SOME FUNDAMENTAL PROPERTIES OF RAW CLAYS INFLUENCING THEIR USES

BY

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Some Fundamental Properties of Raw Clays Influencing Their Uses

I. Introduction

Few materials enjoy such a wide range of distribution and application as clays. The problems of the proper selection of clays and the control of their behaviors in use is one of paramount importance. The situation is made difficult by the great number of variables and by inadequate understanding of some of them and their relationship to each other. Scientific control can be possible only after all properties have been definitely defined and correlated.

The object of this investigation was to obtain information to form the foundation for the general correlation of the properties of clays. It was felt that more could be learned by a general study of many properties than from a detailed study of a few. The ultimate objective, which will not be achieved within the scope of the immediate problem, was to obtain information that will facilitate the selection of the proper clays for a specific purpose, and to enable us to control their behavior in use. It was hoped, however, that information obtained in the present investigation could form the basis of more detailed future investigations.

In formulating a plan for the systematic study of the properties of clays, a consideration of the fundamental relationships involved suggests the most logical method of attack. An outline of these quantities, as shown in Table I, indicates the origin of the properties and points to the possible relationships existing.

If these properties are all related in this way, and the relationships are known, then the complete system can be defined by a few of the properties which are more easily measured.

Table I. Expected Relationships Between Fundamental Properties of Clays

I. Fundamental causes of the differences in clays may be traced to their mineralogical, chemical, and physical characteristics as follows:

- a. The particular clay mineral or minerals present and the relative amounts.
- b. The particle size distribution of each.
- c. Nature and amounts of accessory minerals.
- d. Nature and amounts of soluble constituents present.

II. The following fundamental factors are directly governed by the mineralogical, chemical and physical constitution of clays:

- a. Amount and intensity of hydration (Governed by the adsorption capacity, and the nature and concentration of ions in solution.)
- b. pH changes when soluble salts are added.
- c. Packing characteristics of the particles.

III. Physical properties controlled by (a) or (a) and (c) of II.

- a. Dry strength.
- b. Drying shrinkage.
- c. Flow characteristics of suspensions.
- d. Permeability.
- e. Plasticity.
- f. Stability of suspensions.

Two different plans of attack are thus indicated: First, the determination of the properties listed under III in the outline in Table I, as functions of particle size of pure clay minerals, exchangeable cations and soluble salts.

The second possible method is the one chosen for the present work. This involves the study of a variety of different clays, without regard to purity or composition, to determine whether or not the factors listed under II in Table I fix the properties of the clay. This is feasible, since quantities of II, are the direct results of the mineralogical, physical and chemical constitution of the clays, and the quantities listed under III in the outline are composite manifestations of these basic variables.

If the soluble constituents are controlled, hydration and packing characteristics are the only remaining variables, and these are controlled by the constitution and physical condition of the clay. Thus, by measuring the ion sorption capacity and the pore space of clays, and by controlling soluble salts and water content, the system may be completely defined. If these conditions were shown to hold, the procedure for examining clays would be very much simpler than that required to make particle size and mineralogical analysis.

In this type of investigation, in which several different properties must be measured, a certain amount of accuracy must be sacrificed. Precision measurements, where and if desired, can be taken up later. Some data, such as flow characteristics, could not be obtained in this investigation. This was partly due to the lack of adequate means of testing, but chiefly because of the

the excessive amount of time required to study the three component system, clay-electrolyte-water.

II. Previous Work and Literature

1. General

In the vast majority of investigations of raw clays, the investigators have neglected to take proper account of the basic variables. Most studies relating to ionic exchange (Mattson (1), Ramann (2), Bradfield (3), and Ganssen (4)) have been conducted by attempting to characterize the processes by dissociation constants, true chemical reactions and so forth. Jenny (5), (6), and Cooper (7) have approached sorption phenomena from the point of view of the properties of the participating ions. In recent years the knowledge concerning molecules, atoms and ions has become so well defined that it furnishes a definite basis for the study of ionic processes in connection with the behavior of clays. The first to apply this technique to the study of ceramic clays was Endell and Vageler (8), who investigated the relationship between adsorbed cations and water content of ceramic clays. Endell, Hofmann and Wilm (9) made an extensive investigation of the relation between several properties of natural clays (not single-base clays) and base exchange capacity. Several properties of natural kaolins have been correlated with base exchange capacity of Kleinefelter and co-workers (10).

2. Nature of Certain Cations

In clay-water systems, ions are the most important, if not the only active agents. Cations remain ionized even after adsorption on the colloid. X-ray analyses have shown that clay colloids are not only crystalline but that the crystals are built up of ions (Bragg (11), (12), Debye (13), Goldschmidt (14) and others). These facts have formed the base upon which our knowledge of clays has been pyramided.

Every ion is surrounded by a shell of oriented water; in other words, the ions are hydrated. The mechanism of the hydration phenomenon has been described by Born (15), (16), Drude and Nernst (17), Washburn (18), and Webb (19). The free energies of hydration of chemically unhydrated ions has been obtained as a function of ion radii by calculating the difference in energy necessary to charge the ion in a vacuum and that necessary to charge the ion in water, and to compress the solvent in the vicinity of the ion. The field strength of an ion is proportional to the charge on the ion divided by the square of its radius.

Since water is a permanent dipole, it is tremendously influenced by the presence of ions. Under the influence of an electric field, water molecules become oriented and more tightly packed, forming a "shell" around the ion. Properties of ions influencing the polarizing effects of ions are given in Tables II, III, and IV. The amount of water attracted by an ion is directly proportional to the field strengths of the ions. Thus Na^+ will attract more water than K^+, and H^+ more water than Na^+. The amount of water associated with ions has been determined by Washburn (18) who reports 16.0 mols of H_2O per ion of Na and 11.5 mols. of H_2O per ion of K.

Table II. Pressures Existing in Water at Various Distances From Ion. According to Webb (19).

Distance from ion Å	12.77	5.76	4.16	3.09	2.32	1.95
Field Strength	10^4	5×10^4	10^5	2×10^5	4×10^5	6×10^5
Pressure	0.43	20.9	1.76×10^2	1.28×10^3	6.34×10^3	1.24×10^4

Row 1 gives the distance in Ångström units from the center of the ion.

Row 2 gives the values of internal field strengths corresponding, in c.g.s. electrostatic units.

Row 3 gives the pressure in megadynes per square sentimeter.

Table III. Contraction of Solvent Produced by Ions of Various Radii According to Webb (19)

Radius	4.165	3.090	2.318	1.946	1.715	1.551	1.285	1.122	0.924	0.804
Contraction	1.40	3.59	7.66	10.27	11.84	12.86	14.21	14.83	15.44	15.69

Contraction is given as the total decrease in volume (in cu. cm.) attending the solution of one mole of ions in an infinite quantity of water, as calculated for ions of various radii.

Table IV. Free Energies of Hydration of Individual Ions. According to Webb (19).

Ion	Na^+	K^+	H^+	Zn^{++}	Ca^{++}	Mg^{++}	Al^{+++}
Radius - Å	1.505	1.873	0.5	1.04	$1.06^{(a)}$	$0.78^{(a)}$	$0.57^{(a)}$
Free energy of Hydration	99	81.7	249.6	525	$349.0^{(b)}$	$459^{(b)}$	--

Free energy of hydration is given as kilogram calories per gram ion.

(a) According to Goldschmidt, for crystals.

(b) Quoted by Vageler (20).

3. Mechanism of Adsorption

The structure of the crystalline matter in clays determines the nature of the adsorption phenomena. According to Jenny (6), "The places of attraction in colloidal particles are the negative O^{--} and OH^{--} ions of the rigid crystal frame. Only positive ions will adhere, negative ions as a rule will be repelled and remain in the surrounding liquid. The intensity of fixation follows Coulomb's law according to which the attraction is directly proportional to the product of the charges of the ions and indirectly proportional to the square of the distance between charges, which is of course determined by the size of the ions. Wiegner's (21) contribution in base exchange studies consists in the introduction of the size of the hydrated ions instead of 'crystal ions' in Coulomb's equation. ... The K-ion with its thin water shell can go closer to the O-ion of the crystal frame than the more highly hydrated Na-ion. The attraction between the negative inner layer and the K-ion is therefore greater than for the Na-ion; in other words, K is better adsorbed than Na, and also held more tightly."

Cation exchange is a function of the surface of clays of the kaolinite type. The mechanism is different in the montmorillonite-beidellite-nontronite type of clay minerals. These minerals have a variable (001) spacing into which ions and water are attracted (Gieseking (22)).

III. Experimental

1. The Samples

The samples used in this investigation together with a description of their mineral compositions and source are listed in Table V. These samples were selected with a view to obtaining as wide a range of types as possible which could be studied within the scope of this investigation.

X-ray diffraction patterns of some of the samples are shown in Fig. 1. The mineral constitutions of various clays have been studied in considerable detail by Clark, Riecken, and Reynolds (23), Grim and Bray (24), and others.

Table V. List of Clays Studied, Their Mineral Compositions and Source

Name	Source	Mineralogical Composition
North Carolina Kaolin	North Carolina	Chiefly coarse kaolinite. Some muscovite, quartz, and orthoclase.
English China Clay	England	Chiefly kaolinite. Some white mica, quartz, and feldspar.
Georgia Kaolin	Georgia	Chiefly kaolinite.
Florida Kaolin	Florida	Kaolinite, traces of quartz.
Tennessee Ball No. 7	Tennessee	Kaolinite, some illite.
Tennessee Ball No. 5	Tennessee	Kaolinite, some illite. Organic material, lignite.
Vallendar Clay	Germany	Kaolinite and illite. Quartz, muscovite, and feldspar.
Alton Clay (No. 2 Fire Clay)	Alton, Illinois	Kaolinite. Some illite and organic matter. Quartz and pyrite.

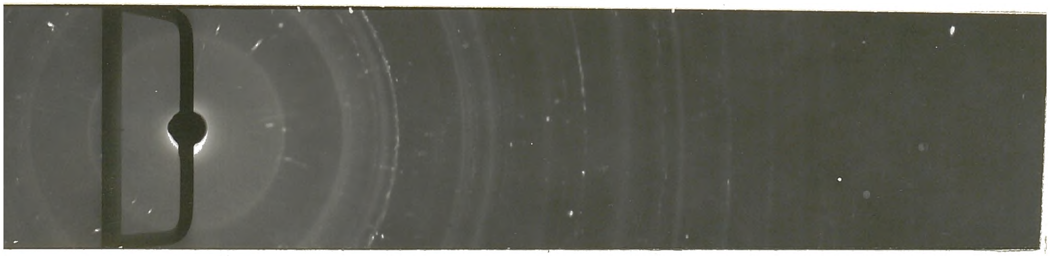
Table V (continued)

Name	Source	Mineralogical Composition
Texas Clay	Dalhart, Texas	Kaolinite and montmorillonite. Some unidentified mineral.
Peat	Northern Illinois	Chiefly lignite. Some quartz, kaolinite, and other minerals.
Bentonite	Wyoming	Montmorillonite.

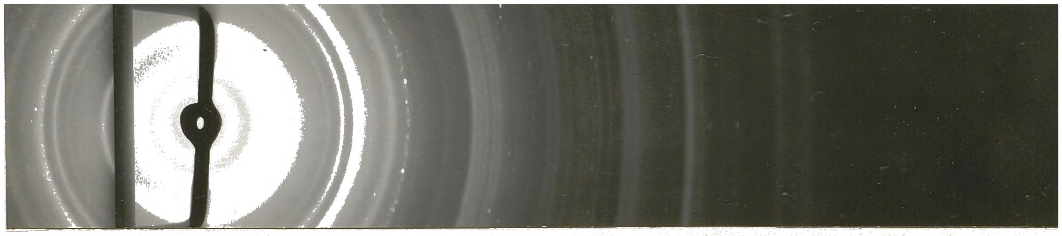
Fig. 1. X-ray Diffraction Patterns of Some of the Samples Used.

