; the results of strength tests and the feasibility of using electrochemical hardening in engineering practice are not included here.

Aluminum was singled out for experimental study for two main reasons. (1) Aluminum anodes are often used in engineering practice for electro-osmotic dewatering. (2) Aluminum can combine with hydroxide ions to form various hydroxy-aluminum compounds in soils. These compounds have interesting properties: they can interlayer with certain clay minerals or precipitate externally in the pore space as amorphous or crystalline hydroxides and thus modify the mineralogy, composition, and presumably the physical properties of the soil. The experiments, physical property determinations, and aluminum extractions

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and analyses were made by Gray at the University of Michigan; the X-ray diffraction and petrographic analyses were made by Schlocker at the Menlo Park, California, center of the Geological Survey.

REVIEW OF PAST WORK

Titkov and others (1965) have demonstrated experimentally that electrolytic alteration and mineralization occur when an electric current is passed through a soil. However, they used very high current densities (on the order of 20–60 mA/cm^2)—well beyond that which could be practically employed for large scale treatment of soils.

Youell (1960) described an electrochemical method for converting montmorillonite to a pseudo-chlorite. His method consisted of electrolytically introducing magnesium and precipitating brucite (magnesium hydroxide) between montmorillonite unit sheets. Converting montmorillonite to pseudo-chlorite should produce a clay with quite different physical properties; however, this aspect was not investigated by Youell.

Murayama and Mise (1953), Shukla (1953), Nettleton (1960), and Esrig (1967) have experimented with electrochemical treatment of clay soils. None of these workers, with the exception of Murayama and Mise, reported evidence of mineralization in the treated soils. Widely different testing conditions, soils, and electrode-electrolyte systems were used by these workers, hence the difficulty of extracting a significant conclusion or consensus from their work. None of these investigators reported attempts to control pH during treatment.

It does not appear that a detailed study has been made of the role played by aluminum when it was electrolytically introduced into a wet clay mass. Aluminum is a particularly interesting ion because of its ability to co-ordinate with hydroxide in different ways and thus form hydroxy-aluminum polymers or compounds. Barnhisel and Rich (1965), Hsu and Bates (1964), and Brydon and Kodama (1966) have investigated the nature of these hydroxy-aluminum compounds, their mode of occurrence in soils, and the conditions favorable to their formation. Brydon and Kodama showed that aluminum hydroxide enters entirely into the interlayer of montmorillonite and assumes a gibbsite-like monolayer structure in amounts up to 8 m-equiv. Al/g of montmorillonite. If sufficient amounts of aluminum hydroxide are made available in this manner, the nature of montmorillonite is radically changed. The basal spacing no longer expands to 18 Å upon absorption of glycerol, and it retains a 12–14 Å basal spacing even upon heating to 700°C, instead of collapsing to 10 Å.

McAtee and Wells (1967) reported the results of an electron microscope study showing adsorption of hydrous aluminum oxides by several clay minerals. In kaolinite, adsorption occurred predominantly on the particle edges, whereas with montmorillonite, adsorption occurred on the basal surfaces of the clay particles. Both types of adsorption suggest a type of bonding action by the aluminum hydroxide. Titkov and others (1965) detected the formation of both amorphous aluminum hydroxide and gibbsite in some of their electrochemically treated samples. Murayama and Mise (1953) likewise reported that aluminum hydroxide was electrolytically precipitated in a few of their samples and that in certain instances this may be an important induration mechanism. They postulated, however, that aluminum oxide deposition would only occur where the soil pH was approximately neutral.

The role of pH in fact deserves more attention in studies of this type than it has received in the past. Unless extreme precautions are taken, an electric field impressed across a wet clay soil will also produce a pH gradient because of electrolysis of the water. The anolyte (or anodic region) will become quite acidic and the catholyte, alkaline. The possibility and effects of pH buffering during electrochemical treatment apparently have not been considered previously.

What has been generally overlooked in past studies is that the pH has a great influence on the type of mineral species that may form and precipitate in an electric field. A related phenomenon—isoelectric focusing—occurs when a direct current voltage is imposed on a porous system saturated with a solution of variable composition. As a result of the impressed electric field, electrolysis will occur resulting in a pH gradient between anode and cathode. An ampholyte species such as aluminum will tend to collect (and likely precipitate as an insoluble hydroxide) at the place in the gradient where the pH corresponds to the isoelectric point (Haglund, 1967).

EXPERIMENTAL PROCEDURE

Materials

Two artificial soils and one natural soil were used in the investigation to provide a variety of soil properties, including a range of clay mineralogy and initial soil pH. The two artificial soils consisted of a mixture of silica flour and grundite (the latter supplied by Illinois Clay Products Co., Goose Lake, Illinois), and silica flour and bentonite (the latter marketed as "Volclay" and mined at Belle Fourche, South Dakota). The silica flour was added to each test sample in a 70 per cent by weight concentration to give the samples the characteristics of a silty clay. The natural soil was a fat clay

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obtained from the U.S. Army Waterways Experiment Station, Vicksburg, Mississippi. The clay, derived from the Vicksburg area, is locally known as "buckshot clay" because it dries into small buckshot-like granules.

The mineralogy and important index properties of the three experimental soils are summarized in Table 1. Note that soils range from acidic (grundite-silica flour, pH = 4·1) to alkaline (bentonite-silica flour, pH = 9·0). The corresponding clay mineralogy ranges from dominantly illitic to entirely montmorillonitic.

The silica flour used in the bentonite and grundite samples was examined separately by X-ray diffraction and the petrographic microscope, and it was found to consist of quartz almost completely free of impurities. The particles were angular and ranged in size from clay to medium sand (0·5–305 μ), but the bulk of it was silt-size grains (55 μ).

The samples were thoroughly mixed with distilled water and remoulded before being packed into a specially designed electrolytic cell. The samples in general had the consistency of stiff paste with water contents either near the liquid limit or midway between the two Atterberg limits. The experimental soils were not subjected to any other pretreatment prior to their use in the experiments.

Electrolytic cell and method of treatment

The experimental procedure consisted of introducing aluminum electrolytically into samples using a direct current power supply. A schematic diagram of the electrolytic cell and test equipment is shown in Fig. 1. The samples were packed into the enclosed central compartment of a specially designed electrolytic cell. This compartment was flanked on two sides by electrode compartments containing the anolyte and catholyte respectively. A thin resin-bonded porous plate separated the sample from the electrolyte solutions on these two sides. The sample chamber itself was cubic, approximately 10 cm on a side.

