

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI[®]

NOTE TO USERS

This reproduction is the best copy available.

UMI[®]

I. A METHOD FOR THE DETERMINATION OF AREA OF EARTH
MATERIALS.

II. SOME FACTORS AFFECTING BASE EXCHANGE IN SOIL
AND SUBSOIL.

BY

Douglas Verne Moses.

A thesis submitted to the Graduate Faculty
for the Degree of
DOCTOR OF PHILOSOPHY.

Major subject Chemical Engineering.

Approved

Signature was redacted for privacy.

In charge of Major work.

Signature was redacted for privacy.

Head of Major Department.

Signature was redacted for privacy.

Dean of Graduate College.

Iowa State College.

1925.

UMI Number: DP14501



UMI Microform DP14501

Copyright 2006 by ProQuest Information and Learning Company.

All rights reserved. This microform edition is protected against
unauthorized copying under Title 17, United States Code.

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

S 593
M 553 m

INDEX.

Acknowledgements.....	3.
-----------------------	----

PART I.

Introduction.....	5.
Current Methods of Estimation of Colloidal Material in Earths.....	6.
Unfree Water as an Indication of Total Surface.....	9.
Experimental.....	10.
(a) Apparatus.....	10.
(b) Procedure.....	11.
Experimental Data.....	15.
Discussion.....	17.
Extracted Colloidal Material.....	19.
Summary.....	23.
Conclusions.....	23.
Literature Cited.....	24.

PART II.

Introduction.....	29.
Theoretical.....	29.
Conditions Affecting Base Exchange in Soils.....	31.
Experimental.....	32.
Treatment of Sample.....	32.

INDEX (CONTD.)

The Effect of Concentration.....	32.
The Effect of Removing the Replaced Base.....	36.
The Effect of Temperature upon Base Exchange.....	37.
The Effect of Time upon Replacement..	38.
The Effect of the Presence of an Alkaline Material upon Base Exchange.....	39.
The Effect of Acidity upon Replacement.....	41.
The Retention of Alkaline Materials by Soils.....	42.
A Method of Determining Combined Replaceable and Soluble Potassium in Soils.....	44.
Summary.....	46.
Conclusions.....	46.
Literature Reviewed.....	47.

ACKNOWLEDGEMENT.

The author wishes to express his sincere gratitude to Dr. O. R. Sweeney, professor of Chemical Engineering, under whose direction this work was carried out and to Dr. J. A. Wilkinson, professor of Chemistry, for his many helpful suggestions. He is also indebted to Mr. J. R. Boyd of the United States Bureau of Roads and to Dr. M. S. Anderson of the United States Bureau of Soils for samples used in the investigation.

I. A METHOD FOR THE DETERMINATION OF AREA OF EARTH
MATERIALS.

INTRODUCTION.

With increased attention being given earth materials, a simple method of determining their surface has become essential. It is quite generally recognized that the finer portions with their large surface exert a great influence on the properties of earths. Earth materials are of great importance to the engineer for roadmaking and for foundation support. Studies are being made in an effort to correlate the properties of these materials in a quantitative way with colloids or the related factor, total surface. (1)(2)

It has been the practice to split earths into fractions. Different investigators have set various arbitrary limits upon the diameter of the particles making up the fractions. (3)(4) Schloesing allowed suspensions of the fine fractions to settle several months to obtain his "argile colloïdale". (5) Hilgarde termed "colloidal clay" any particles which failed to settle through a column of water eight inches high in 24 hours. Investigators with the United States Bureau of Soils (6) term "ultra clay" that portion of the soil which remains in suspension after being subjected in a centrifuge for three minutes to a force of 17,000 times gravity.

The exact nature of the colloidal, or ultra clay, having particles within the colloidal range has not been definitely established, but there is no reason for assuming that they have sharply different properties from particles immediately

above the colloidal range. Inside of the colloidal range, there is opportunity for a wide variation due to the possibility of the major portion of the particles approaching either the upper or lower limit of the colloidal dimensions. Because of this, it is unlikely that a close connection between mass and adsorption or other surface properties exists in the colloidal or near colloidal fractions of the earths. In the study of soil characteristics it is, therefore, more desirable to use a relative indication of surface than to attempt a reduction to percent colloidal content.

CURRENT METHODS OF ESTIMATION OF COLLOIDAL MATERIAL IN EARTHS.

Perhaps the oldest and most widely used method of arriving at the colloidal content of an earth is the separation or mechanical analysis. Methods of this type depend upon the dislodging and dispersing of the light particles by shaking, brushing or rubbing repeatedly and separating by settling or centrifuging ⁽⁶⁾⁽⁷⁾⁽⁸⁾ the water suspension.