Tennessee No. 7 Ball Clay

Tennessee No. 5 Ball Clay



No. 2 Fire Clay - Alton, Illinois



Texas Clay

Peat

Bentonite

2. Preparation of the Samples

One hundred to two hundred grams of each sample were converted to hydrogen-clay either by leaching or by electro-dialysis. The dialyzing apparatus used was similar to the one described by Bradfield (25). These samples were then air dried and sealed in jars until needed. A portion of the Alton Clay was treated with H_2O_2 to remove the organic material.

The sodium-clays were prepared by adding NaOH to the hydrogen-clays in amounts equivalent to the respective base exchange capacities.

3. Methods of Measuring properties.

a. Base Exchange Capacity

The base exchange capacities were determined by the ammonia distillation method. The clays were leached with normal neutral ammonium acetate solution and the excess ammonium acetate removed by washing with neutral absolute methyl alcohol. The adsorbed NH_4 was replaced by washing with 0.1 Normal HCl and the displaced NH_4 determined by the Kjeldahl method.

b. Heat of wetting

Heat of wetting was determined by a method devised by Janert (26). The apparatus consisted of a Dewar flask, which was suspended inside another, larger, Dewar flask. It was covered by a well insulated lid, bored to accommodate a Beckman thermometer, a stirrer, and the sample bottle.

In making measurements, the calorimeter was charged with a quantity of water such that the volume of the water plus the volume of the sample was always 300 cc. The samples were contained in glass capsules with ground glass caps. The samples were dried at

Fig. 2. Heat of Wetting of H-Kaolin (Eng. China Clay)
Wt. Sample Dried at 105°C 39.847 gr.
Heat of Wetting - 1.04 Cal. per gm.

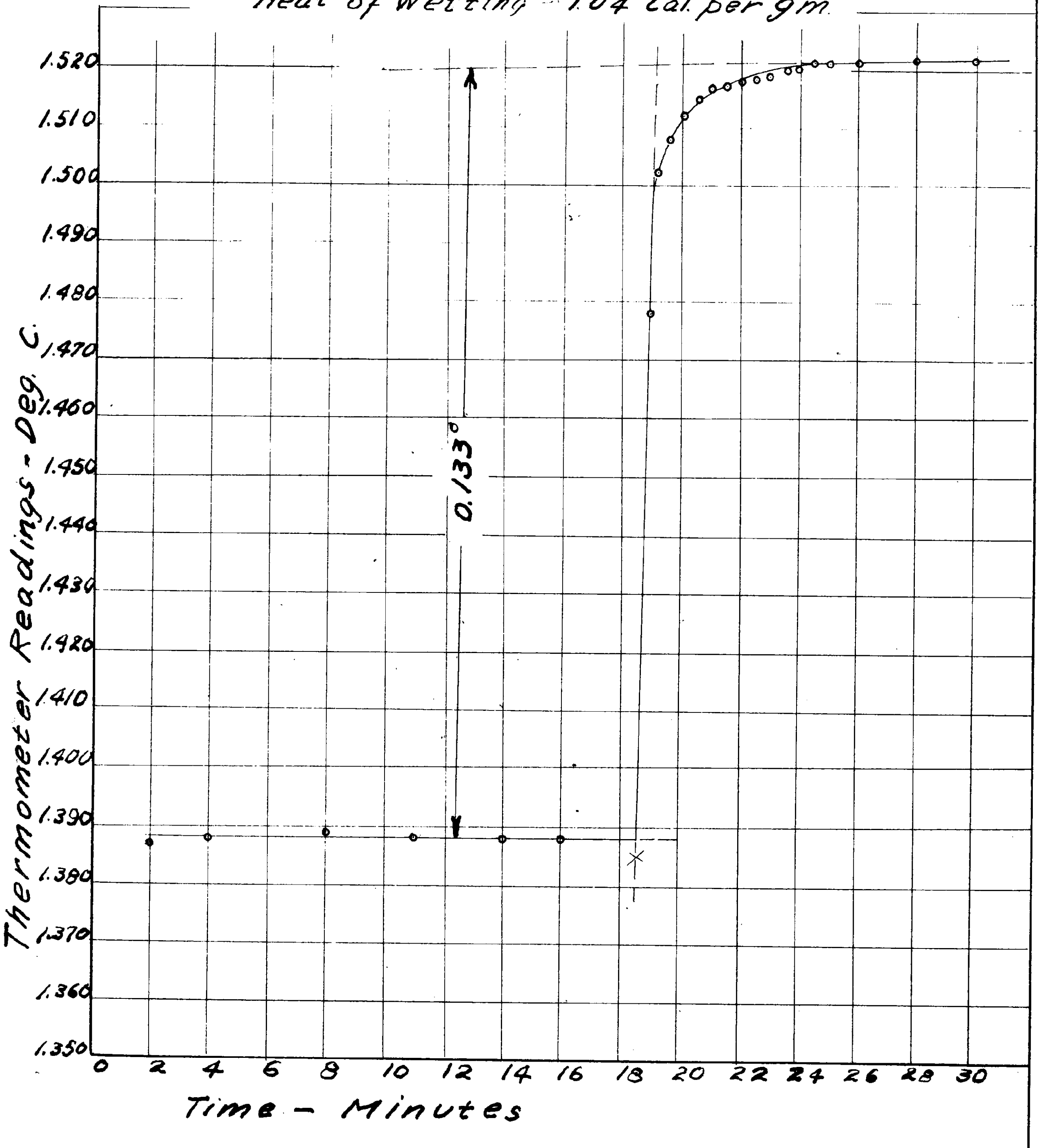
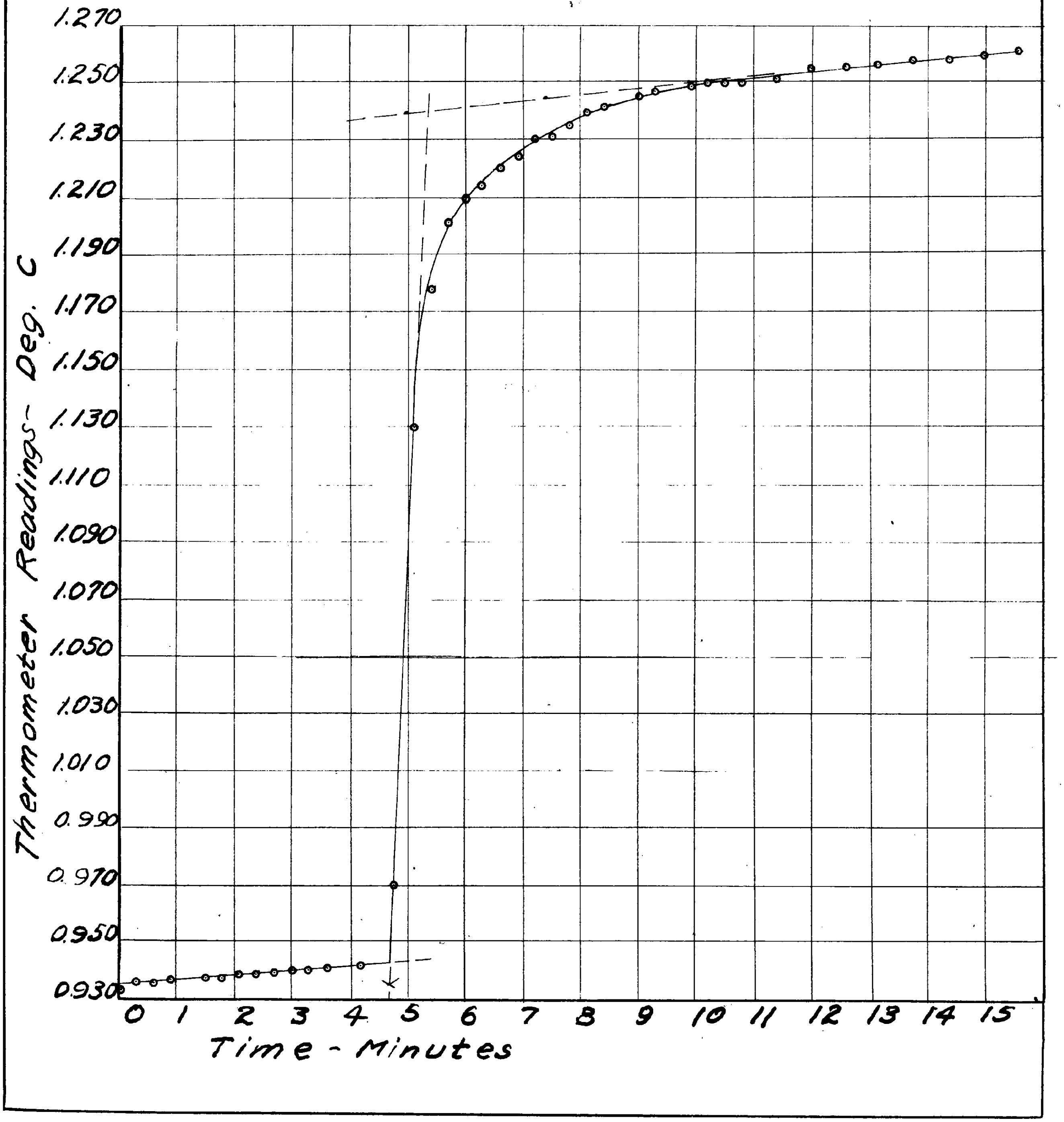


Fig. 3. Heat of Wetting Data for H-Bentonite
Wt. Sample Dried at 105°C – 5.045 gm.
Heat of Wetting – 18.72 Cal. per gm.



105° C., weighed, and the caps sealed with paraffin. Sealed sample was then immersed in the water in the calorimeter and allowed to stand over night to attain thermal equilibrium. When ready to make the test, the water in the calorimeter was gently stirred and a record kept of temperature and time. The sample was then quickly removed and the clay dumped into the calorimeter. With constant stirring, observations were made of temperature and time, so that curves such as Figs. 2 and 3 could be plotted. Heats of wetting were calculated from the temperature rise, weight of sample, weight of water and apparatus constant. The calorimeter was calibrated by the heat of solution of sodium carbonate.