Provisions were included in the experimental equipment for monitoring the voltage gradients which developed across the samples, electrical energy input, voltage loss at the electrode-electrolyte interface, pH and electrical conductivity of the electrolyte solutions, and sample temperature. Platinum wire voltage probes were inserted directly into the side of the sample to record the voltage gradient across the soil. Sample temperature was measured with a thermistor inserted into the top of the soil. Both sample temperature and voltage were monitored and recorded continuously during treatment.

Current electrodes (placed in the electrolyte

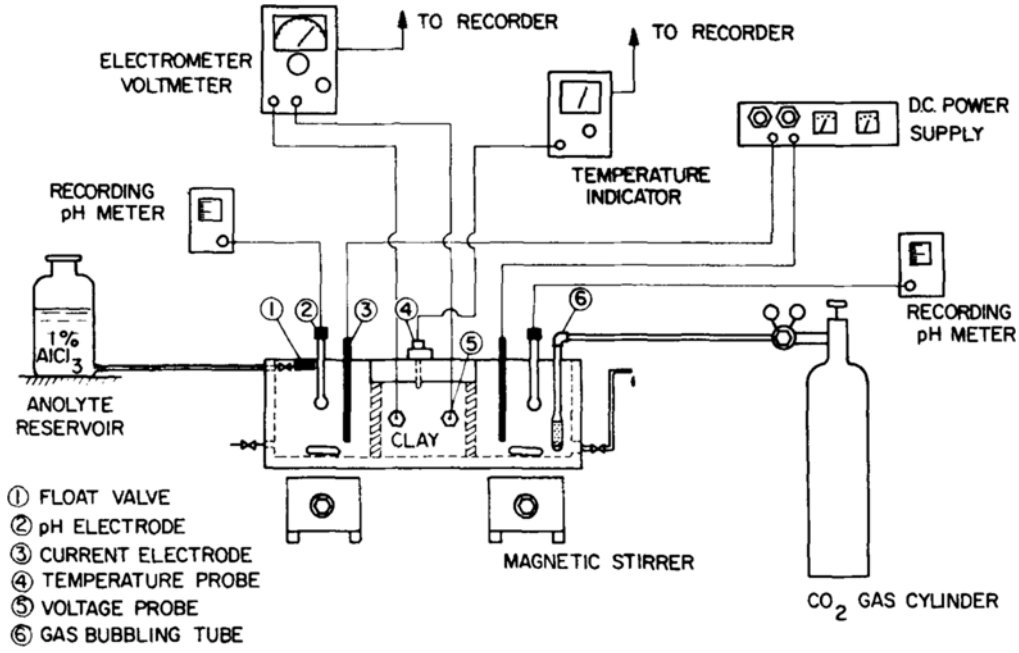


Fig. 1. Schematic diagram of test equipment.

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Table 1. Mineralogy and index properties of experimental soils

Soil	Mineralogic* composition	Atterberg limits LL	PL	Unified soil classification	Principal exchange ions	pH	Source‡
30% bentonite 70% silica flour	Quartz-71% Montmorillonite-27 Feldspar-2	168	23	C	Sodium	9·0	American Colloid Co. Belle Fourche, S.D.
30% grundite 70% silica flour	Quartz-76% Illite-17 Kaolinite-3 Mixed layer-4	27	19	CL	Calcium magnesium	4·1	Illinois Clay Products Co., Goose Lake, Ill.
Vicksburg "Buckshot" clay	†Illite-25% Montmorillonite-25 Quartz-20 Feldspar-20	50	24	CH	Not determined	6·3	U.S. Army Waterways Exp. Station, Vicksburg, Miss.

Notes: *Per cent by weight composition is approximate.
†Less than 74 μ fraction.
‡Silica flour is "Agsco 140", supplied by American Graded Sand Co., Des Plaines, Ill.

compartments) were connected to a constant current d.c. power supply with a maximum rated output of 1 A at 300 V. Current densities on the order of 1–5 mA/cm² were used in the experiments. A 1/16-in. thick copper plate was used as the cathode and a 1/16-in. thick aluminum plate or a 2-in. diameter graphite rod (samples nos. 9–12), as the anode.

A 1 per cent solution of hydrated aluminum chloride constituted the anolyte in every case and a 0·5 per cent solution of sodium chloride, the catholyte. The external source of aluminum was either the aluminum anode, the aluminum chloride anolyte or possibly both. The concentration of aluminum chloride in the anolyte was selected to provide sufficient aluminum ions for electrolytic transfer into the soil and to keep the resistance of the system low enough in order not to exceed the voltage limitations of the power supply. The anolyte was replenished during the course of a test because of evaporation and electro-osmotic losses. Sodium chloride was selected as an inexpensive electrolyte which would not precipitate at the high pH values expected in the catholyte during treatment. Its concentration (0·5 per cent) was selected to give the catholyte the same initial electrical conductivity as the anolyte. Both electrolyte solutions were stirred vigorously during treatment in order to prevent electrode polarization and to improve electrolytic transfer.

The original plan was to apply a direct current for a long enough time to transfer electrolytically into each sample sufficient aluminum to satisfy the requirement for a "gibbsite interlayer filling". This requirement, according to Brydon and Kodama (1966, p. 886) is 16 m-equiv Al/g of montmorillonite for a perfect gibbsite layer. Time, current-voltage limitations, and the development of high resistances during the course of treatments made it difficult to adhere to this original plan. Accordingly, treatment times were selected based on experimental convenience and energy inputs not to exceed 30 k Wh/yd³ of treated soil. This energy input represents a probable upper economic limit based on a survey of energy requirements reported in the literature for a large number of electro-osmotic field installations. A record was kept of the total charge and specific electrical energy input into each sample during the present investigation.

pH Buffering

The effect of pH buffering on the progress and extent of electrochemical induration by aluminum was studied by bubbling CO_2 gas into the catholyte in a number of experiments. This procedure effectively maintained the catholyte pH in the neutral range. The use of aluminum anodes effectively buffered the anolyte at a pH of 3·8. With neither of these provisions, i.e. with graphite anodes in lieu of aluminum ones and *no* CO^2 buffering in the catholyte, the pH extended as low as 1·2 in the anolyte and as high as 12·8 in the catholyte. Tests nos. 7, 10 and 12 employed CO_2 buffering and were essentially duplicate runs of preceding experiments (nos. 6, 9, and 11 respectively) which were unbuffered.