Various means including evaporation, ultrafiltration and coagulation, are used for the recovery of the dispersed ⁽⁶⁾⁽⁷⁾⁽¹⁰⁾ fraction. The heavier portion is classified further by sieve analysis. Figures obtained by these methods are very valuable in giving insight into the range of size in the coarser fractions, but complete separation of the fine

material is very difficult if not impossible. It has been shown that there is a considerable amount of colloidal material present after many extractions. (11)

Adsorption methods based on the decolorization of various dye solutions have been proposed. Ashley (12) measures the capacity of a soil to partially decolorize an excess of malachite green solution. This is regarded as a relative measure of the colloids. The United States Bureau of Soils (13) uses a modification of this method in determining the ratio of soil and extracted colloidal material. The United States Bureau of Roads uses a method devised by Dr. E.C.E. Lord (7) which measures the capacity of a soil to completely decolorize standard crystal violet solution as it percolates through a weighed sample. Many other methods based upon adsorption of dyestuffs are described.

There is considerable evidence that adsorption of dyestuffs by earths bears no simple relation to colloidal content. (14)(15) There is also some indication that the so-called adsorption is a combination of chemical and physical reactions. (16) This would seem to indicate that the dye adsorption value, while valuable in certain instances, is not to be regarded as a direct measure of active surface.

One of the most constant properties of earth colloids seems to be their power to adsorb water vapor from an atmosphere of known humidity. Originated by Mitscherlich (17) and

modified by workers in the United States Bureau of Soils,⁽¹³⁾
this test seems to bear a direct relation to total surface.
Essentially it consists in allowing the soil to become
saturated in an atmosphere over sulfuric acid of a known
concentration and measuring the water driven off by drying.
In the study of a large number of soil extracts made by the
Bureau of Soils' workers, it was found that an average of
0.298 gram of water was adsorbed per gram of soil colloid.
The maximum variation from the average was 23 percent. This
variation was probably due to the lack of uniformity of the
colloidal particles themselves.

Some attention has been given the microscopic examination
of clays and the estimation of colloidal content by micro-
scopic methods.⁽¹⁸⁾ Fry⁽¹⁹⁾ describes a method of determin-
ation, using a petrographic microscope, which seems very
reliable but which is too long and too specialized for
routine application.

Some of the latest attempts to find a readily measurable
function which may be used as a colloidal index have been
along the lines of heat of wetting. Bouyoucos⁽¹⁹⁾ and
Anderson⁽²⁰⁾ have obtained promising results in this way. The
methods which are very similar, measure the temperature rise
when soils are wetted, assuming that all heat generated is
from adsorption.

A number of other methods of arriving at some idea of
colloidal content have been devised. These include digestion

(21) with acid, shrinkage when dried (22) and adsorption of
(13) ammonia.

UNFREE WATER AS AN INDICATION OF TOTAL SURFACE.

One of the characteristics of many colloidal substances is the capacity to adsorb water and prevent its freezing at normal freezing temperature. Foote and Saxton (23)(24)(25) studied the freezing of water adsorbed in various colloidal materials and found that a certain rather definite portion remained unfrozen. Their investigation is especially noteworthy in that it is the first in which the dilatometer was used to determine the amount of frozen water. Bouyoucos (26) later applied the method to the study of amounts and kinds of water encountered in soils. It was found that some water froze at its normal freezing temperature, some at a lower degree, while some did not freeze even at a very low temperature. Further study showed that the presence of soluble salts had little or no effect upon the amount of water which could not be readily frozen. Bouyoucos termed the tightly bound water "unfree".

It was noted from Bouyoucos' work and later from studies in this laboratory that the amount of water remaining unfrozen in soils at low temperatures was different for different soils. Sandy soils held relatively small amounts while heavy clays prevented much more from freezing. Preliminary comparison of the unfree water with the amount adsorbed in the

Bureau of Soils' water vapor method showed some connection. The possibility of using the unfree water as an index to the total surface was noted and further studies carried out.

EXPERIMENTAL.

Apparatus.

On account of the size sample which it was desired to use and to facilitate changing samples, the ordinary form of dilatometer was modified. The form used by Bouyoucos was found to be too fragile and to have openings which were too small for convenient changing of samples. A small sized show bottle was fitted with a two-hole rubber stopper carrying a thermometer graduated in tenths of a degree and a two cc. pipette having 0.02 cc. divisions. Cork and ground glass stoppers were tried without success; the former absorbing gasoline and the latter invariably leaking. The rounded neck of the show bottle allowed the rubber to expand inside and make a very tight seal. No change of volume was noted due to expansion of stoppers; the expansion evidently being equal to the volume absorbed. The freezing baths were made by placing one gallon jars inside of three gallon jars. The intervening space was filled with sawdust for insulation. Moisture determinations of the usual sort were made in aluminum dishes. An ordinary filter pump was used in exhausting the air from samples in the dilatometer.