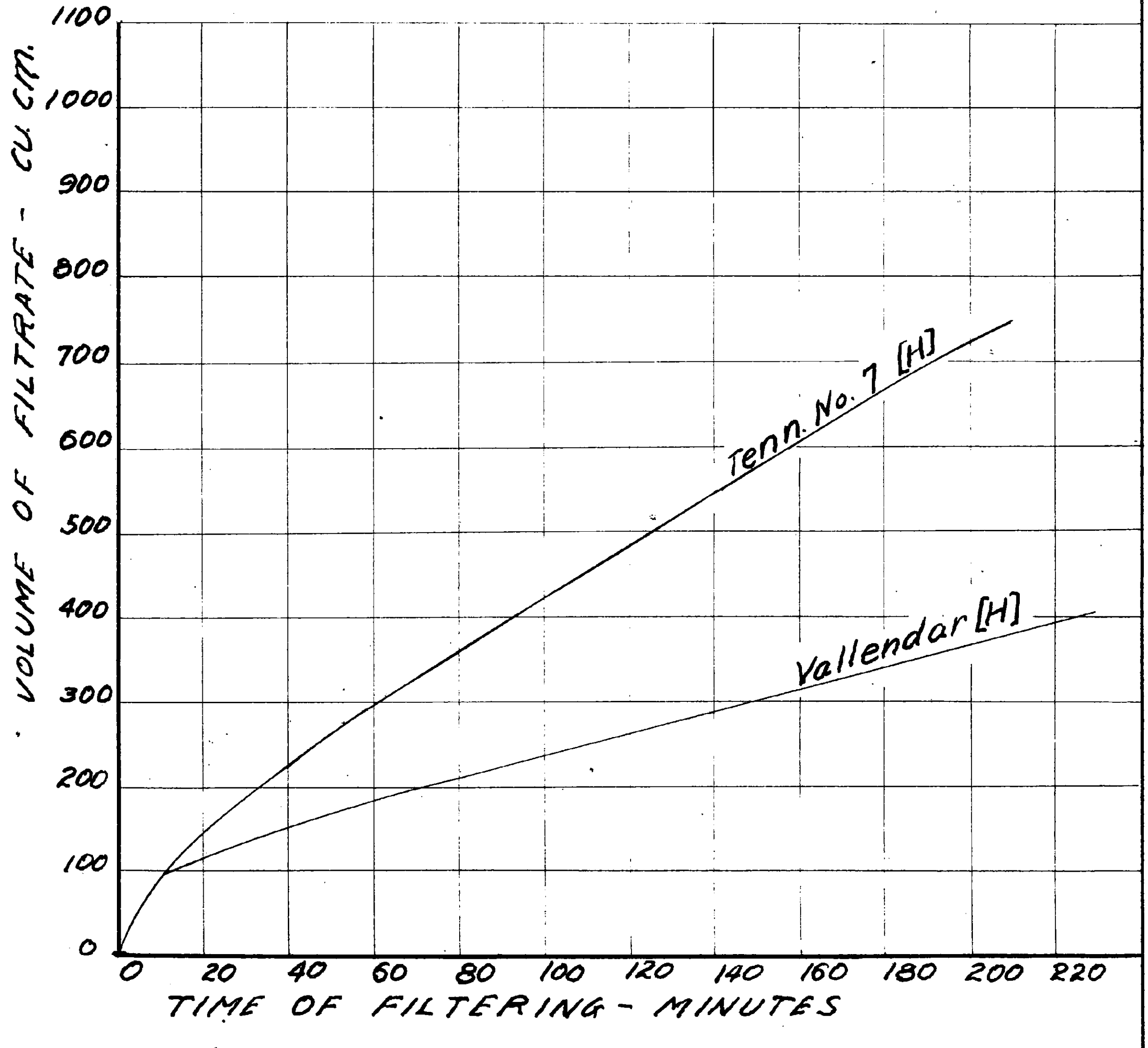
c. Measurements of pH

The clays were mixed with water to form a thick slip containing 0.5 gram of clay per cc. of slip. A Beckman pH meter was used in the determination.

d. Equilibrium moisture

Three general methods are available for the study of equilibrium moisture. The three methods are, (a) the ordinary desiccator method, (b) a chamber at atmospheric pressure in which the air is kept well stirred, and (c) dynamic method. For the purpose at hand, the ordinary desiccator method was used, in which the clay samples were brought to equilibrium with the vapor above appropriate sulfuric acid solutions. This method is open to criticism in several respects, but it proved to be satisfactory for the purposes of this investigation. All the samples were left in contact with the vapor for six months at approximately 25° C.

Fig. 4 Example of Permeability Data by Method No. 2



c. Permeability

In order to obtain a comparison of the relative permeabilities of the various clays, the following tests were devised.

Method No. 1. A 10 gram sample of clay was weighed to an accuracy of ± 0.1 gram. Fifty cc. distilled water were added to the sample, and the suspension was allowed to stand 12 hours. A 9-cm. Buchner funnel was prepared using No. OK filter paper, and made to set as nearly level as possible. A vacuum of 29 in. was applied and the suspension transferred to the funnel. Ample time was allowed for the clay layer to form; then the vacuum was released and a graduated cylinder plased inside the flask so that the funnel when replaced had its spout inside the graduated cylinder. The vacuum was again applied and records made of the time required for 5.0 cc. of liquid to pass through the clay membrane. The temperature during all runs was near 24° C.

Method No. 2. 10.0 grams of clay were added to 50 cc. of distilled water in a flask. The clay was shaken 72 hours by a mechanical agitator, then transferred to a Buchner funnel. The time required for 20 cc. portions of distilled water to pass the clay membrane was noted. Fig. 4 shows an example of the type of data obtained by this method.

Method No. 3. Ten grams of clay and 50 cc. of water were put into a flask and the clay deflocculated by additions of NaOH. After 72 hours of mechanical agitation, the sample was flocculated by a few drops of HCl and transferred to the funnel, and the chlorine ions leached out. The filtration rate was then measured.

f. Rate of drying.

The clays were made plastic and adjusted to a plasticity (*) number of about 1.5, then formed into cylindrical test specimens. These specimens were made one square inch in cross section with a height equal to the diameter. The samples were set on the laboratory table and weighed periodically to determine the rate of water loss. This simple test was all that could be carried out with the limited amount of sample available and with clays of so wide a range of drying characteristics.

g. Drying shrinkage.

Drying shrinkage was measured on the "rate of drying" samples. The plastic volumes were determined by weighing the bars suspended in carbon tetrachloride. Dry volumes were calculated from the weights of bars saturated and suspended in carbon tetrachloride.

h. Porosity measurements.

The porosity of dried bars was calculated from their respective dry volumes, weights, and true densities.

i. Plasticity.

An apparatus patterned after the one described by Endell (27) was used for the plasticity measurements in this investigation. The plasticity of clays cannot be defined by a single figure, and can be adequately described only as a function of the two component system, clay-water. The quantity of sample available in this investigation was so limited that this could not be accomplished. The plasticity apparatus was used only as an aid in bringing all plastic samples to approximately the same plasticity before testing.

(*) Cylindrical test specimens were subjected to simultaneous compression and torsion. The plasticity number was the product of the deformation and load at the time of rupture.

j. Dry Strength.

The compressive strengths were determined on cylindrical specimens approximately 1 inch in diameter and 1 inch in height, using a small hydraulic press. For modulus of rupture, specimens 1/2 inch in diameter were loaded at the mid-point of a span of six centimeters.

IV. Results and Conclusions

1. Base exchange capacity

Since base exchange capacity is one of the fundamental factors influencing the properties of clays (see Table I), and is comparatively simple to adequately determine, it will be used as a function against which all others are plotted to test correlation. This can be done on the premise that all properties which are functions of base exchange capacity, are also functions of, or related to, each other.

The identity of the individual clays will not be indicated on most of the graphs, but may be recognized by their base exchange values by reference to Table VI.

Table VI. Base Exchange Capacities.

Clay	Base Exchange Capacity. Milli-equivalents per 100 grams.
North Carolina Kaolin	4.0
South Carolina Kaolin	4.9
English China Clay	5.9
Florida Kaolin.	8.0
Tennessee Ball Clay No. 7	10.2
Tennessee Ball Clay No. 5	12.1
Vallendar Clay.	13.8
Alton Clay.	21.9
Alton Clay (treated with H_2O_2).	20.3
Texas Clay	33.3
Peat.	76.7
Bentonite	85.1

2. Heat of Wetting

The mechanism of water adsorption has long been a matter of controversy. Heat of wetting data, interpreted in the light of modern science, has done much to clarify this question. Janert (26), reasoning that polar adsorption should be closely correlated with exchangeable bases, and consequently the heat of hydration of adsorbed cations, discovered some important facts. He was able to show that the ratio of the heat of hydration of the adsorbed ions to the heat of wetting is a constant. The values for these ratios are as follows: H-clays 11.8, Mg-clays 9.0, Ca-clays 7.0, K-clays 5.1, and Na-clays 4.9. These results were taken as proof that the adsorbed ions are the source of activity in clay-water systems. Since the cations are more or less bound to the alumino-silicate complex, only a certain fraction of the total heat of hydration can reappear when the dry clay is wetted. This proportion differs considerably for the different cations. The adsorption is strongest for hydrogen, and therefore only 1/11.5 (8.7%) of the total heat is returned as heat of wetting. Sodium is but little adsorbed and 1/4.9 (20%) appears in the heat of wetting. The other cations fall between and follow the well known order intensity of adsorption.

The values of heat of wetting used in constructing the curves plotted in Fig. 5 were calculated by the following equation:

$$\text{Base exchange capacity} = \frac{\text{100 K x heat of wetting}}{\text{heat of hydration}}$$

where K is Janert's ratio of heat of hydration to heat of wetting. This ratio was checked in the present investigation for three H-clays, the values being indicated in Fig. 5.

Janert failed to point out that perhaps the most important application of this generalization is the prediction of the behavior of untried cations in clay-water systems. The greater the portion of ionic energy which is used up in its adsorption by the colloid, the closer the system approaches an iso-electric point. Conversely, cations which retain a high percentage of their energy should be good dispersing agents. It is possible to evaluate these factors precisely and conveniently by heat of wetting measurements.

3. pH

The pH data can be interpreted in the same manner as heat of wetting. If none of the energy of the hydrogen were utilized in adsorbing on the surfaces of the silicate complex, the pH would be

Fig. 5 The Relation Between the Heat of Wetting of Clays and Adsorbed Cations

Curves Calculated from Data by Janert.

Points Show Data on Hydrogen-Clays Obtained in Present Investigation.