Physico-chemical analyses

A selective extraction procedure was used to determine the form or mode of occurrence of aluminum in the treated samples. This procedure consisted of leaching a small sample of soil with 1N KCl followed by successive extractions on the same sample with 1N $NH_4C_2H_3O_2$ (buffered to pH 4·8), and a 2·5-min boiling extraction in 0·5N NaOH. The amount of aluminum released after each extraction was determined colorimetrically using the Aluminon method (McClean, 1965). The entire leaching-extraction procedure was also run on untreated samples so that comparisons could be made.

According to McClean (1965) and Jackson (1965) the potassium chloride leaching removes only the readily exchangeable aluminum; the ammonium acetate extraction removes soluble aluminum hydroxide and some hydroxy-aluminum polymers which may be strongly absorbed by the clays; the sodium hydroxide extraction removes amorphous aluminosilicates, free alumina (including gibbsite), and the balance of the precipitated, interlayer alumina. The sodium hydroxide extraction is too brief to attack and dissolve appreciable aluminum from the clay structure.

X-ray diffraction analyses

Untreated material was analyzed by X-ray diffraction in order to characterize its mineralogy. Some material was also examined under the petrographic microscope to aid in identification and description. Treated samples were re-analyzed by X-ray diffraction in order to look for evidence of hydroxy-aluminum interlayering in the clays or for the presence of new mineral phases.

Samples for diffraction analysis were disaggregated ultrasonically in deionized water and allowed to settle for a few seconds. The material that remained suspended was transferred by pipette to a porous ceramic tile. Water was removed by vacuum through the tile, and the soil was dried at 21°C in a low-humidity atmosphere.

The samples were analyzed by X-ray diffraction with a Picker Nuclear X-ray unit using Cu$K\alpha$ radiation at a scan rate of 2° 2θ/min from 2 to 35°

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2θ after (1) drying at 21°C at a low humidity; (2) glyceration; (3) heating to 300°C for 30 min; (4) heating to 550°C for 30 min; (5) heating to 700°C for 2 hr.

RESULTS AND INTERPRETATION

Distribution of aluminum in treated samples

The results of analyses for the various forms of aluminum are shown by means of bar graphs in Figs. 2 and 3. These graphs show respectively the amount of KCl-exchangeable, $NH_4C_2H_3O_2$-extractable, and NaOH-extractable aluminum from both anodic and cathodic regions of the treated samples. The results of tests on untreated samples of the three different soils are also shown.

Test No. 3 was not typical in that it employed aluminum electrodes and aluminum chloride electrolyte solutions in both chambers, pH buffering in the catholyte, and a polarity reversal two thirds of the way through the experiment.

Very little exchangeable aluminum was found in the cathodic region of treated samples when the current was not reversed. In two experiments (Nos. 8 and 9) there was no evidence of aluminum deposition of any form near the cathode.

In the case of the bentonite-silica flour samples, the additional aluminum appeared almost entirely in *non*-exchangeable form. On the other hand, in the grundite–silica flour samples, the additional aluminum appeared almost entirely in exchange-

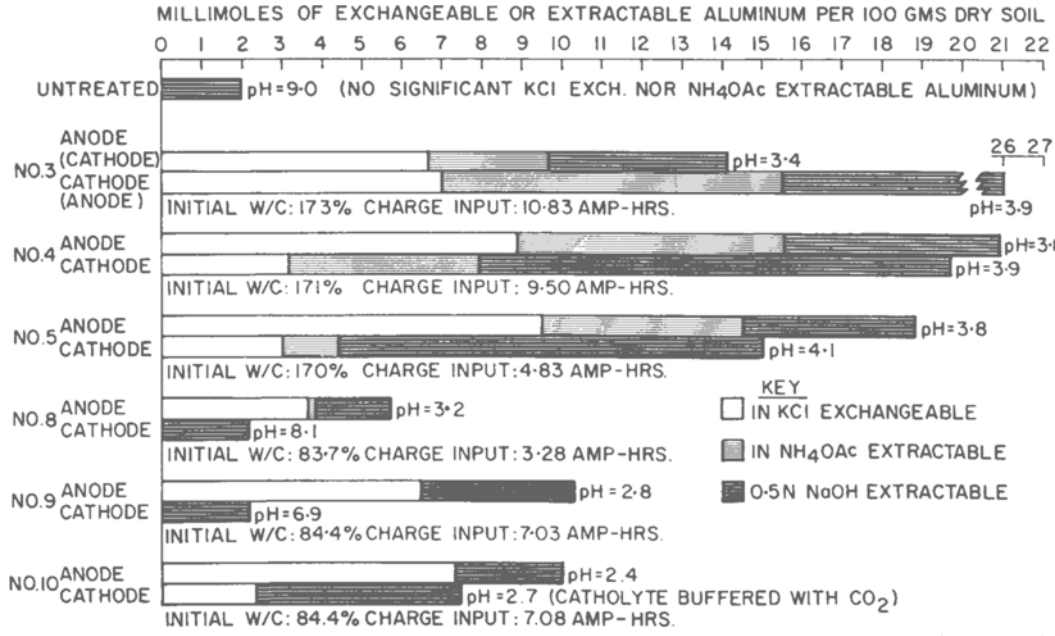


Fig. 2. Final pH and distribution of aluminum in treated samples of bentonite-silica flour.

Initial water content, charge input, and soil pH are also indicated on the diagrams. The effect of initial water content, pH buffering, and charge input on the extent of "aluminization" can best be observed by comparing the results of experiments with the bentonite-silica flour samples as summarized in Fig. 2.

Certain aspects of these analyses deserve comment. At approximately the same charge input, the higher water content samples have a higher aluminum content. Conversely, at a given water content, the aluminum concentration increases with increasing electric charge input.

able form. The natural soil, buckshot clay, was intermediate in this respect. This soil exhibited a comparatively large concentration of extractable aluminum before treatment – probably due to the presence of allophane or another amorphous alumino-silicate.

