The Effect of Electrodialysis on Several Kaolins

by

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Approved:

In Charge of Major Work

Head of Department

Dean of Engineering

Chairman, Graduate Committee
Acknowledgement

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Abstract

Six Kaolins were chosen at random. These Kaolins were electrodialyzed in a Mattson type dialysis cell. Titration curves were run on these both before and after being dialyzed to determine base exchange capacity and optimum pH. Debye-Scherrer x-ray powder diffraction patterns were made on each Kaolin both untreated and electrodialyzed in order to determine if electrodialysis had any effect on the crystal structure of the Kaolin. Quantitative spectrographic analyses were made to determine what elements and how much of each element was removed by dialysis. The same process was run and tests were made on Tennessee Ball Clay and Bentonite as a basis of comparison. It was confirmed that the Bentonite was decomposed by electrodialysis.
Introduction

In present day research in many fields, the tendency is becoming more and more prevalent to attempt to explain physical phenomena in terms of the atomic theory or its corollaries. It is assumed that any physical or chemical change in a substance has its fundamental explanation in the behavior of the molecules, atoms or ions in this substance.

This investigation is an attempt to explain the process of electrodialysis in just such a manner when such a process is carried out on Kaolin. In addition to this study of the process, an attempt is made to classify the clays studied according to their base exchange capacity by means of their optimum pH. Such information would eliminate, without further tests, the uncertainties of work with electrolytes on these clays. This is important in ceramic work with slips and their flocculating and deflocculating qualities.

Clays, as they are mined, have a number of adsorbed ions present, adhered to the surface of the clay. These ions are present in different amounts depending on the Kaolin and the amount of impurities to which it has been exposed, by the working of the Kaolin and the refining processes to which it has been subjected.

In this investigation a Mattson type Electrolysis cell is used to replace the cations with the H ions and the anions with OH ions. This process is studied by means of titration curves, spectrographic analysis and x-ray analysis. Except for the use of pH measurements this is believed to be the first time electrodialysis has been studied by such measurements. These latter two measurements have the advantage of giving information, not only of the kind of ion, acid or basic, which has been replaced but specifically the element from which the ion was derived and quantitative measurements of this ion. X-ray studies gave specific information of the effect of electrodialysis on the crystal structure of the substance. In one instance this was considerable.

Barker and Truog explain optimum pH in the following manner.

To a series of 20 gram samples of the clay, contained in beakers, 50 c.c. of distilled water with varying amounts of sodium carbonate ranging from 0.1 to 1.0 percent, based on the dry weight of the clay, are added to each of the beakers. After mixing, the pH of each of these mixtures is determined with a Beckman pH meter using a glass electrode. The results are plotted with pH values on the vertical axis and percent of sodium carbonate on the

horizontal axis. At a certain stage, this curve usually flattens out and becomes practically horizontal. The pH range which corresponds to this stage in the curve is the optimum pH range for the clay under consideration.

The above expression, optimum pH, should not be confused with ultimate pH which is explained by Henry and Taylor. Electro-dialyzed clay, having only H ions and OH ions adsorbed, may be expressed as H-clay-OH. From this complex, in aqueous suspension, H ions and OH ions may be thought of as dissociating until an equilibrium is reached. The hydrogen ion concentration of this suspension is known as the ultimate pH. In other words, it is the pH of the clay suspension when all the adsorbed ions have been replaced by either H ions or OH ions.

The first question this investigation attempts to answer is, are the ions which are assumed to be adsorbed actually present. This immediately presents the next problem. If they are present what are they and how much is present. This work has been done to answer the above questions and further to show that the process of electrodialysis will remove these adsorbed ions and to what extent this removal is affected. It is further attempted to show

that in Kaolin the crystal structure of the Kaolinite is not affected but in some other substances the structure may be affected and the purifying process of electrodialysis becomes useless.