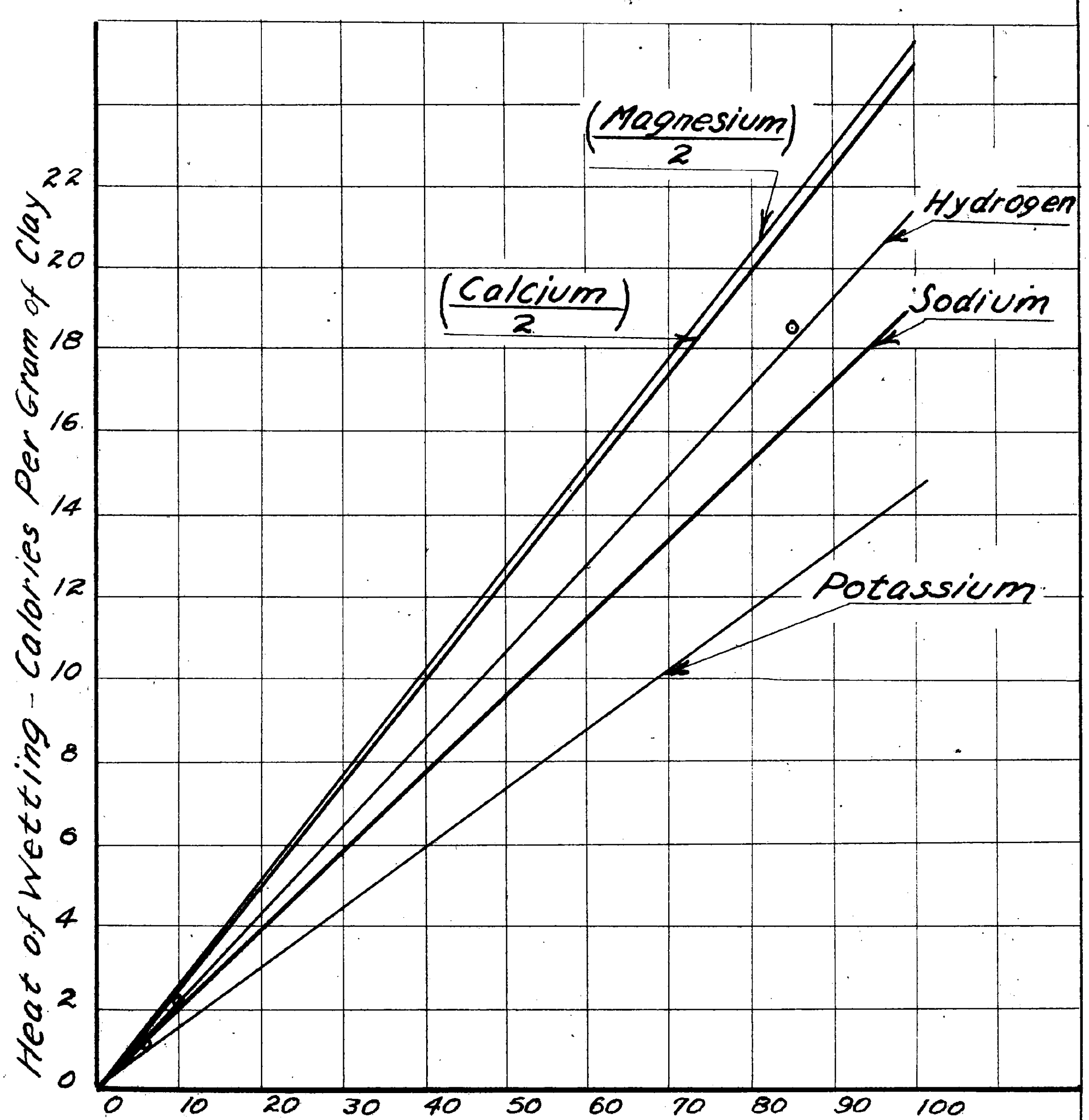
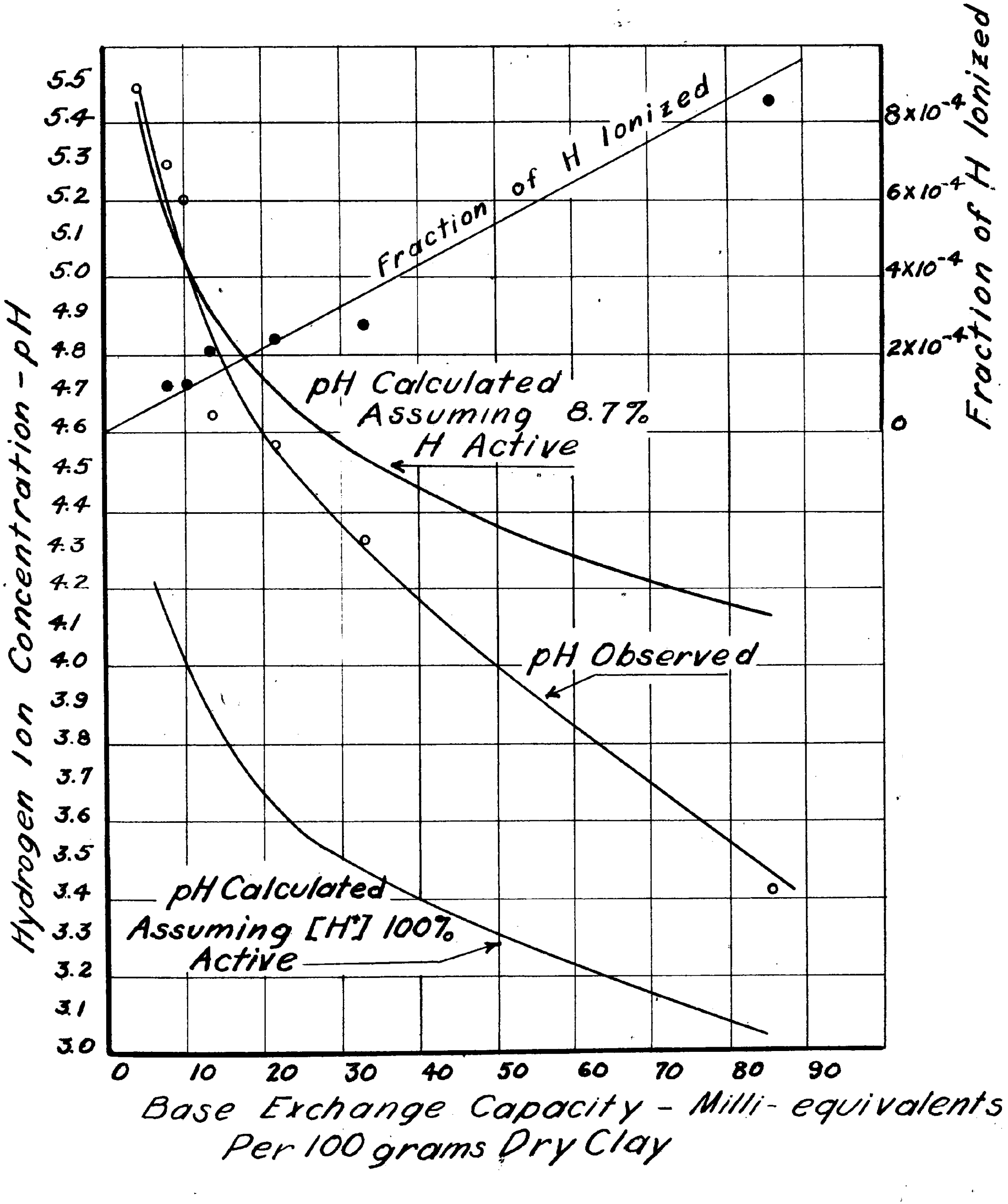


Fig. 6. Hydrogen Ion Concentration of H^+-Clays



as shown in Fig. 6 for the curve labeled "pH Calculated assuming 100% of H Active." The curve calculated assuming 8.7% (Janert's factor) of H active is much closer to the observed values. The observed values could not be expected to check with those calculated from the 8.7% factor since the water to clay ratios are radically different in the two cases. The heat of wetting measurements were taken at practically infinite dilution (considering only the ions), while the pH measurements were made on samples containing 0.5 gram clay per cc. of suspension. The difference between the computed and observed pH values simply means that the intensity of adsorption of the cations varies with water content. More electrolyte would have to be added to a plastic clay than to thick slip, and more to thick slip than to dilute slip (per gram of clay) to produce the same degree of change.

The method of calculation of pH is obvious from Table VII. The fraction of hydrogen ionized and the dissociation constants were calculated according to the usual means of the physical chemist. These calculations involve the assumption that clay acts as a polyvalent acid in which the silicate is the anion and the adsorbed hydrogen the cations.

Table VII. pH of H-clays, Observed and Calculated.

	a	b	log $\frac{1}{b}$	pH observed	$\propto$	K
North Carolina Kaolin	4 x 10^{-5}	34.8 x 10^{-7}	5.46	5.5		
Florida Kaolin	8 x 10^{-5}	69.0 x 10^{-7}	5.15	5.30	1.25 x 10^{-4}	0.625 x 10^{-9}
Tenness No.7 Ball	10.2 x 10^{-5}	88.7 x 10^{-7}	5.05	5.21	1.26 x 10^{-4}	0.80 x 10^{-9}
Vallendar Clay	13.8 x 10^{-5}	119.7 x 10^{-7}	4.92	4.65	2.18 x 10^{-4}	3.26 x 10^{-9}
Alton Clay	21.8 x 10^{-5}	189.7 x 10^{-7}	4.72	4.58	2.42 x 10^{-4}	5.65 x 10^{-9}
Texas Clay	33.3 x 10^{-5}	290 x 10^{-7}	4.54	4.33	2.80 x 10^{-4}	13.1 x 10^{-9}
Bentonite	85.3 x 10^{-5}	742 x 10^{-7}	4.13	4.43	8.73 x 10^{-4}	340.8 x 10^{-9}

a = equivalents of H per gram of clay.

b = equivalents of H per gram of clay x 0.087 (0.087 is Janert's factor for heat of wetting).

log 1/b = calculated pH

$\propto$ = fraction of H ionized - calculated.

K = dissociation constant - calculated.

It can be inferred from what has been shown that if pH is to be used as a control in clay work, the relations must be determined empirically for each individual case. The same pH can of course be obtained in solutions containing a variety of different cations. Since the behavior of clay-water systems is largely dependent upon the particular type of cation present, pH in poly-ionic systems is incidental and not fundamental.

4. Equilibrium moisture.

The moisture in equilibrium with several H-clays is shown in Fig. 7. This is tantamount to plotting equilibrium moisture against the vapor pressure of the equilibrium moisture. The drop in vapor pressure, as the moisture content decreases, shows that the water is under strong restraining influence due to the attraction by the adsorbed cations.

The water in equilibrium with atmospheres of 10%, 50%, and 70% relative humidities is plotted against the base exchange capacities of the respective clays in Fig. 8. With certain exceptions, there is excellent linear correlation. The Texas clay is wild in all the curves, possibly due to an error in determining the base exchange capacity. According to this curve it should be about 40. All the other points not correlating, are low, and all these clays contain organic matter. The sample of peat, which is essentially lignite, has a very low water adsorbing capacity per exchangeable ion. Further proof that organic matter in clays is characterized by low water adsorption capacity is shown by the fact that the Alton clay, after the extraction of the organic material, falls on the curve.