The source of the aluminum which was detected in the treated samples was not determined exactly. The clays themselves are a potential source; they can give up structural aluminum in very acidic environments. It appears unlikely, however, that this was the major source of the aluminum in the experiments reported herein. This view is based

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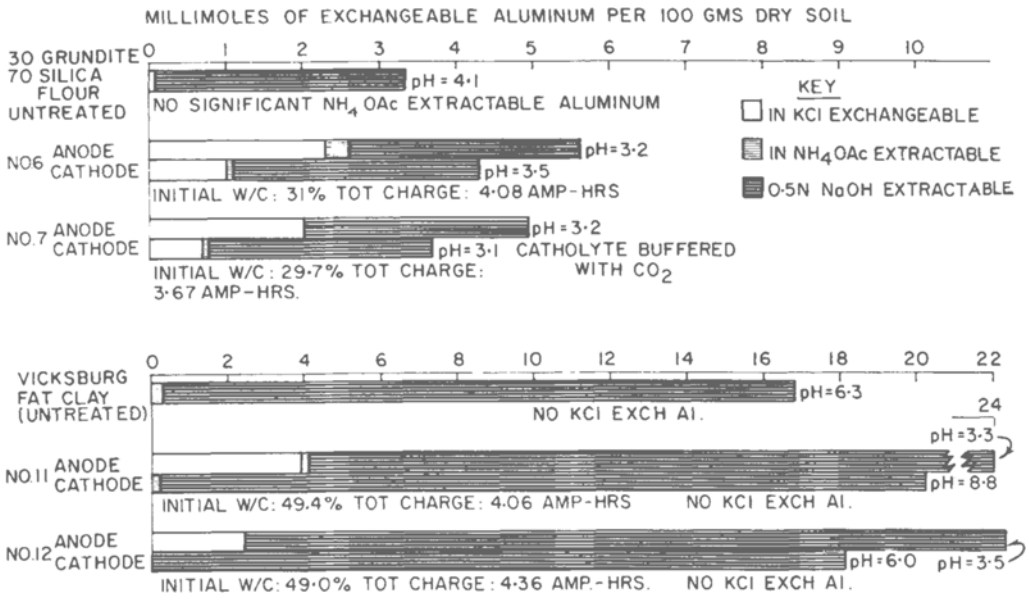


Fig. 3. Final pH and distribution of aluminum in treated samples of grundite-silica flour and Vicksburg "Buckshot" clay.

on the large amounts of both exchangeable and extractable aluminum found in the anodic portions of Samples Nos. 3–5 in which the anolyte was buffered to pH 3·8.

Progress of treatment and energy requirements

The voltage/current relationship and fluctuation in the pH and electrical conductivity of the anolyte and catholyte during the course of a treatment is shown in Figs. 4–6. Even though the conductivity of the external electrolyte solutions increased, the voltage gradient across the samples fell off almost exponentially with time. This was typical of all runs. The *total* voltage required to maintain a constant current, meanwhile, increased to the point where it was necessary periodically to cut back on the current level.

The reason for the decrease in voltage gradient across the sample with time is not clear. The total voltage increase across the system with time was caused in some instances by the behavior of the aluminum anodes. When aluminum is used as an anode, it tends to develop large resistance to current flow (Jenny, 1940). Typical voltage-time curves for aluminum anodes in various electrolyte solutions at constant current density are shown in Fig. 7.

Typical electrical energy requirements (based only on voltage drops across the samples themselves) were on the order of 20–30 kWh/yd^3 of bulk soil treated.

Role of soil pH and pH buffering

The initial soil pH seems to be an important factor in determining the form of aluminum deposited in the treated clay soils. Electrolytically introduced aluminum appears in exchangeable form in the acidic, grundite-silica flour soil and in both exchangeable and non-exchangeable (hydroxy-alumina interlayer) forms in the basic, bentonite-silica flour soil as shown in Figs. 2 and 3.

The pH buffering in the catholyte with CO_2 increased the rate and extent of electrochemical induration. This was true primarily of the more alkaline, bentonite-silica flour soil. The effect of pH buffering is shown quite clearly by comparing the extent of aluminum deposition in the cathodic zones of Samples Nos. 9 and 10 as shown in Fig. 2. Both these samples had identical initial water contents and received the same electrical charge and energy inputs. The buffered sample (No. 10) had a much higher rate of electrolytic aluminum transfer into the cathodic zone.

This difference in rate and extent of electrochemical induration between buffered and non-buffered samples was also indicated by the rate at which the "electrochemical front" moved across the sample from anode to cathode. The position of the front was marked by a sharp color and textural contrast in the bentonite-silica flour samples but was less clearly defined in the other samples. The effect of pH buffering and initial water content on the rate of the electrochemical advance is shown

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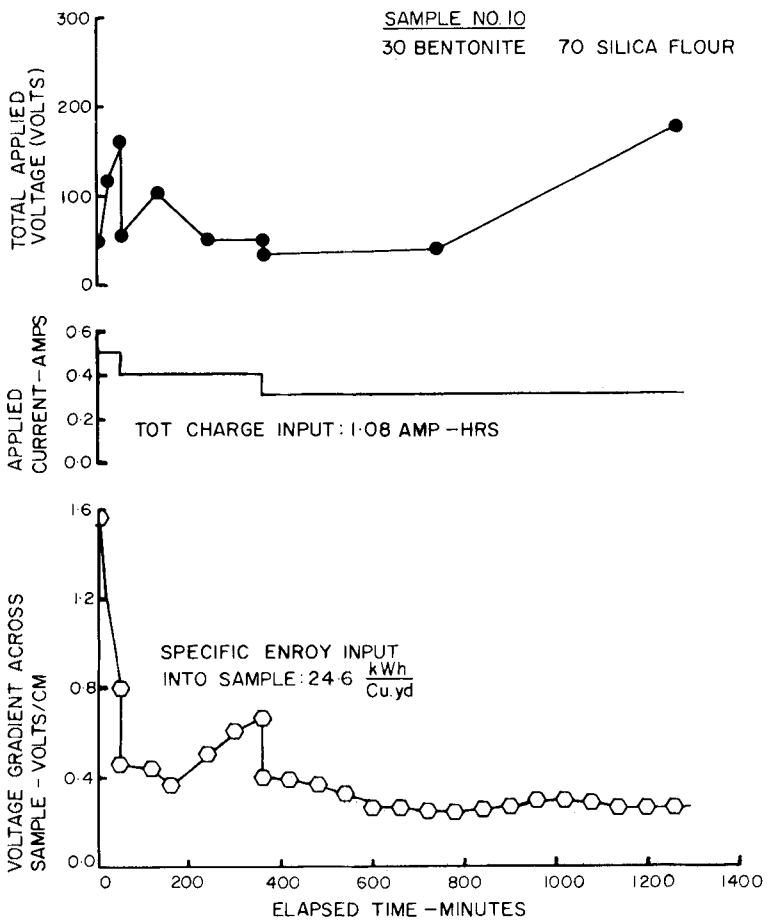


Fig. 4. Energy requirements and voltage-current relationship during electrochemical treatment of sample no. 10.