Procedure.

A quantity of earth ranging from 150 to 200 grams was placed in a casserole and just enough water added to make it stick together. A considerable excess of water over the amount which the soil prevented from freezing caused a large expansion, sometimes breaking the dilatometer. It was also noted that a large excess of water affected the results so an effort was made to keep the moisture as low as possible and still have enough present to show some expansion. After being worked and stirred until the moisture was uniformly distributed, the sample was covered and allowed to stand for approximately an hour. This provided time for moisture to penetrate any small lumps. At the end of that time, the sample was pressed flat on a glass plate and cut into many thin strips. Every third strip was removed. This provided two samples containing equal percentages of moisture, but one sample approximately twice the size of the other. The larger portion was placed into the previously weighed dilatometer and the smaller in a tared moisture dish. Both dish and dilatometer were again weighed. The moisture dish was placed in an oven and dried to constant weight at 110 C.

The dilatometer was nearly filled with gasoline and connected through a Kjeldahl connecting bulb to a filter pump to remove the air. The bulb allowed the gasoline to

boil vigorously under the reduced pressure without being drawn into the bulb. In order to note whether or not all the air had been expelled after a period of pumping the dilatometer was tilted until some of the bubbles were entrapped under the shoulder and the vacuum broken. Bubbles of gasoline vapor condensed immediately while air remained as small permanent bubbles. After the air had been removed the dilatometer was completely filled with gasoline and fitted with the stopper carrying the pipette and thermometer. To retard evaporation of gasoline, the end of the pipette was stoppered as tightly as possible with cotton.

The cooling process was accomplished in two steps. After adjusting the height of the gasoline at room temperature to near the middle of the pipette, a reading was taken. The dilatometer was then placed in a bath of pure ice and water and was allowed to remain until 0 C. was reached, when another reading was taken. It was then transferred to a bath maintained at as near -4 C. as possible for the freezing. Equilibrium throughout the sample was indicated by the gasoline column reaching a constant level. When this condition was reached and the thermometer indicated a temperature of -4 C., the final reading was taken. The dilatometer was removed and allowed to stand in the air until it reached room temperature again. A comparison of the height of the gasoline column with its height before freezing

indicated whether or not leaking had taken place. Observations were made only upon the first freezing due to the fact that successive freezings affect the colloid and decrease the amount of unfree water.

The total expansion was taken as the difference between the reading at -4°C . before freezing and the reading after freezing. Because of difficulties in supercooling some earths to -4°C . without freezing, this reading was not taken directly but was found by extrapolation of the values taken at room temperature and 0°C . Cooling curves for gasoline alone and for gasoline and dry earth were found to be straight lines.

Calculations were made on the basis that one gram of water in freezing expands 0.0932 cc. This value was obtained by Foote and Saxton.⁽²⁴⁾ A determination made with the large dilatometer containing ignited and washed sand with a known quantity of water gave results which closely checked this value.

The amount of water frozen was found by dividing the expansion by this figure. From the moisture determination the total amount of water in the frozen sample could be found; the difference between the frozen and total representing the unfrozen water. The unfrozen or unfree water was expressed as a percentage of the weight of the dry soil.

The entire calculation is given in the following formulae:

$$\text{Expansion when frozen} = h_f - h_o + \frac{4(h_r - h_o)}{T_r}$$

when:

h_f Final reading of gasoline column in cc.

h_o Zero.

h_r Room temperature reading of gasoline column in cc.

T_r Room temperature in degrees C.

$$\text{Percent unfree water} = \frac{\left(\frac{LW}{W} \cdot 0.0932 - E\right) 100}{.0932 \left(W - \frac{LW}{W}\right)}$$

which may be reduced to the form:

$$\text{Percent unfree water} = \frac{(LW - 10.73EW)100}{W(W - L)}$$

when:

w Weight of the moisture sample.

W Weight of the sample frozen.

L Loss of weight of moisture sample.

E Expansion when frozen.

In addition to unfree water, determinations were made of extractable clay using the Bureau of Roads mechanical analysis method, ⁽⁵⁾ of dye adsorption numbers by the Lord method, ⁽⁵⁾ and of water vapor adsorption by the Bureau of Soils method. ⁽¹³⁾

EXPERIMENTAL DATA.