Finally knowing the answers to the above questions an attempt is made to classify it and thus add to the store of fundamental information about Kaolin.
Review of Literature

A review of literature revealed such a wealth of material that even to list the publications would be impractical. However, most of this work on base exchange was done on whole soils. A few papers were found which confined the work to the materials in which ceramic engineers are interested.

S. E. Mattson gives a description of the three chambered electrodialysis cell which he has used in the study of electrodialysis of soils. This cell has become known as a Mattson type cell. Enough information is given so that any person desirous of building such a cell could do so from this description.

The exchangeable bases are usually regarded as being present in the adsorbed condition. It is further stated that bases are present in two conditions defined as exchangeable and nonexchangeable. Hissink has assumed that the exchangeable bases are adsorbed on the surfaces of soil particles.

König, Hasenbaumer and Kuppe studied the amount of material removable from different soils by an electric current and found that there was some correspondence between the

material removed by electrodialysis and that removed by steam and hydrogen peroxide. Treatment over a period of time removed all lime, soda and sulphur but only a small part of the magnesia potash and other elements. Mattson found that electrodialysis is similar to ordinary dialysis but it is much more rapid and it also affects a separation of the diffusible ions of opposite charge.

Kelley, Dore and Brown showed that the chief effect of grinding soil colloids was to increase the replaceability of their magnesium to a great extent.

Henry and Taylor state that almost all of the information on the chemical behavior of soils is applicable to the study of the behavior of ceramic clays. They state that clays show adsorption, flocculation and deflocculation, gel formation and swelling under the influence of dilute electrolyte solutions, and that clay particles in aqueous suspension assume a charge and migrate toward an electrode when subjected to the influence of a direct current. They further point out that although adsorption seems to be a surface phenomenon it is a function of both the amount of surface and the amount of surface activity.


In this same line Meyer\textsuperscript{8} states that a clay with larger particles may show more adsorptive power than a clay with smaller particles and consequently larger surface, because the larger particles have a greater surface activity.

Graham and Sullivan point out that there are two types of base exchange reactions recognized.\textsuperscript{9} One is the replacement of one cation in the outer Helmholtz double layer with another cation. In the other, cations of the crystal lattice are replaced by other cations which assume the geometric position of those they displace. This gives a lattice which has different optical properties than the original.

In their discussion of the electrodialysis of bentonite it was stated that the electrodialysis of bentonite did not reach completion even in 72 hours and it was believed that the bentonite was decomposed. They list and compare the following methods of determining exchangeable bases:

1. Analysis by electrodialysis
2. Analysis by leaching
3. Analysis of Exchanged Metallic Bases
   a. Ultimate method
   b. Proximate carbonate method
   c. Proximate sulfate method


Barker and Truog \(^\text{10}\) show how the process of clay treatment may be controlled through the use of pH measurements. They use the pH curve for obtaining this information. They list three different pH curves and discuss them and the manner of using them in control of plant operations. Kelley, Dore and Brown \(^7\) show a number of \textit{x-ray powder diffraction patterns of the effect of grinding of bentonite on crystal structure}. However, nothing could be found which supported through \textit{x-ray analysis} Graham and Sullivan's statement concerning the decomposition of bentonite. There are a number of standard works on \textit{x-rays and crystal structure} as well as spectral analysis on which the work of this investigation is based. These publications are listed in the bibliography.

Procedure

Construction of cell:

The cell used in this investigation was a Mattson type\textsuperscript{4} which is described and diagramed in Norton's Refractories.\textsuperscript{11} The basis of the cell was the case of a discarded storage battery. This battery case was cut into three parts along the partition of the cells in the battery. This separated the case into three parts as is shown in figure 1.

![Figure 1.-Dialysis cell with upper clamp removed showing how cell separates into three parts for the insertion of the parchment paper.](image)

The edges which would come into contact were ground with carborundum powder on a lap to make a water tight seal. From 3/8" x 12" bolts were used to clamp the three component parts together. Parchment paper especially manufactured for

electrodialysis cells was obtained from Arthur H. Thomas Company for use in the cell. A sheet of this parchment was placed between each component part of the cell. This was reinforced by a cloth backing. The assembled cell then consisted of a container divided into three parts by the cloth reinforced parchment paper, the whole being water-tight. The middle compartment had a capacity of 2500 c.c. and each of the end compartments had a capacity of 1500 c.c. In one end compartment a carbon cathode was suspended and in the opposite end compartment a copper anode was suspended. Any source of D.C. will suffice as long as it has a voltage of 90 volts or greater. Current, of course, depends on the resistance through the cell.