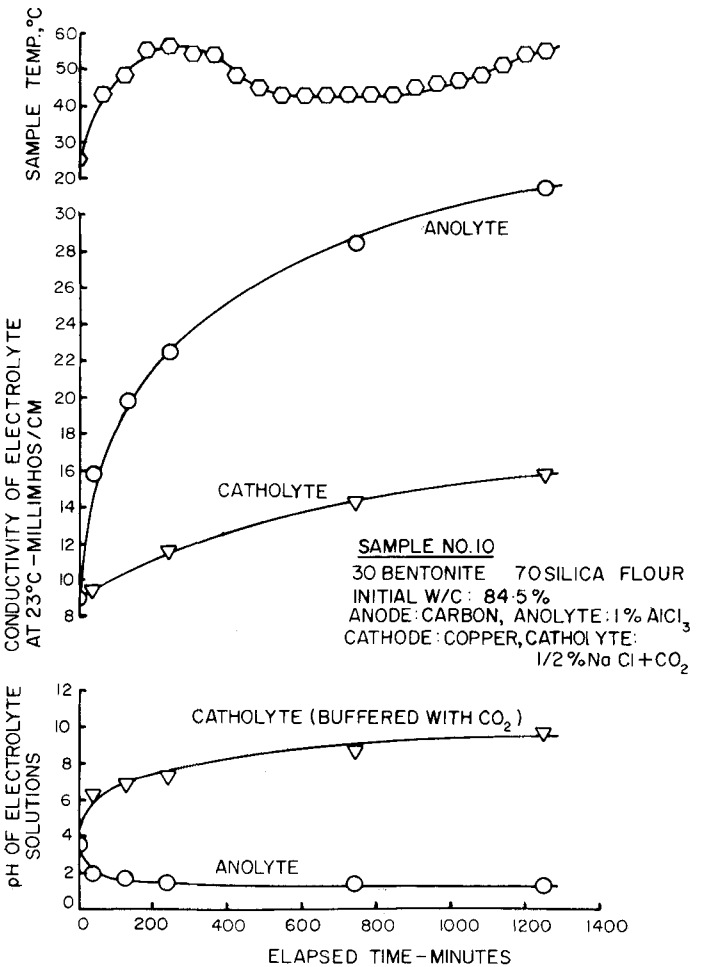


Fig. 5. Temperature, conductivity and pH changes during electrochemical treatment of sample no. 10.

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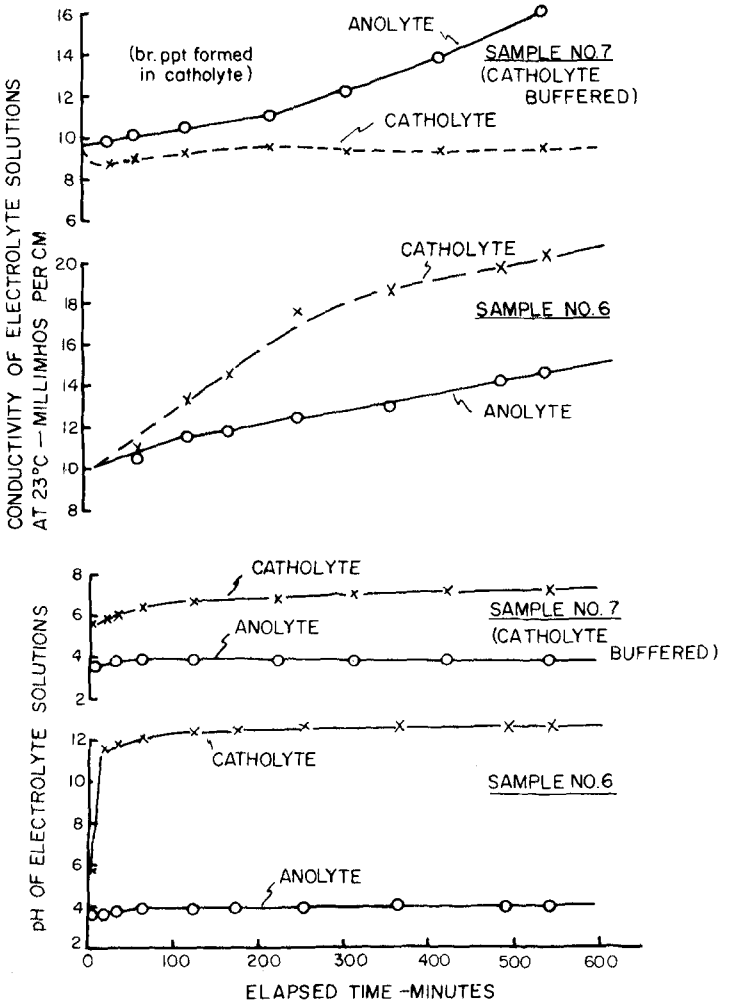


Fig. 6. Effect of CO_2 buffering during electrochemical treatment on the pH and conductivity of electrolyte solutions (grundite-silica flour samples).