Fig. 7. Moisture in Equilibrium With H-Clays at Different Relative Humidities

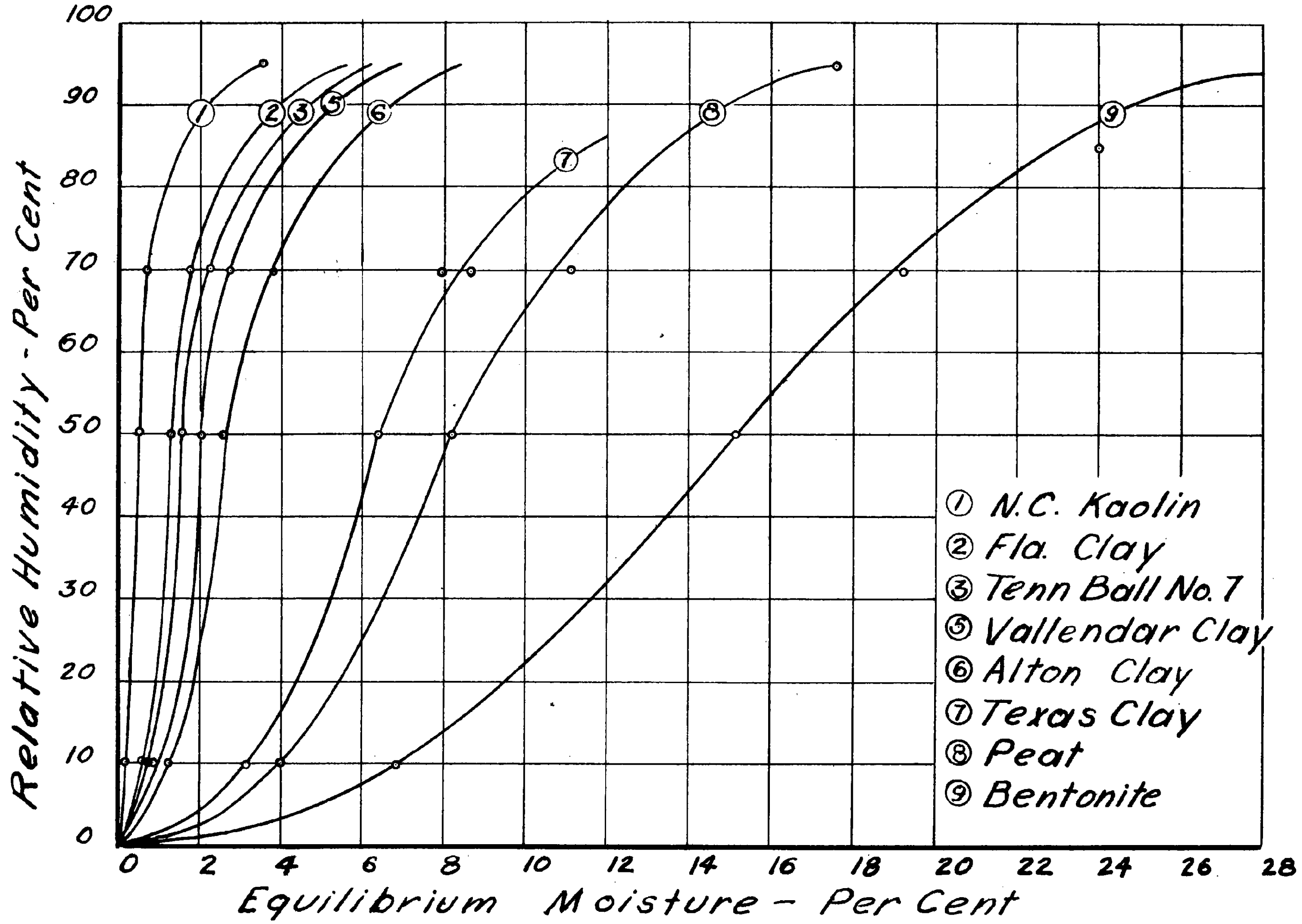
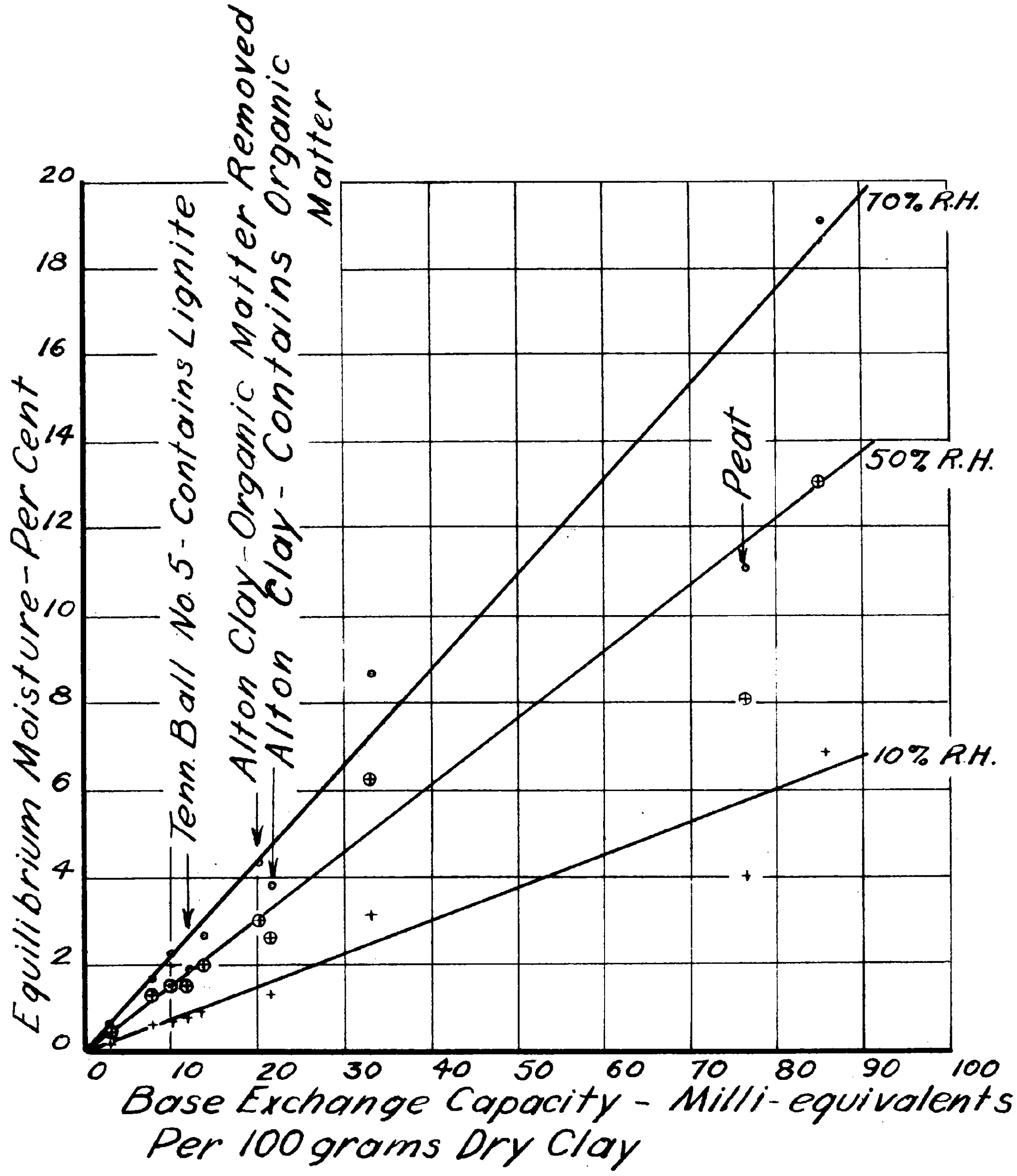


FIG 8
Moisture in Equilibrium With Various Hydrogen Clays at Different Relative Humidities. Temperature 25°C.



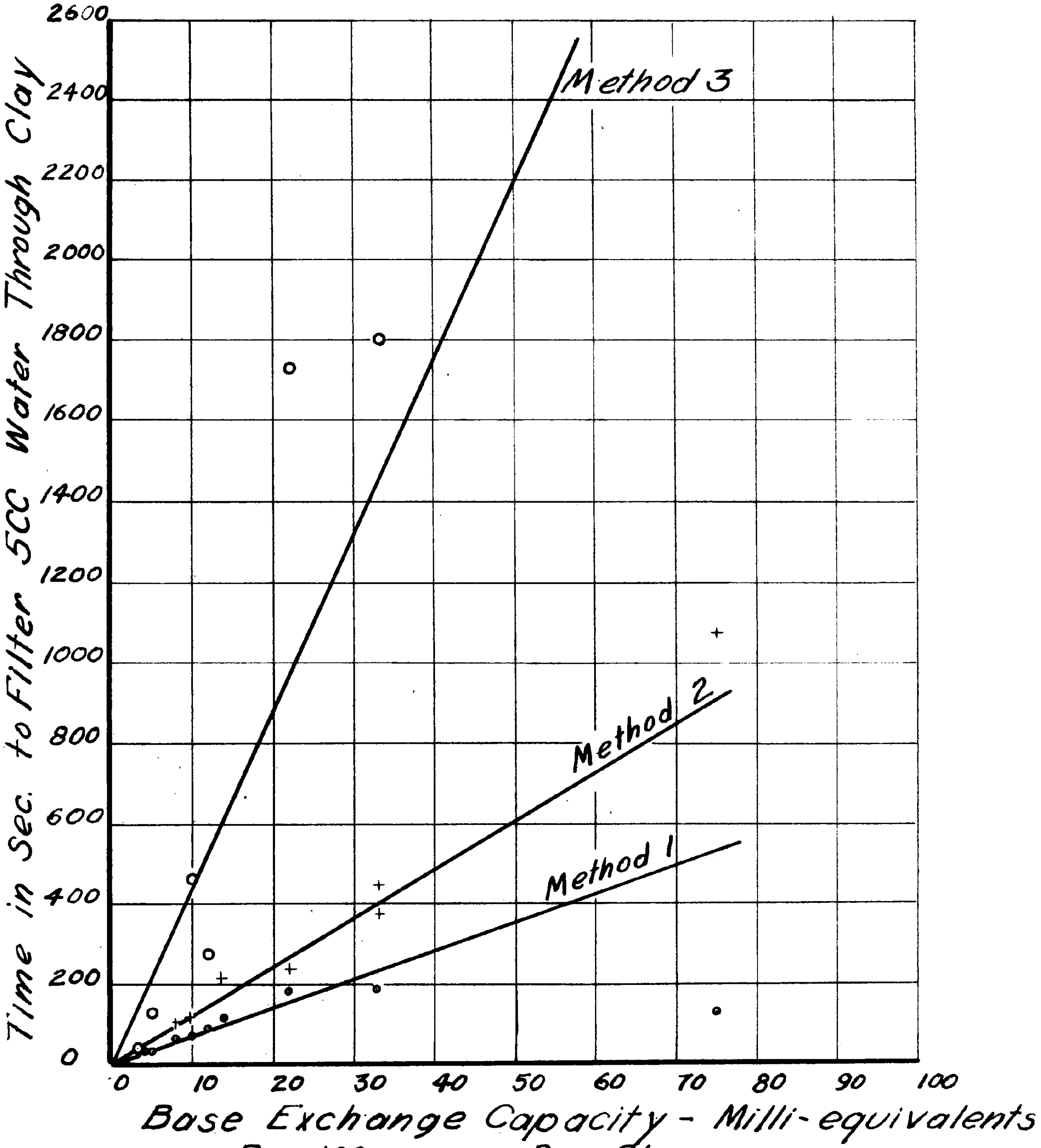
Organic material in clay is somewhat soluble, and some of it apparently dissociates to form cations of a character quite different from hydrogen. They are less strongly adsorbed than hydrogen, their behavior resembling somewhat that of sodium ions. The well known and characteristic ease with which lignitic clays disperse in water has never been explained. The postulation that organic matter dissolves and ionizes to produce cations of low field strength would explain the anomalies found here, as well as others to be pointed out below. Such clays could never be made single-base clays due to the continual solution of this constituent.

Possibly the best method to evaluate the organic matter content of clays would be a determination of its equilibrium moisture in comparison to clays not containing it. Another possibility is to be found in heat of wetting measurements which show a similar anomaly.

5. Permeability.

The permeability data shown in Fig. 9 brings out first of all that there is a general relationship between permeability and base exchange capacity, but the correlation is not exact. This is the first of the properties discussed which could be related to the packing characteristics of the particles (See Table I, item II D). This relation is clearly indicated here from two different aspects. In method 1 (see part 3 of Experimental), the powdered clays are merely allowed to soak over night, so the permeabilities are partly dependent upon the slaking rates of the clays. More thorough agitation tightens up the clays, but the values still fell far short of the limiting case brought about by complete dispersion (Method 3).

Fig. 9. Permeability of Hydrogen Clays
Temperature 25°C.