A rotating paddle actuated by an electric motor was introduced into the center compartment to keep the clay suspension agitated. Although this stirring is not absolutely necessary it will hasten the process to completion. Figure 2 shows the complete cell with rectifier.

In this apparatus the source of current was the standard 110 volt A.C. line. This current was rectified by the use of two 866A mercury rectifiers connected in parallel. The circuit diagram of this rectifier is shown in figure 3. This gave a D.C. output voltage of 160 volts and a maximum current of 3 amperes. No filtering was used in the D.C. circuit. A milliammeter was connected in series with the D.C. circuit and a voltmeter across it.
Figure 2.-Dialysis cell with electrodes in place and connected to rectifier. A frame holds the stirring motor in place over the cell.

Figure 3.-Diagram showing rectifier and D.C. circuit through the dialysis cell.
Operation of the Cell:

A sample of 200 grams of the clay to be electrodialyzed was placed in a mechanical mixer and about 1 liter of distilled water added. The mixer was run until the suspension was of uniform consistency. The suspension was then transferred to the center compartment of the cell and enough distilled water added to fill the compartment completely. The end compartments were filled with distilled water. The electrodes were inserted in the water in the end compartments and the current turned on. A reading of the current on the milliammeter was recorded. From time to time the pH of the catholyte and the pH of the clay suspension being treated was taken. Also a reading of current was made. This was done in order to determine when the process reached completion. When these readings reached a constant value it was decided that the process had reached or was very close to completion. In each case this was about 50 hours but each Kaolin was dialyzed for 72 hours. It was necessary to add water from time to time to all compartments to make up for leakage and evaporation.

When the process had reached completion the clay suspension was removed and placed in a dryer at 110°C. to remove all water.
Titrations:

A standard 0.01N solution of sodium carbonate was made up. Sodium carbonate was used because it was not deliquescent and a standard solution could be made quite accurately with it.\footnote{12} This solution was used to standardize a 0.01N solution of HCl. These two solutions were not used in working on the clay but were used to standardize one tenth normal solutions of NaOH and HCl. This insured having a constant standard by which the working solutions could be measured.

Into each of fourteen Erlenmeyer flasks 5 grams of the clay to be titrated were placed. Into the first flask 5 c.c. of 0.01N NaOH were run. This made one milliequivalent of base \footnote{15} (see page \textit{Appendix}). Two M.E. of base were run into the second flask. This was continued until there were nine flasks containing successively the following M.E. of base 1, 2, 3, 4, 5, 6, 8, 10, 15. This was repeated with the 0.01N HCl using four of the five remaining flasks. Acid was run into the flasks in the amounts of 1, 2, 3 and 4 M.E. No acid or base was added to the remaining flask. Enough distilled water was added to each flask to make the contents up to 75 c.c. These flasks were stoppered, packed in the jars of

\footnote{12} E. F. H. Fish, \textit{Quantitative Analysis}, Blakiston's Son & Co., Inc., Philadelphia (1931)
a pebble mill with cloth and rotated in the mill for three hours to make certain the contents were thoroughly mixed.\textsuperscript{13}

A milliequivalent is one-thousandth of a gram equivalent weight. One equivalent weight of NaOH being 40 grams, one milliequivalent is 0.04 gram.\textsuperscript{14} This means that 0.04 gram of NaOH must be added to 100 grams of the clay to give 1 milliequivalent of base per 100 gr of clay.