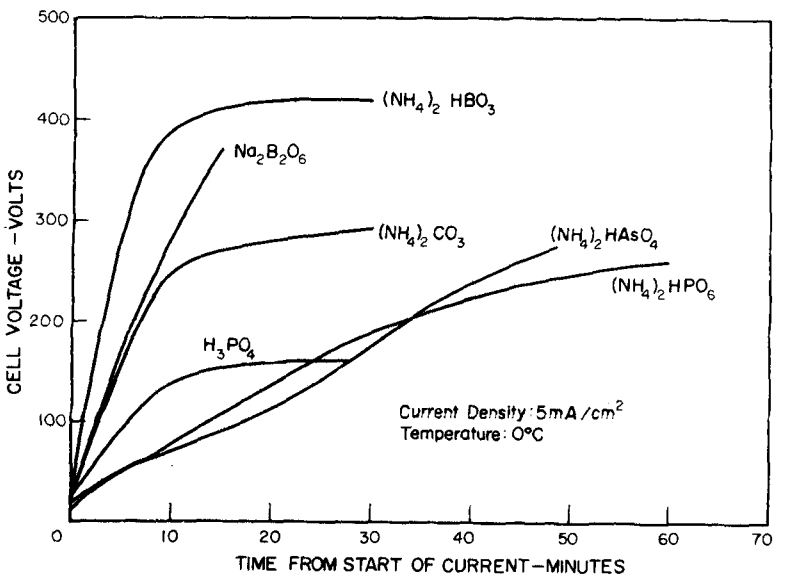


Fig. 7. Development of anodic voltage loss of aluminum with time in different electrolytes (after Jenny, 1940).

in Fig. 8. Note the effectiveness of pH buffering in the catholyte (Samples 3, 8, 10) in actually accelerating the advance, in contrast to the unbuffered runs (Nos. 5 and 9) in which the rate of advance was constantly slowed.

The effectiveness of buffering with CO_2 in maintaining the pH of the catholyte near neutrality (pH = 7) is shown in Fig. 6. The tendency of the aluminum anodes to buffer the anolyte at pH = 3·8 is also shown in Fig. 6. A secondary effect of buffering the catholyte with CO_2 is indicated by the atypical catholyte conductivity for Sample No. 6 (Fig. 6). The atypical conductivity was caused by precipitation of magnesium and calcium carbonate after these ions were displaced from the soil (they are the principal exchange ions in grundite) towards the cathode. This precipitate was present in the cathode chamber.

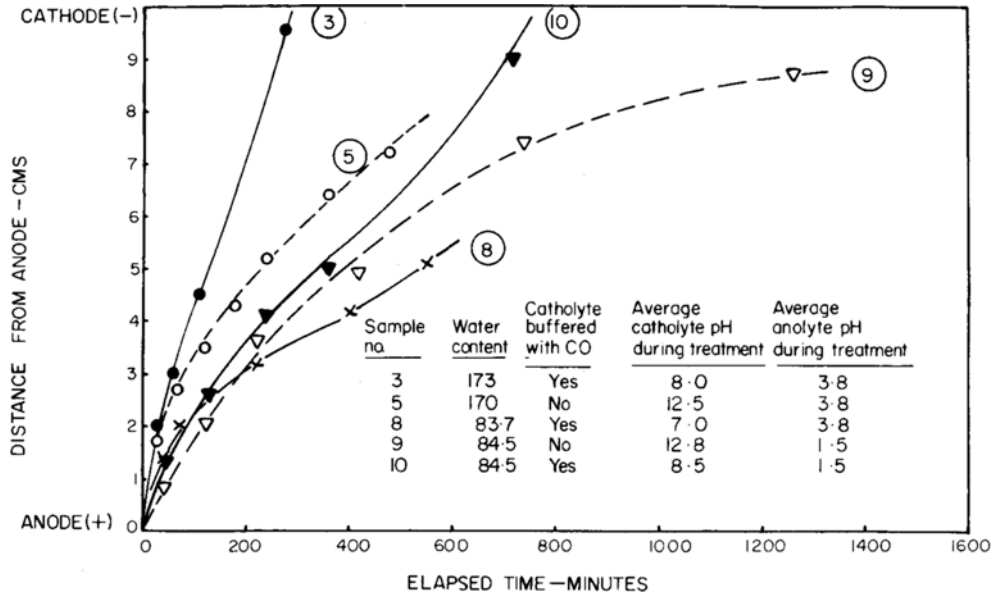


Fig. 8. Effect of initial water content and pH on rate of electrochemical front movement in bentonite-silica flour samples.

X-ray diffraction results

Mineralogy of soils before treatment. The buckshot clay is predominantly montmorillonite, which upon glyceration shows a strong basal spacing at 18·3 Å and a second order spacing at 9·1 Å; higher orders are weak or absent. Present in smaller amounts are illite, kaolinite, quartz, feldspar, and possibly vermiculite and gibbsite. A peculiarity of the montmorillonite in buckshot clay is that it remains expanded to 15·2 Å upon heating to 300°C for 30 min. Under the same heat treatment much of the montmorillonite in the bentonite soil collapses to 10 Å. Grundite consists of illite, mixed layered mica-montmorillonite, kaolinite, and quartz. X-ray diffraction analyses of bentonite before mixing with silica flour showed it to consist predominantly of montmorillonite that upon glyceration shows a rational series of prominent X-ray peaks to the 6th order and traces of gypsum, mica, feldspars, and quartz.

Changes after treatment. X-ray diffraction analysis on soils shortly after electrochemical treatment showed important changes in the bentonite-silica flour soil, but little or none in the grundite-silica flour and the buckshot clay soils.

The important changes created by the treatment show in results of X-ray diffraction analysis in samples heated to 300°C, 550°C, and 700°C. Figure 9 shows typical results of X-ray diffraction analyses of bentonite-silica flour soils heated to 300°C for 30 min. In the untreated soil much of the montmorillonite has collapsed to the 10 Å spacing indicating removal of water between clay layers. Montmorillonite in the treated soils collapsed only to 15·7 and 12·6 Å near the cathode and anode respectively.

Figure 10 shows results of X-ray diffraction analyses of bentonite-silica flour soils heated to 550°C. In the untreated soil a sharp, strong peak at