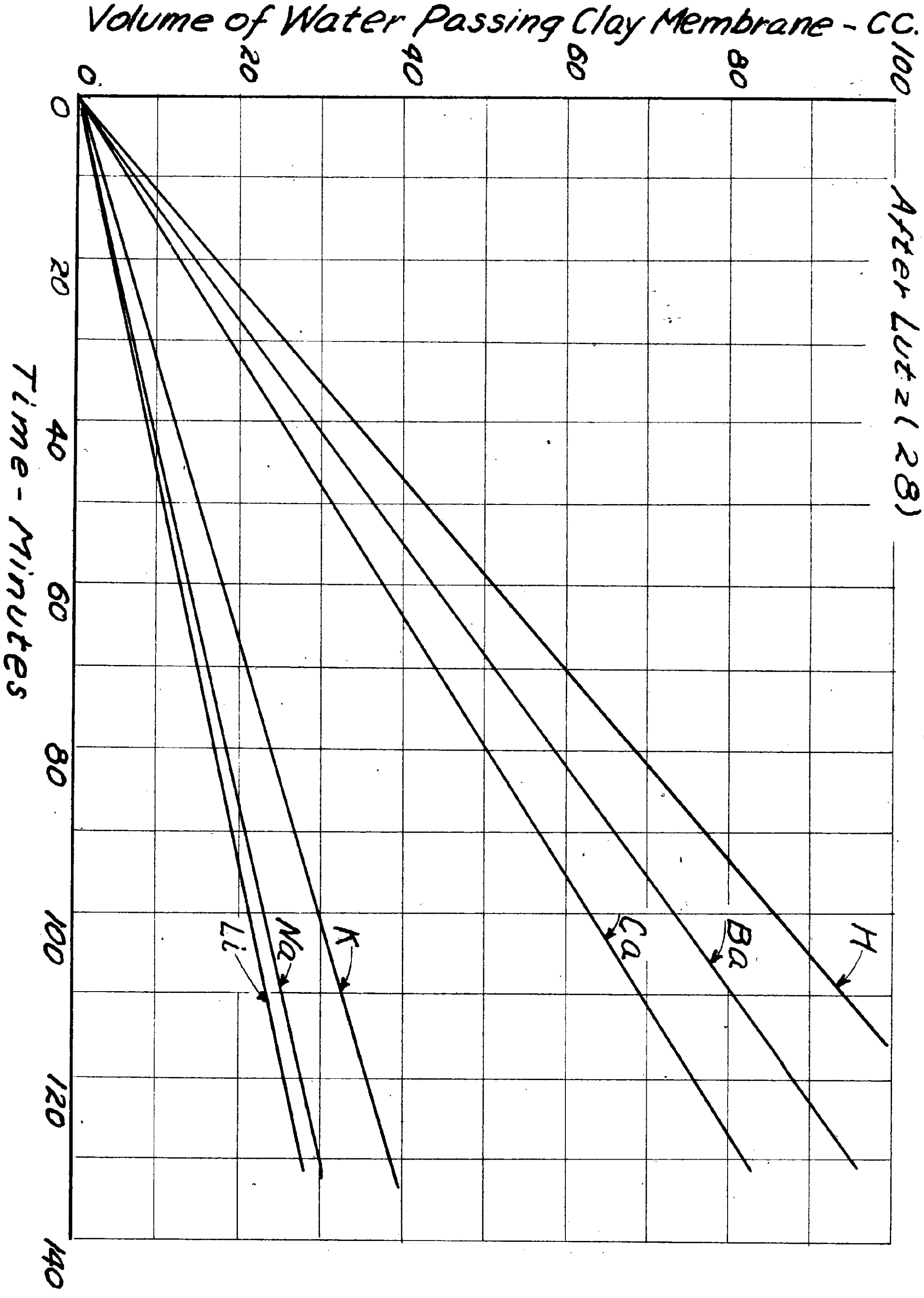


Fig.10. Effect of different Cations on the Permeability of Clay
After Lutz (28)

The correlation for method 3, which may be considered the limit, is very poor. This evidently means that permeability is dependent, not only on base exchange capacity, but upon packing as well, and that there is no definite relationship between base exchange capacity and packing. Note that here again the clays containing organic matter do not fall on the curves. This could have been predicted from the equilibrium moisture data. The less highly hydrated organic ions can pack much closer and develop a denser structure.

The effect of different cations on the permeability of clays has been shown by Lutz (28). Some of his data are shown in Fig. 10. The order of increasing permeability is the same as would be expected from a calculation of the field strengths and hydration power for the respective ions. (See section II).

Information of this sort has several practical applications. The theory can be applied to the modification of drying properties, casting rates, dry strengths, drilling muds, etc. Another thing that should be pointed out is that Fig. 9 offers a partial explanation for some of the frequently observed anomalous behaviors of clays and ceramic mixes in practice. It may be very difficult, if not impossible, to always obtain the same degree of dispersion of the clays during processing, which would have a marked influence on several important properties.

6. Rate of drying.

Figs. 11 and 12 show the results of some simple tests on the rates of drying of several of the clays. The only new facts brought out by this data were the difference in the shapes of the time-water loss curves of the Na- and H-clays. The H-clays dry in the

Fig. 11. Rates of Drying of Hydrogen-Clays
Dried in Open Air at Room Temperature

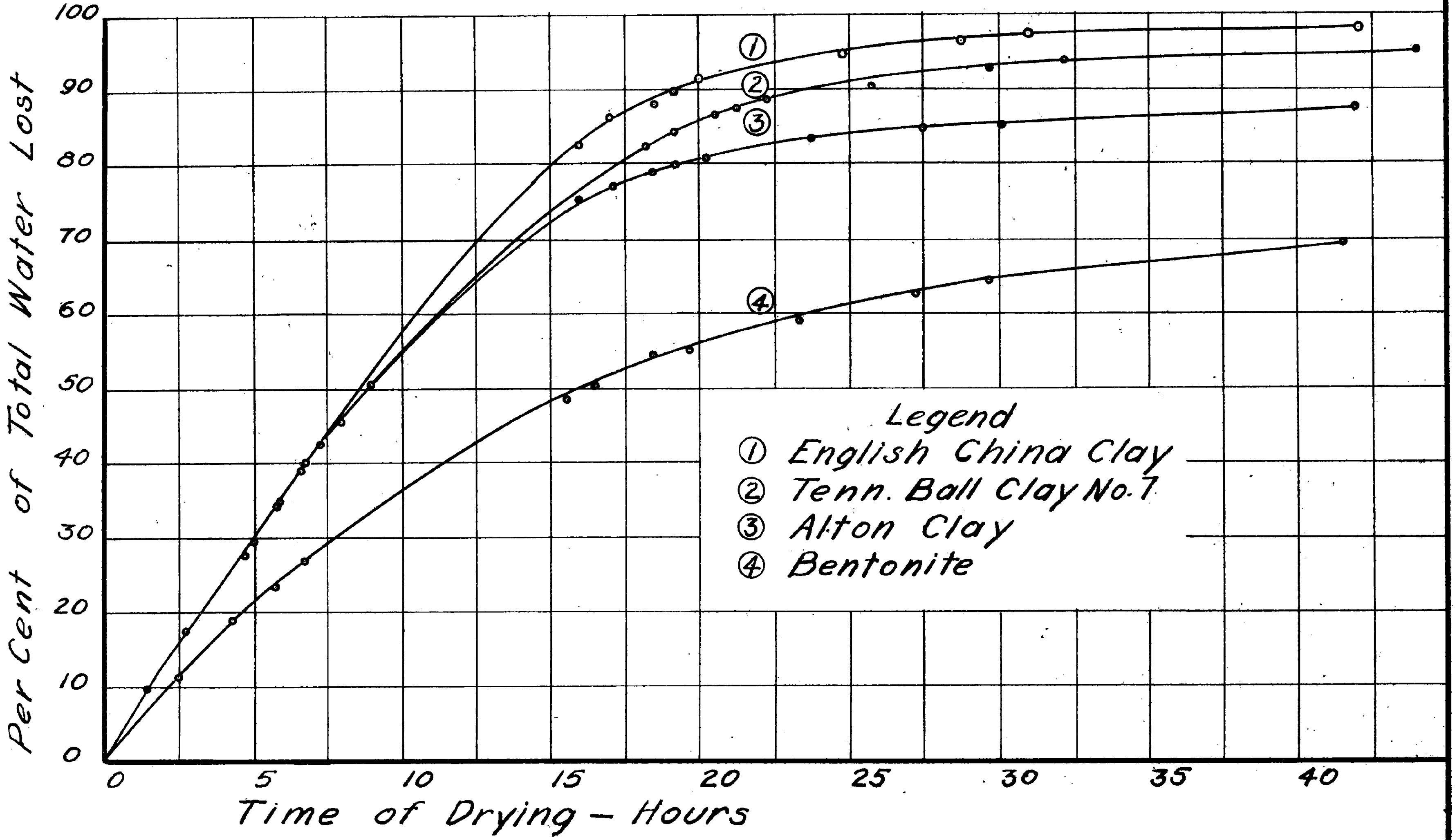
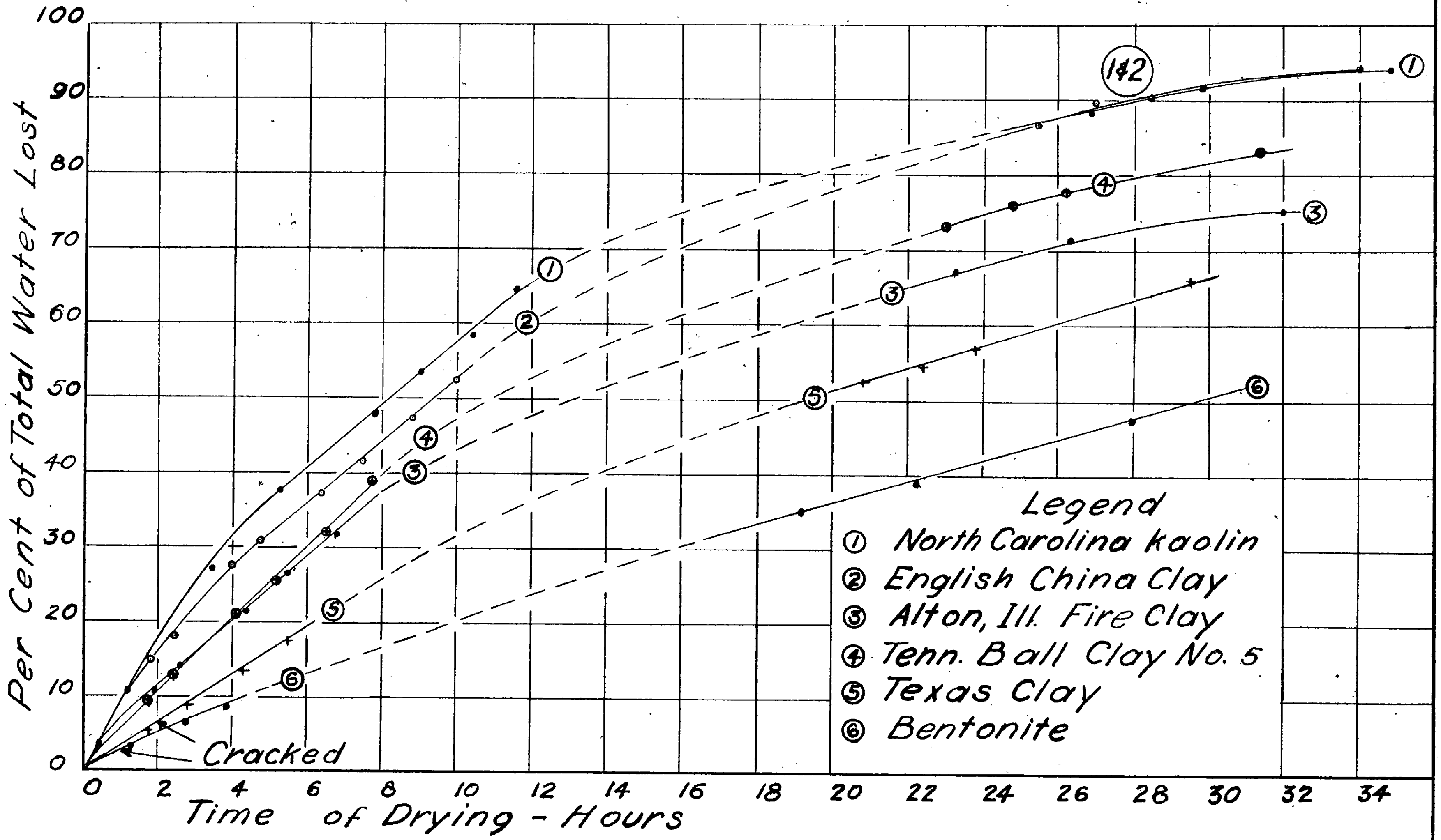


Fig. 12. Rates of Drying of Sodium-Clays Dried in Open Air at Room Temp.



usual characteristic manner, but the Na-clays have two constant rate periods. The only explanation seems to be that the type of packing is so different in the two cases as to drastically alter the structure of the capillary system. The H-clays of course are in a flocculent condition, and the floccules of clay pack in a rather loose, unstable structure. As drying progresses and shrinkage takes place the internal stress is relieved by shiftings of the particles composing the floccules. This not only brings about a more stable and dense packing, but continually changes the pore structure in such a manner as to cause a continually decreasing rate of drying.