The pH of the contents of each flask was determined with a Beckman pH meter using a glass electrode. A duplicate run was made in determining pH because the solutions and the pH meter were both very sensitive to the slightest impurity. If the two readings did not check within 0.5 of a pH unit a third run was made on that particular mixture. If this did not check the meter was checked with a standard (pH-7) solution and the sample checked for contamination. The pH meter was checked with the standard solution before and after each run. The pH readings taken on the mixtures were recorded and used to plot the curves from which the optimum pH was obtained. The pH of the contents of the flask of dialyzed clay which had neither base nor acid added gave the ultimate pH of that clay.

The results were plotted on a graph with milliequivalent

\textsuperscript{13} A. L. Johnson and F.H. Norton, Preparation of a Purified Kaolinite Suspension, Jour. Amer. Cer. Soc., 24, 64 (1941)

of acid or base per 100 grams of clay along the horizontal axis and pH along the vertical axis. The Optimum pH of the clay was obtained from this curve.

The x-ray analysis\textsuperscript{15}

The powder method of crystal analysis makes use of the random orientation of crystal planes in powdered specimen. In this investigation monochromatic radiation produced by filtration was used.

\textbf{Figure 4.}–X-ray tube with two Debye–Scherrer powder diffraction cameras in place. A one RPM motor is in place on the right hand camera.

\textsuperscript{15} W. Richardson - Notes on x-ray lecture by Prof. Richardson given at V.P.I. winter quarter 1947
This was obtained from a copper target in the x-ray tube filtered by a nickel foil filter. This gave monochromatic radiation of x-rays in which the wavelength was 1.539\AA. Such an x-ray apparatus with two Debye-Scherrer powder diffraction cameras in place is shown in figure 4. Lead shields are generally employed to give protection for the worker but have been removed to afford a better view of the instrument. The crystals were oriented by use of the Debye-Scherrer powder diffraction camera so that the correct angle $\theta$ for diffraction will take place according to the Bragg equation, $\lambda = 2d \sin \theta$. In the Debye-Scherrer camera the film is placed on the circumference of a cylinder with the sample at the center as is shown in figure 5.

**Figure 5.** A diagram of the Debye-Scherrer x-ray powder diffraction camera. The distance, $S$ in mm, is measured on the circumference between the two sides of the angle of diffraction.
A monochromatic beam of x-rays as defined above will pass through the pin hole system, strike the specimen and be diffracted to the sides of the camera giving an effect on the photographic film. The main beam will pass out the opposite side of the camera through the hole cut in the film for the purpose. The developed film was the negative from which the prints were made which are shown in the results. The hole cut in the film prevents fogging of the film due to scattering of the x-ray from the film and also prevents spurious back reflection lines from the silver in the emulsion.

![Figure 6](image)

**Figure 6.** - A comparator with millimeter scale used in measuring powder diffraction patterns.

The angle $\theta$ may be measured directly from this film. It will be noted in figure 5 that the x-ray will be diffracted on both sides of the specimen. Half of the angle formed by
the two diffracted rays will be the angle \( \theta \). This angle may be measured directly by flattening out the film, measuring the distance between any two corresponding points with a comparator, figure 6, and taking half of this distance. The camera is so constructed with a diameter of \( \frac{180^\circ}{\pi} = 57.3 \text{ mm} \) that this distance expressed in mm. will be numerically equal to the angle \( \theta \) in degrees. The mathematics involved in this design are given below. From the data so obtained it is possible to calculate the facts concerning the crystal structure of the specimen. A great many facts may be calculated but a complete crystal analysis of the Kaolins studied is beyond the scope of this paper. The principle interest is the answer to the question: Is the crystal structure changed? This is explained in the discussion.