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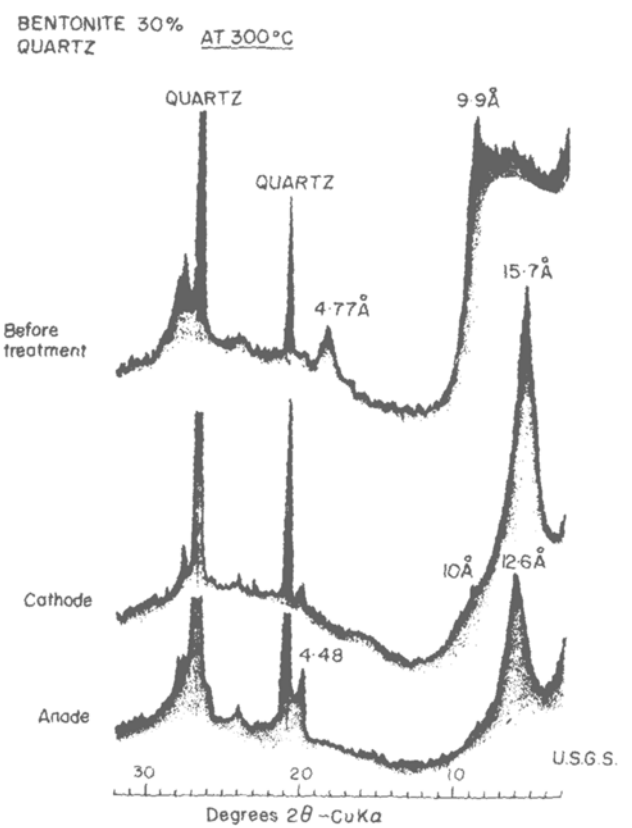


Fig. 9. Typical X-ray diffractograms of bentonite-silica flour soil, before and after electrochemical treatment. Samples for X-ray analysis heated to 300°C for 1/2 hr.

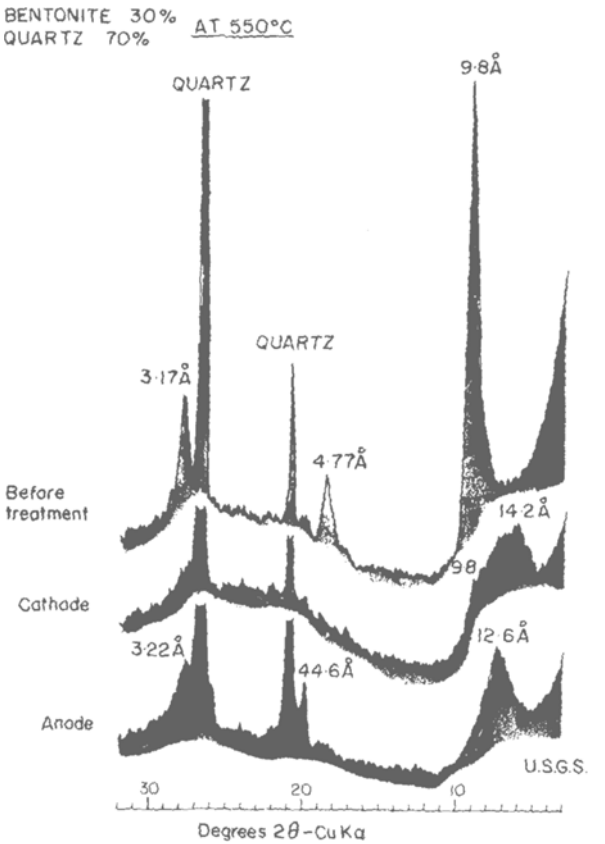


Fig. 10. Typical X-ray diffractograms of bentonite-silica flour soil, before and after electrochemical treatment. Samples for X-ray analysis heated to 550°C for 1/2 hr.

9·8 Å indicates the removal of interlayer water and the collapse of montmorillonite. In contrast, the treated soils show broad peaks. The soil near the cathode shows some montmorillonite collapse to 9·8 Å, but the bulk is held open to higher spacings and peaks at 14·2 Å. The soil adjacent to the anode shows a broad peak with a maximum at 12·6 Å.

In the case of the bentonite-silica flour soils heated to 700°C, the untreated soil is little changed from the 550°C heating, showing a sharp, strong peak at 9·8 Å. The soil from the cathode region shows a broad peak that gives spacings from 9·9 to 12·6 Å. The soil from the anode region gives a broad peak that culminates at 10·2 Å, but ranges from about 9·9 to 11·6 Å.

Summary and conclusions from X-ray diffraction analyses. Electrolytic treatment causes significant changes in the interlayer spacing of montmorillonite in the bentonite-silica flour soil. Little or no change was observed in X-ray diffraction analyses of the buckshot clay or grundite-silica flour soils.

Plasticity tests

The results of liquid limit tests before and after treatment are shown in Fig. 11. Electrochemical treatment reduced the liquid limit of the bentonite-silica flour soil to almost half its original value. The decrease was more pronounced for the anodic region than the cathodic. This may have been caused by a higher electrolytic transfer of aluminum into the anode zone as shown in Fig. 2.

Electrochemical treatment had virtually no effect on the liquid limit of the grundite-silica flour soil, and slightly increased the liquid limit of the buckshot clay.

CONCLUSIONS

Aluminum ions were electrolytically introduced into clay soils, thereby altering their composition and physical properties. By means of X-ray diffraction analyses and selective chemical extraction procedures it was possible to determine the distribution and mode of occurrence of aluminum

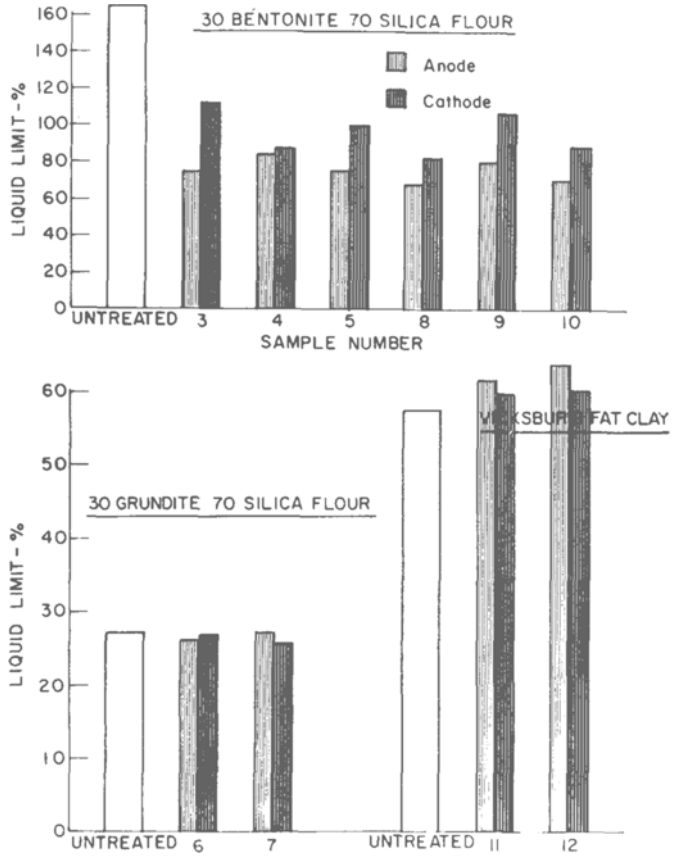


Fig. 11. Effect of electrochemical treatment on the liquid limit of the experimental clay soils.