The Na-clays, being deflocculated, are difficult to work unless they possess almost a minimum of water content. This results in a stable system of packing which does not change materially as drying progresses. Clays with such a capillary system should dry at a nearly constant rate over a considerable period. There being no other means of relieving excess stress, excepting to crack, such clays are difficult to dry safely.

Any of the large cations of low charge, such as the postulated organic ion, would be expected to act in the same manner toward clays.

7. Drying Shrinkage.

Figure 13 indicates that if clays are made up to the same plasticity, the drying shrinkage is proportional to the base exchange capacity, and the effect of the nature of the adsorbed cation is very little. This is perhaps due to compensating effects of more water and higher porosity in the hydrogen clays, and less water and lower porosity in the sodium clays. The relations

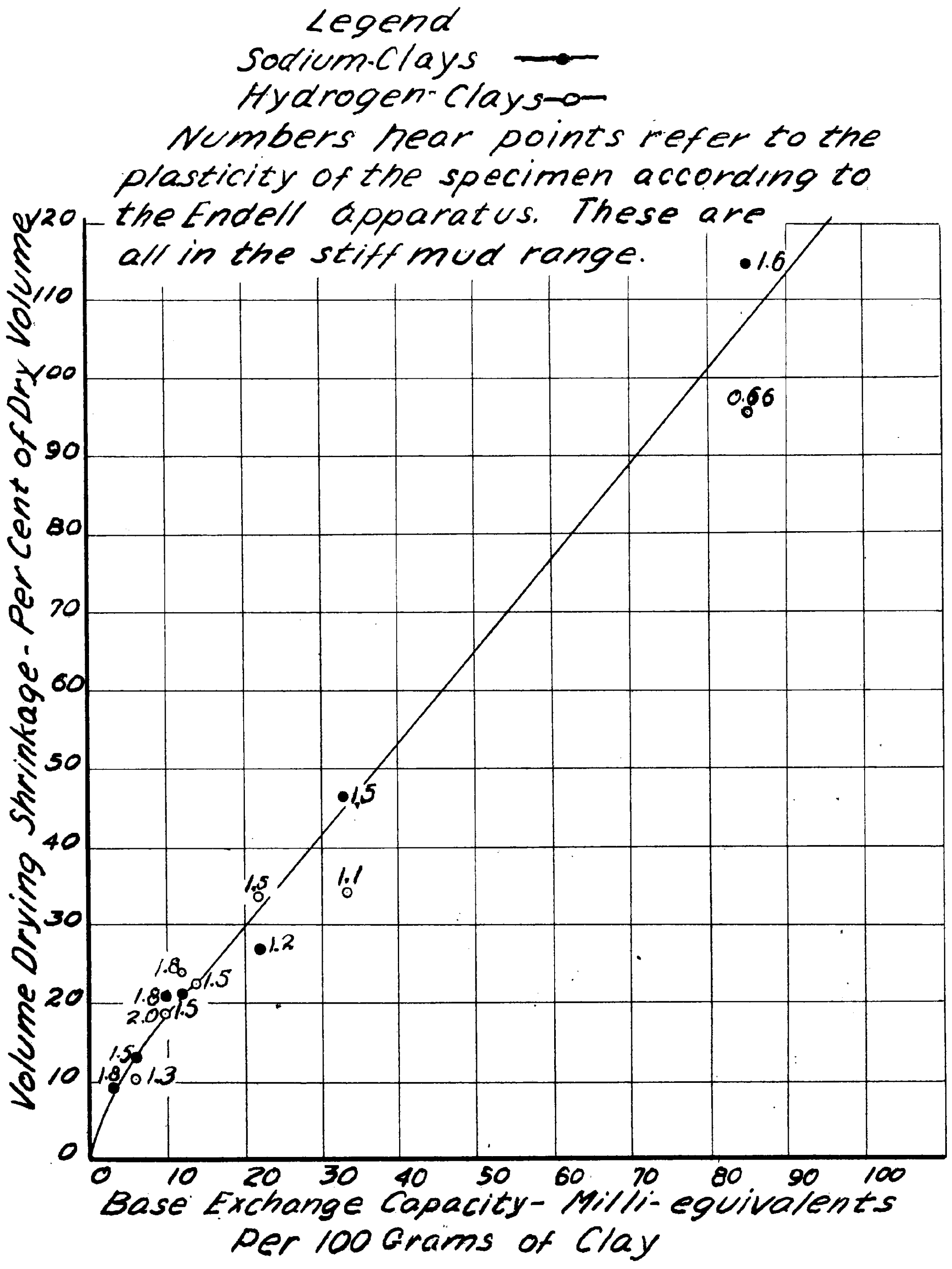


Fig. 13 Drying Shrinkages of Clays

between drying shrinkage, tempering water and porosity for a single clay are shown in Fig. 14.

6. Dry strengths.

Analysis of the dry strength data shown in Figs. 15 and 16 brings out some interesting points. The same points that were wild on the equilibrium moisture and permeability diagrams are also out of place here, and in the same direction. Dry strengths are vastly increased by replacing hydrogen with sodium. Organic matter has a similar behavior.

The difference in strength is probably due difference in packing characteristics. The data shown in Fig. 17 indicate that this is the case. The clays containing organic matter which showed poor agreement in Figs.8, 9, 15, and 16 appear normal in Fig. 17.

The porosity-strength curves for the H-clays and the Na-clays do not coincide. This indicates that the pore structures of the Na- and H-clays are of different types. The dry strength would apparently be a function of porosity for a given type of pore structure.

V. General Conclusions

The cation adsorption capacity and the nature of the adsorbed cation are very closely related to the heat of wetting, pH and equilibrium moisture. In fact, they appear to be different manifestations of the same phenomena. For a given adsorbed cation, these properties relate directly to the intensity of adsorption of the ion.

It is feasible to postulate the existence of organic cations (originating from the solution of organic matter in clays) of large radius, small charge and low hydrationenergy, which will explain

Fig. 14. The Effect of Tempering Water on the Shrinkage and Porosity of Clay – (Tenn. No. 7 Ball)