The diameter of the camera is chosen so that:

\[
\frac{3 \text{ mm.}}{2} = \theta
\]

\[
\frac{76.2}{2} = \theta
\]

\[
38.6 = \theta
\]

where:

\[
\frac{1}{d^2} = \frac{4 \sin^2 \theta}{\lambda^2}
\]

\[d = \text{grating space in Angstrom} \]

\[
\frac{1}{d^2} = \frac{4 \sin^2 38.6}{1.539^2}
\]

\[\lambda = \text{wavelength of x-ray used} \]

\[
\frac{1}{d^2} = 66 \text{A}
\]

\[\theta = \text{angle of diffraction} \]

\[d = 1.23 \text{ A} \]

This is the grating space which diffracted the x-ray beam.
Figure 7.—Shows the parabolic mirror and the film plate holder. Camera was set under the grating pointing away from it.

Figure 8.—Shows the grating with the slit just to the left. The disk with the motor for reducing the amount of light is shown at the left. Camera was set in front of and pointing away from the plate holder.
Figure 9.- A diffraction grating mounted in parallel light.
The Spectrographic Analysis:

Spectrograms were made of each Kaolin D.C. carbon arc. The arc gives a discontinuous spectra which are radiated from atoms or molecules in a vapor state which have stored up excess energy and then radiates it as luminous energy. Quantitative spectrochemical analysis is based on the fact that when an element is present in a matrix in smaller and smaller quantities the spectral lines of this element grow weaker and disappear in definite order. A straight line relationship exists between the concentration of the element and the concentration of the element and the intensity of the spectral lines caused by the element.\(^6\)

Spectrograms of each of the Kaolins were made before and after the clay was electrodialyzed. A grating having 30,000 lines per inch mounted in parallel light was used, figures 6, 7 and 8. Since the amount of Silica in the Kaolin was assumed to be the same both before and after electrodialysis the Silicon in each Kaolin was used as an internal standard. In making each spectrogram a few milligrams of the clay were used and in each case the sample was vaporized completely.

After developing, a principle line was identified for each element to be studied. These lines were purposely picked near one of the lines of Silicon as this line was to be the standard. After these lines were identified and marked on the

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spectrogram their densities were measured. In each case the
density of the Silicon line in the particular spectrogram was
also measured.

The decrease in the quantity of the element in each case
was calculated in the following manner:

The intensity of the spectrum of each
element was calculated by the following
expression:

\[ \log \frac{S_1 - S_0}{S_2 - S_0} = D \]

- \( S_0 \): The density of the darkest line on the spectrogram or a standard dark line
- \( S_1 \): density of the spectrogram in the region of the line of the element
- \( S_2 \): density of the line of the element
- \( D \): The intensity of the line of the element

Since it is practically impossible to make two or more
runs on any spectrograph the same the Silicon content of the
sample was used as in internal standard. This enables the
operator to calculate his results on the same basis.
In sample No. 1 and 1E.

No. 1 
\[ \log \frac{S_1-S_0}{S-S_0} = D \]
\[ \log \frac{13.8-4.8}{9.5-4.8} = D \]
\[ \log \frac{9}{4.7} = D \]
0.282 = D This is the relative intensity of the Si line in sample No. 1

No. 1E 
\[ \log \frac{S_1-S_0}{S_2-S_0} = D \]
\[ \log \frac{11.3-4.8}{6.6-4.8} = D \]
0.582 = D This is the relative intensity of the Si line in sample No. 1E

Now in each sample the spectrum of Si was made by the same amount of Si. This means that each measurement made on the spectrogram of sample No. 1 has the relative intensity of 0.282 and this must be brought up to 0.582 before a comparison can be made. This is done by multiplying each intensity in No. 1 by the factor \[ \frac{582}{282} = 2.06 \]

To calculate the amount of CaO the intensity of the spectral line of a Ca in both samples is calculated.
Log \[ \frac{31 - 3_0}{3_2 - 3_0} = D \]

Log \[ \frac{13.8 - 4.8}{6.3 - 4.8} = D \]

0.410 = D Sample No. 1

Log \[ \frac{31 - 3_0}{3_2 - 3_0} = D \]

Log \[ \frac{11.7 - 4.8}{6.3 - 4.8} = D \]

0.517 = D Sample No. 1E

However, D for sample No. 1 must be multiplied by 2.06 to bring it to the same basis as sample No. 1E.