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in the treated samples. Aluminum was present in both exchangeable form and as a hydroxy-aluminum interlayer in the treated bentonite soil and was found primarily in exchangeable form in the treated illite soil.

Electrolytic treatment with aluminum anodes (or anolyte) changed the character of the montmorillonite in the bentonite soil. Montmorillonite in the treated soil did not collapse to 10 Å upon heating and showed interlayer spacings as great as 12·6 Å upon heating at 700°C for 2 hr. No evidence was found for deposition of gibbsite or other crystalline forms of aluminum hydroxide in the treated soils.

Buffering the pH of the catholyte with carbon dioxide increased the rate and extent of penetration of aluminum into the bentonite soil.

The liquid limit and hence the plasticity of the bentonite soil was greatly reduced by electrochemical treatment. On the other hand, the liquid limit of the illite soil was virtually unaffected by treatment, and slightly increased in the case of the buckshot clay.

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Résumé—La composition et les propriétés physiques de trois sols argileux ont été modifiées par l'introduction d'aluminium sous un gradient électrochimique afin de définir le rôle du pH dans le contrôle des changements affectant la composition des sols et la possibilité d'amortir le pH au cours du traitement électrochimique. Les méthodes de diffraction des rayons X et d'extraction chimique sélective ont été utilisées pour déterminer la distribution et le mode d'intervention de l'aluminium dans les prélèvements traités. L'aluminium a été détecté dans les prélèvements traités à la fois sous la forme échangeable et en tant que couche intermédiaire d'hydroxy-aluminium. Les minéraux d'oxyde d'aluminium tel que le gibbsite n'ont été détectés dans aucun des échantillons traités. La minéralisation par les ions d'aluminium a été activée et intensifiée dans les sols de bentonite en amortissant le catholyte avec de l'oxyde de carbone. La plasticité des échantillons de sols de bentonite du Dakota du Sud a été réduite notablement par le traitement électrochimique, tandis que la plasticité d'un sol illite de l'Illinois et un sol illite-montmorillonite du Mississippi n'était pratiquement pas affectée. Presque tous les échantillons traités ont montré quelque degré d'induration électrochimique ou de minéralisation. L'induration était plus prononcée dans les échantillons de sols bentonite avec des teneurs en eau élevées et un pH alcalin surtout à cause des couches intermédiaires d'hydroxy-aluminium dans l'argile. D'autre part la couche intermédiaire était négligeable dans les échantillons de sols illites avec pH faible: le principal effet du traitement électrochimique dans ce cas était l'apport d'aluminium dans les zones d'échange.

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Kurzreferat – Die Zusammensetzung und die physikalischen Eigenschaften von drei Ton-Erden wurden durch Einführung von Aluminium unter Steuerung der elektrochemischen Merkmale eingeführt, um die Rolle des pH-Wertes bei der Regelung von Änderungen in der Bodenzusammensetzung und die Möglichkeit einer pH-Pufferung während elektrochemischer Behandlung zu untersuchen.

Sowohl Röntgendiffraktions-als auch selektive chemische Extraktionsmethoden wurden angewandt, um die Verteilung und Erscheinungsform des Aluminiums in den behandelten Proben zu bestimmen. Das Aluminium wurde in den behandelten Proben in sowohl austauschbarer Form als auch als Hydroxy-Aluminium-Zwischenschicht gefunden. Aluminiumoxydminerale wie Gibbsit wurden in keiner der behandelten Proben festgestellt. Die Mineralisierung durch Aluminium-Ionen wurde in Bentonit-Erden durch Pufferung des Katholyten mit Kohlendioxyd beschleunigt und verstärkt.

Die Plastizität der Bentonit-Erdproben von Süd-Dakota wurde merklich durch elektrochemische Behandlung reduziert, während die Plastizität einer Illit-Erde aus Illinois und einer Illit-Montmorillonit-Erde aus Mississippi verhältnismäßig unberührt blieb. Fast alle der behandelten Proben wiesen eine gewisse elektrochemische Verhärtung oder Mineralisierung auf. Die Verhärtung war in Bentonit-Erdproben mit hohem Wassergehalt und alkalischem pH besonders beachtlich, vor allem wegen der Hydroxy-Aluminiumschichtung im Ton. Andererseits war die Schichtung in Illitbodenproben mit niedrigem pH-Wert vernachlässigbar gering. Die Hauptwirkung der elektrochemischen Behandlung bestand in diesem Fall in der Bereicherung der Austauschpunkte mit Aluminium.

Резюме—Состав и физические свойства трех глинистых грунтов были изменены добавлением алюминия при электрохимическом градиенте для определения роли pH в контролируемых изменениях состава почвы и возможности буфферного действия на pH электрохимической обработки. Для определения распределения и формы нахождения алюминия в обработанных образцах использованы как дифракция рентгеновских лучей, так и селективные химические вытяжки. Алюминий в обработанных образцах обнаружен как в обменной форме, так и в виде гидроксиалюминиевых межслоевых выделений. Минералы свободной окиси алюминия например гиббсит, ни в одном из обработанных образцов обнаружены не были. Минерализация при участии иона алюминия была ускорена и усилена в бентонитовых грунтах при использовании углекислоты в качестве буфера католита.

Пластичность образцов бентонитового грунта из Южной Дакоты заметно уменьшалась после электрохимической обработки, тогда как пластичность иллитового грунта из Иллинойса и иллито-монтмориллонитового грунта из Миссисипи практически не изменилась.

Почти все обработанные образцы обнаружили некоторую степень химического затвердевания или минерализации. Затвердевание было наиболее отчетливым в образцах бентонитового грунта с высоким содержанием воды и щелочной реакцией, в основном благодаря наличию гидрооксиалюминиевых межслоевых выделений в глинистом минерале.В образцах, иллитового грунта с низкими pH межслоевые выделения были весьма незначительными, главным эффектом электрохимической обработки в этом случае было увеличение содержания обменного алюминия.

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