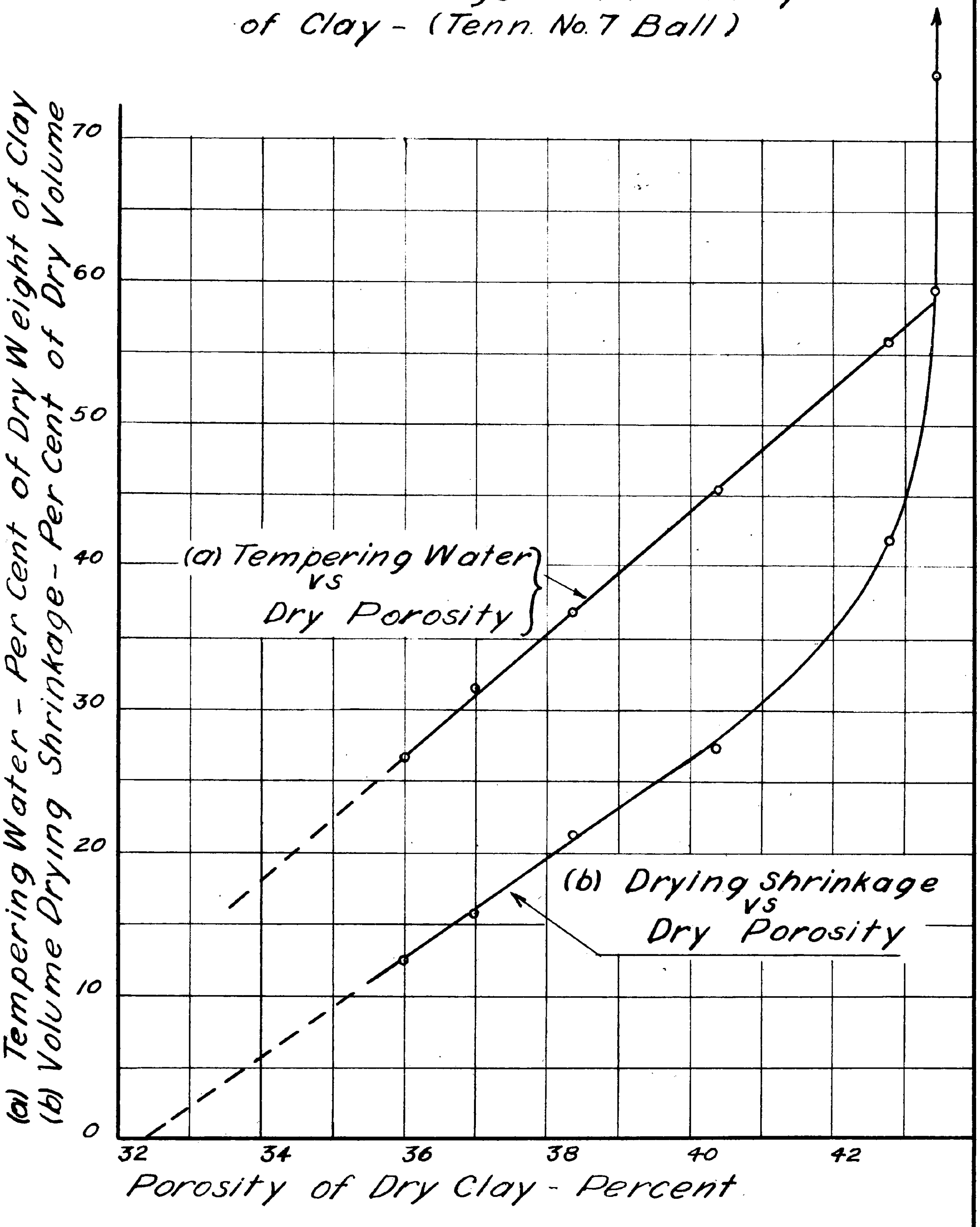


Fig. 15. Modulus of Rupture of Sodium And Hydrogen Clays in The Dry State

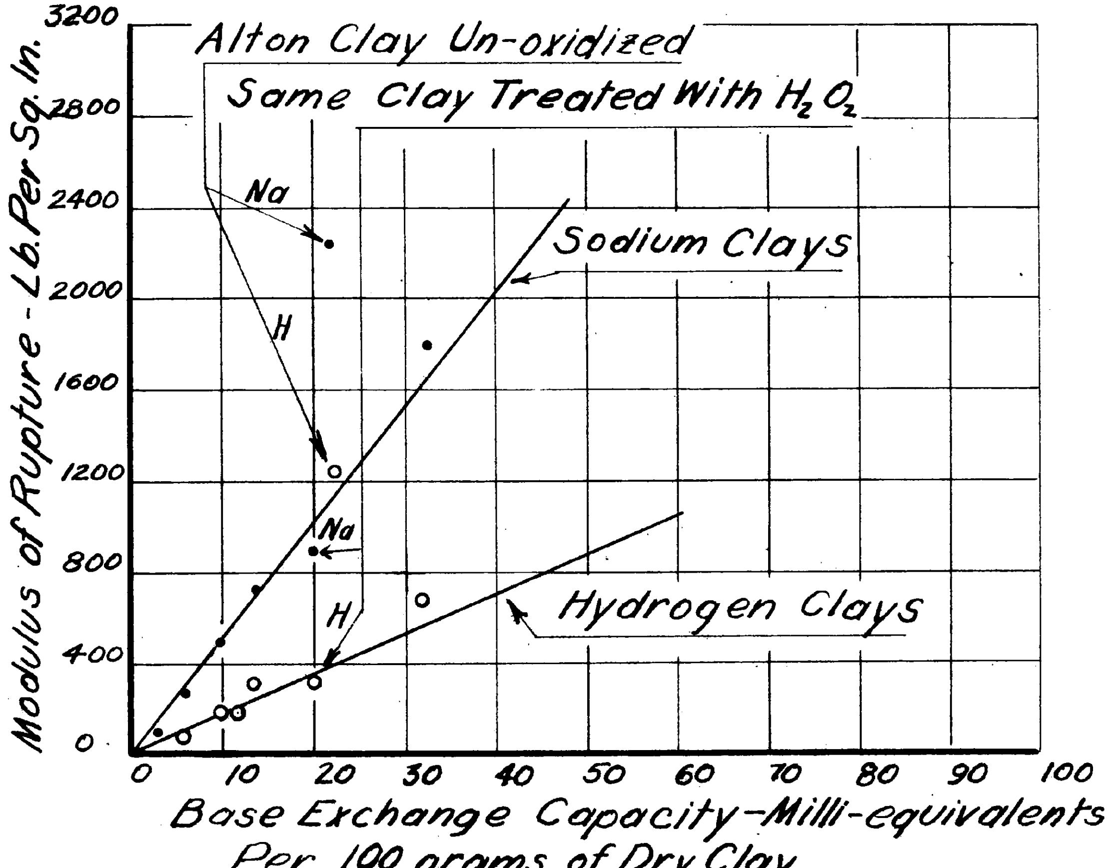


Fig. 16. Compressive Strengths of Dry Clays as a Function of Base Exchange Capacity and as Influenced by Adsorbed Sodium and Hydrogen Ions and The Presence of Organic Matter

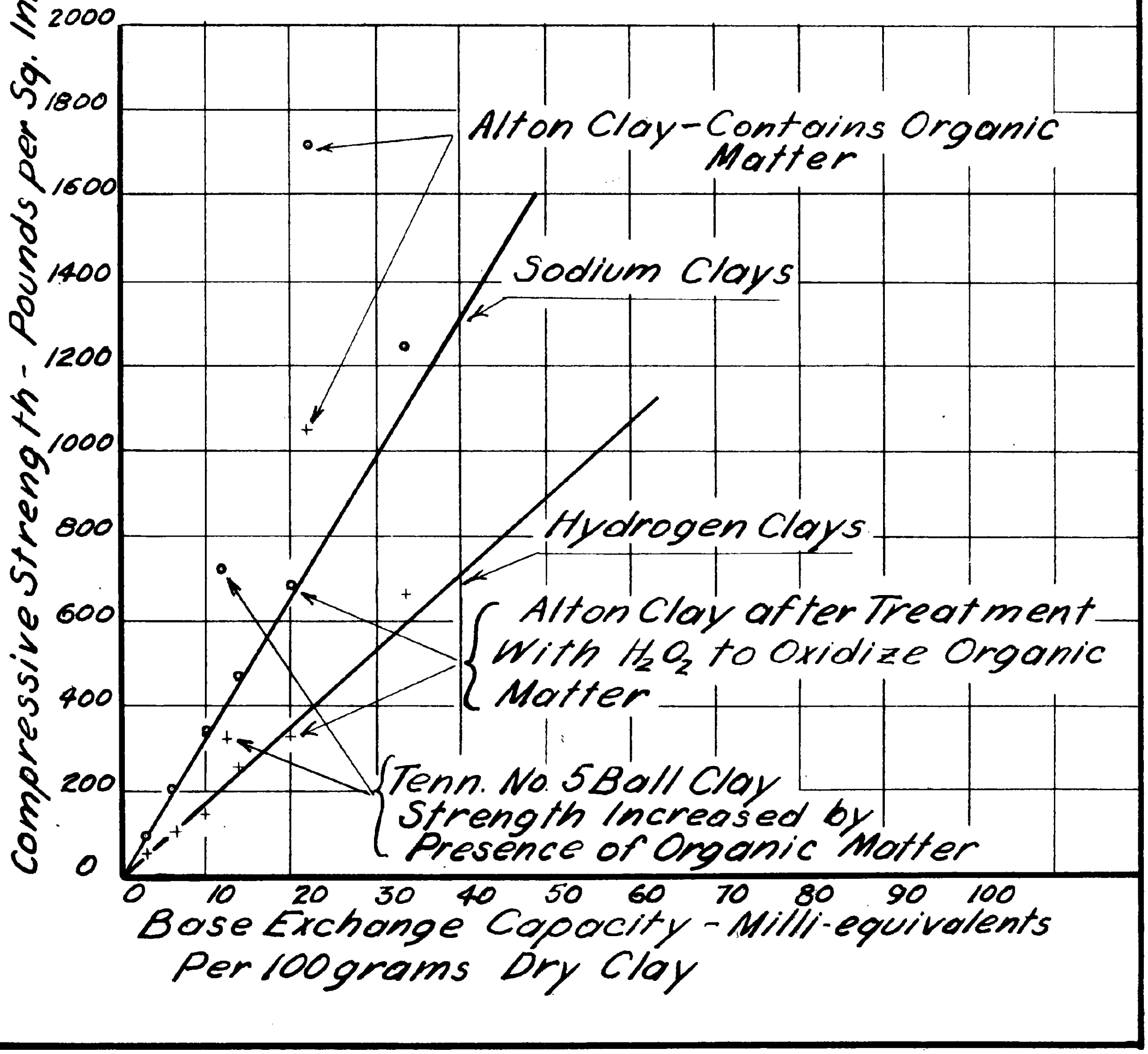
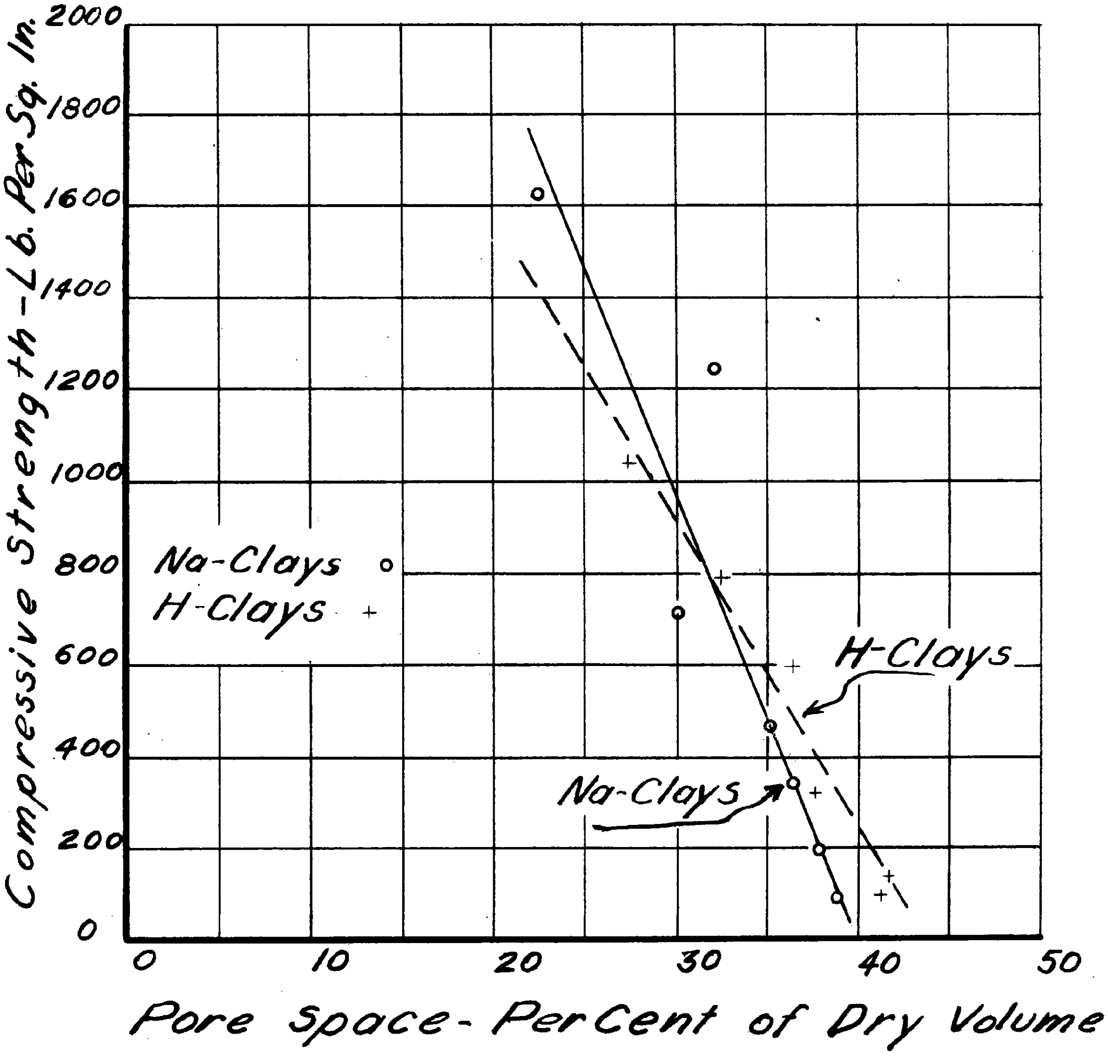


Fig. 17 Compressive Strengths of Dry Clays As A Function of Their Porosities



the anomalous behavior of clays containing organic matter.

Permeability, drying rates and dry strengths (for single-base clays) are very closely correlated, and are dependent upon pore structure and pore volume as well as upon base exchange capacity. Pore structure is in a large measure dependent upon the character of the cation present. Large, weak ions, when present, bring about a dense, stable pore structure which imparts difficult drying characteristics, high dry strength and low permeability. Small strong ions, such as hydrogen, induce the reverse effects.

The properties of clays may be defined as functions of ion sorption capacity, nature of the adsorbed cation, and porosity, providing the water content and soluble salts are controlled.

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VIII. Vita

Cameron Gerald Harman was born in Grayville, Illinois, July 7, 1905. He attended various public schools and was graduated from Olney Township High School in 1924. He entered the University of Illinois in 1924 and was graduated from that institution in 1929 with the degree of Bachelor of Science in Ceramics. He received the degree of Master of Science in Ceramic Engineering from the same institution in 1935.

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