0.410 \times 2.06 = 0.845

This intensity of the line is proportional to the amount of Ca present in each of the samples.

Therefore:

\[ \frac{0.517}{0.845} \times 100 = 61.2\% \]

Sample No. 1E has 61% as much Ca as sample No. 1.

Knowing the amount of CaO in sample No. 1, it is simple to calculate the amount of CaO in No. 1E.

0.10 \times 0.61 = 0.061% CaO in 1E

It follows that 0.039 gr of CaO per 100 grams of clay has been removed by electrodialysis.

In a similar manner, the amount of element removed by electrodialysis can be calculated. These amounts are tabulated in a table in Results.
LAKELAND FLORIDA KAOLIN
United Clay Mines

Optimum pH
Electrodialyzed
Untreated

Ultimate pH

Milliequivalent per 100 grams of clay

M.E. HCl
NaOH

1 2 3 4 5 6 7 8 9 10

pH 5 4 3 2
FLORIDA KAOLIN
E.P.K. Company

Optimum pH
Ultimate pH

Untreated
Electrodialyzed

M.E. HCl
NaOH

Milliequivalent per 100 grams of clay
NO KARB KAOLIN
E.P.K. Company

Optimum pH

Ultimate pH

Untreated
Electrodialyzed

Milliequivalent per 100 grams of clay

M.E. HCl

NaOH
Debye Scherrer X-Ray Powder Diffraction Patterns

Figure 10.- Lakeland Florida Kaolin, United Clay Mines Untreated

Figure 10A.- Lakeland Florida Kaolin, United Clay Mines Electrodialyzed

Figure 11.- Putnam Florida Kaolin, United Clay Mines Untreated

Figure 11A.- Putnam Florida Kaolin, United Clay Mines Electrodialyzed
Debye Scherrer X-Ray Powder Diffraction Patterns

Figure 12.-Florida Kaolin, E.F.K. Company
Untreated

Figure 12A.-Florida Kaolin, E.F.K. Company
Electrodialyzed

Figure 13.-No Karb Kaolin, E.F.K. Company
Untreated

Figure 13A.-No Karb Kaolin, E.F.K. Company
Electrodialyzed
Debye Scherrer X-Ray Powder Diffraction Patterns

Figure 16. - Tenn. Ball Clay No. 5, Ky.-Tenn. Clay Company Untreated

Figure 16A. - Tenn. Ball Clay No. 5, Ky.-Tenn. Clay Company Electrolytically

Figure 17. - Bentonite, American Colloid Company Untreated, Run 30 minutes

Figure 17A. - Bentonite, American Colloid Company Electrolytically, Run 30 minutes
Debye Scherrer X-Ray Powder Diffraction Patterns

Figure 17B.- Bentonite, American Colloid Company
Electrodialyzed, run 60 minutes

Figure 17C.- Bentonite, American Colloid Company
Electrodialyzed, run 120 minutes
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The following figures are prints made from the spectrograms of the Kaolins investigated. Each spectrogram has been given a key number which is printed on it. The key numbers are given below:

K1 - Lakeland Florida Kaolin - Untreated
K1E - Lakeland Florida Kaolin - Electrodialyzed
K2 - Putnam Florida Kaolin - Untreated
K2E - Putnam Florida Kaolin - Electrodialyzed
K3 - Florida Kaolin - Untreated
K3E - Florida Kaolin - Electrodialyzed
K4 - No Karb Kaolin - Untreated
K4E - No Karb Kaolin - Electrodialyzed
K5 - Klondyke Washed Kaolin - Untreated
K5E - Klondyke Washed Kaolin - Electrodialyzed
K6 - X-Pulverized Crude Kaolin - Untreated
K6E - X-Pulverized Crude Kaolin - Electrodialyzed
T - Tennessee Ball Clay No. 5 - Untreated
TE - Tennessee Ball Clay No. 5 - Electrodialyzed
B - Bentonite - Untreated
BE - Bentonite - Electrodialyzed
### Intensity Readings of Spectrograms

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Table showing grams of compound per 100 grams of clay before and after electrodialysis

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* The original amount is not known. Percentage given is percent of the original amount which still remains in the sample after electrodialysis.
Discussion

The ability of all solids to retain on their surfaces a layer of any gas or solute with which they are in contact is called adsorption.

Adsorption is a surface phenomenon which depends on concentration, temperature and the nature of the adsorbent and adsorbed substance. The empirical equation of Freundlich was developed to show the relations of adsorbed material to adsorbent when equilibrium is reached. (See Appendix) Later and improved experiments tend more and more to support the theory of Langmuir when adsorption is not great. The formula of Langmuir (see next page) is based on the fact that crystalline structure is made up of atoms arranged in orderly fashion making a unit cell which repeats itself over and over. The hypothesis of Langmuir assumes that the adsorbed layer is only one molecule thick.

Studies of adsorption on Kaolin are of special interest. It has been found that only the cation of an electrolyte shaken up with Kaolin is adsorbed while the anion remains in the solution with practically unaltered concentration. Because the solution must remain electrically neutral cations must be removed from the adsorbent, Kaolin, to maintain this balance. This type of adsorption is known as exchange adsorption.17

17. F. H. Getman and F. Daniels, "Outlines of Physical Chemistry," 7, 257-8, (1943) John Wiley and Sons, Inc. 1943
1. Empirical adsorption equation of Freundlich.\textsuperscript{16}

\[
\log \frac{x}{m} = n \log c + \log k
\]

\(k\) and \(n\) = constants to be determined for each temperature, solute and adsorbent

\(c\) = concentration of solution

\(x\) = weight of adsorbed substance

\(m\) = weight of adsorbent

2. Langmuir formula for weight of adsorbed material.\textsuperscript{19}

\[
\frac{x}{m} = y = \frac{a b c}{1 + c}
\]

\(y\) = weight of adsorbed material per unit of surface

Constants, \(a\) and \(b\) = \(1 - \frac{m}{x}\) ratio of molecules that adhere

\(c\) = concentration of solution

\textsuperscript{16} F. H. Getman and F. Daniels, "Outlines of Physical Chemistry", 7, 256, John Wiley and Sons, Inc. 1943

Crystals are built up of atoms or molecules in definite rows and parallel planes. A unit cell is defined as the smallest possible subdivision which has the properties of the visible macrocrystal and which, by the repetition or translation of itself in all directions, builds the crystal. Figure 21 shows one of the common crystal forms of Kaolin. With a little imagination it can be seen that repetition of the unit cell a, b, c in all directions would form a crystal as shown A, B, C. Each point of intersection of the lines in the figure may be thought of as the position of an atom which makes up the crystal. Any point in the interior of the crystal has six lines meeting at that point. Any point on the surface of the crystal has five lines meeting, leaving one unsatisfied bond. Along the edge there will be two unsatisfied bonds and at each corner three unsatisfied bonds. It is to these unsatisfied bonds that the ions of the adsorbed substances adhere. A process such as dialysis is required to replace these ions completely with the H⁺ and OH⁻.

Barker and Truog have obtained three curves which they designate as A, B and C. The A type curve is one which shows a rapid uniform rise in pH and flattens abruptly at the optimum pH. The clay giving this type of curve responds readily to pH adjustment and offers no difficulties in the pH adjustment.

process. In a clay of this type there is assurance that the treatment will give beneficial results.

A type B curve is one in which there is a slight preliminary flattening which reverses itself and rises again before there is a permanent flattening. This is considered evidence that there are considerable amounts of soluble salts present. These salts must be inactivated before pH adjustments will give beneficial results.

A type C curve rises gradually and has no abrupt flattening. Laboratory tests made by Barker and Truog give evidence that pH adjustment will make these clays more plastic and lessen the amount of water required.

One method of determining exchange capacity of a clay is to titrate the clay with hydroxide noting the amount required to bring the suspension to a given pH such as 7.0 or 8.0.

Lakeland Florida Kaolin:

This clay has a base exchange capacity of 2 M.E. The titration curve is classed as a type B showing the presence of soluble salts. This clay would probably give difficulty in a manufacturing process which required the use of electrolytes for deflocculation.

Putnam Florida Kaolin:

This clay has a base exchange capacity of 1 M.E. The titration curve is type A indicating little difficulty when subject to pH adjustments in manufacturing processes.
Florida Kaolin, E.F.K. Company:

This clay has a base exchange capacity of \( \frac{3}{4} \) M.E. The titration curve is type A. There is some difference indicated in the optimum pH of the untreated and dialyzed condition but since both curves are the same type it is considered that the adsorbed material will give no difficulty in pH adjustments.

No Karb Kaolin:
Klondyke Washed Kaolin:
Crude Kaolin:

Each of these clays is similar to the other. All have a base exchange capacity of about \( \frac{3}{4} \) M.E. The titration curves are all of the type A indicating they should respond well to the process of pH adjustment.
The X-Ray Analysis:

Although complete analysis of any of the materials by x-rays is far beyond the scope of this paper it is considered that enough work has been done to show the effect of electrodialysis on the crystal structure of the substances under investigation. In order to make clear the results of the x-ray analysis it will be necessary to discuss briefly some of the principles involved.

It is a fact of x-rays that an x-ray of wavelength \( \lambda \) will be diffracted at an angle \( \theta \) and only at that angle. This angle depends on the grating space \( d \) of the crystal in question. The mechanism of diffraction of x-rays by crystals is very complicated and involved but Bragg showed that the operation may be reduced to simplicity and the laws of reflection applied, the reflection taking place according to the equation \( n \lambda = 2d \sin \theta \).

In the powder diffraction method, which is used in this investigation, a monochromatic x-ray is used and the angle \( \theta \) obtained by rotating a sample of clay. In this sample the crystals of the clay are oriented at random and by rotating the sample in the beam of the x-ray it is assured that the x-ray will strike the crystal at the angle \( \theta \) once each revolution. The diffraction of the x-ray will depend on the crystal structure of the sample because the angle \( \theta \) depends on the grating space \( d \). Any change in the structure of the crystal will give a change in

d and consequently a change in $\Theta$. Conversely any change observed in $\Theta$ will show a change in crystal structure of the substance.

It can be readily understood that the more crystals that are present in the sample which is rotated the more intense will be the diffracted beam of the x-ray. Conversely a less intense beam of the x-rays shows a lesser amount of the crystal present. An amorphous substance would give no diffraction at all. Since the results show that there was no change in diffraction pattern in any of the Kaolins it follows that the crystal structure was not changed.

The Bentonite pattern, although not showing a change in pattern when electrodialyzed, showed a great loss in intensity of the diffracted beam. It follows, as explained above, that the crystal structure of some of the Bentonite was not changed but some was decomposed giving an amorphous product. The exact nature of this product is not known although there is reason to believe that a silica gel has been formed as described in Searle.  

Spectrographic Analysis:

The spectrographic analysis is practically self explanatory. The tables show in each case the amount of the element which was removed by electrodialysis. In case the amount of original element was not known the percent of that element which still remains in the dialyzed sample is reported.

In the method used only the metal will give a line on the spectrogram. Therefore the compound may be reported on the same basis as in the original sample.
Conclusions

1. Kaolins are not decomposed by electrodialysis and therefore this process may be used in removing adsorbed materials from the Kaolin.

2. Bentonite is decomposed by electrodialysis and therefore this process becomes useless as a means of removing adsorbed materials.

3. From ten percent to ninety percent of the adsorbed material may be removed from a Kaolin by electrodialyzing it one time.

4. Lakeland Florida Kaolin has a type B titration curve indicating that difficulties should be encountered when this clay is subjected to the process of pH adjustment.

5. All other Kaolins investigated have type A titration curves indicating little or no difficulty should be encountered when these clays are subjected to the process of pH adjustment.
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