Results of the method as applied to 27 samples of soil from various parts of the United States are shown in Table I. Included in the table are the results of the other tests. The results are averages of two check determinations varying not more than five percent in all cases except the dye adsorption with which the results varied from five to ten percent. For convenience in comparison, the results are arranged in ascending order of their percent unfree water.

TABLE I

:Sample:	Original Location:	Extract-*	Dye ads.*	Adsorb-	Unfree:
:No.	: of Sample	:able clay:	Number	:ed Water:	Water %:
:	:State: County	: %	:	:	:
: 1	:Va. : Arlington	: 11.4	: 2.0	: 1.03	: 1.32
: 2	:Va. : Arlington	: 9.6	: 7.5	: 1.17	: 1.55
: 3	:R. I.:	: 16.8	: 0.0	: 1.45	: 2.10
: 4	:Iowa : Story	: 13.2 [Ⓢ]	: 12.0 [Ⓢ]	: 1.80	: 2.20
: 5	:Minn : St. Louis	: 4.9	: 8.0	: 2.11	: 2.59
: 6	:R. I.:	: 19.5	: 0.0	: 1.80	: 3.24
: 7	:Iowa : Story	: 24.4 [Ⓢ]	: 25.0 [Ⓢ]	: 4.41	: 5.50
: 8	:Va. : Arlington	: 24.6	: 11.0	: 5.28	: 5.98
: 9	:Minn : St. Louis	: 26.4	: 29.0	: 4.77	: 5.99
: 10	:Iowa : Cerro Gorda	: 25.2	: 56.0	: 4.66	: 6.04
: 11	:Ohio :	: 48.5	: 37.5	: 5.94	: 6.94
: 12	:Iowa : Cerro Gorda	: 27.8	: 26.0	: 4.85	: 6.95
: 13	:Iowa : Story	: 30.6 [Ⓢ]	: 60.0 [Ⓢ]	: 4.65	: 8.00
: 14	:Ore. : Douglas	: 40.0	: 30.0	: 7.38	: 8.92
: 15	:Ohio :	: 56.0	: 25.0	: 8.39	: 9.80
: 16	:Va. : Arlington	: 33.2	: 40.0	: 9.46	: 10.67
: 17	:Va. : Arlington	: 45.8	: 26.0	: 9.39	: 12.05
: 18	:Minn : St. Louis	: 61.6	: 62.5	: 11.65	: 12.10
: 19	:Iowa : Story	: 36.0 [Ⓢ]	: 75.0 [Ⓢ]	: 9.56	: 12.80
: 20	:Iowa : Story	: 50.7 [Ⓢ]	: 100.0 [Ⓢ]	: 11.52	: 14.20
: 21	:Cal.I. : Los Angeles	: 56.8	: 152.5	: 12.81	: 15.90
: 22	:Iowa : Floyd	: 40.6	: 118.0	: 13.23	: 15.92
: 23	:Minn : St. Louis	: 78.9	: 100.0	: 16.83	: 18.30
: 24	:Iowa : Floyd	: 44.6	: 45.0	: 15.25	: 18.81
: 25	:Ky. : Hardin	: 76.4	: 50.0	: 18.52	: 20.0
: 26	:Ohio :	: 94.9	: 97.5	: 18.99	: 21.73
: 27	:Ore. : Tillamook	: 80.5	: 135.0	: 18.16	: 21.90

* With the exceptions noted the results under these headings were furnished through the courtesy of the United States Bureau of Public Roads.

@ Determinations made in this laboratory.

DISCUSSION.

It can be seen from the results that there is a close connection between water vapor and unfree water. Nearly as much water is adsorbed from the atmosphere over the 3.3 percent sulfuric acid as is held in the unfree state. Evidently the attraction is not entirely satisfied by the adsorbed water and the film adsorbed and prevented from freezing is slightly thicker.

It is believed that a break should occur in a vapor pressure curve plotted with a constant temperature and varying moisture content when the unfree water content is reached. At that point evaporation of the water should begin to require more energy because of the forces holding it. There is, however, the possibility that the break would appear only as a change of slope due to the shading off of the adsorptive forces. Little or no data is available on this point at the present time.

It is possible to calculate with a fair degree of accuracy the amount of water which will be adsorbed in the Bureau of Soils test if the unfree water is known or vice versa. Figure (1) shows this relation. If one gram of colloid adsorbs 0.3 gram of water as the Bureau of Soils workers have found, ⁽²⁹⁾ it will prevent 0.36 gram from freezing at -4 C. Percentage of colloids may be calculated from these figures, but it is believed that the relative measure expressed as percent unfree water is much more valuable.

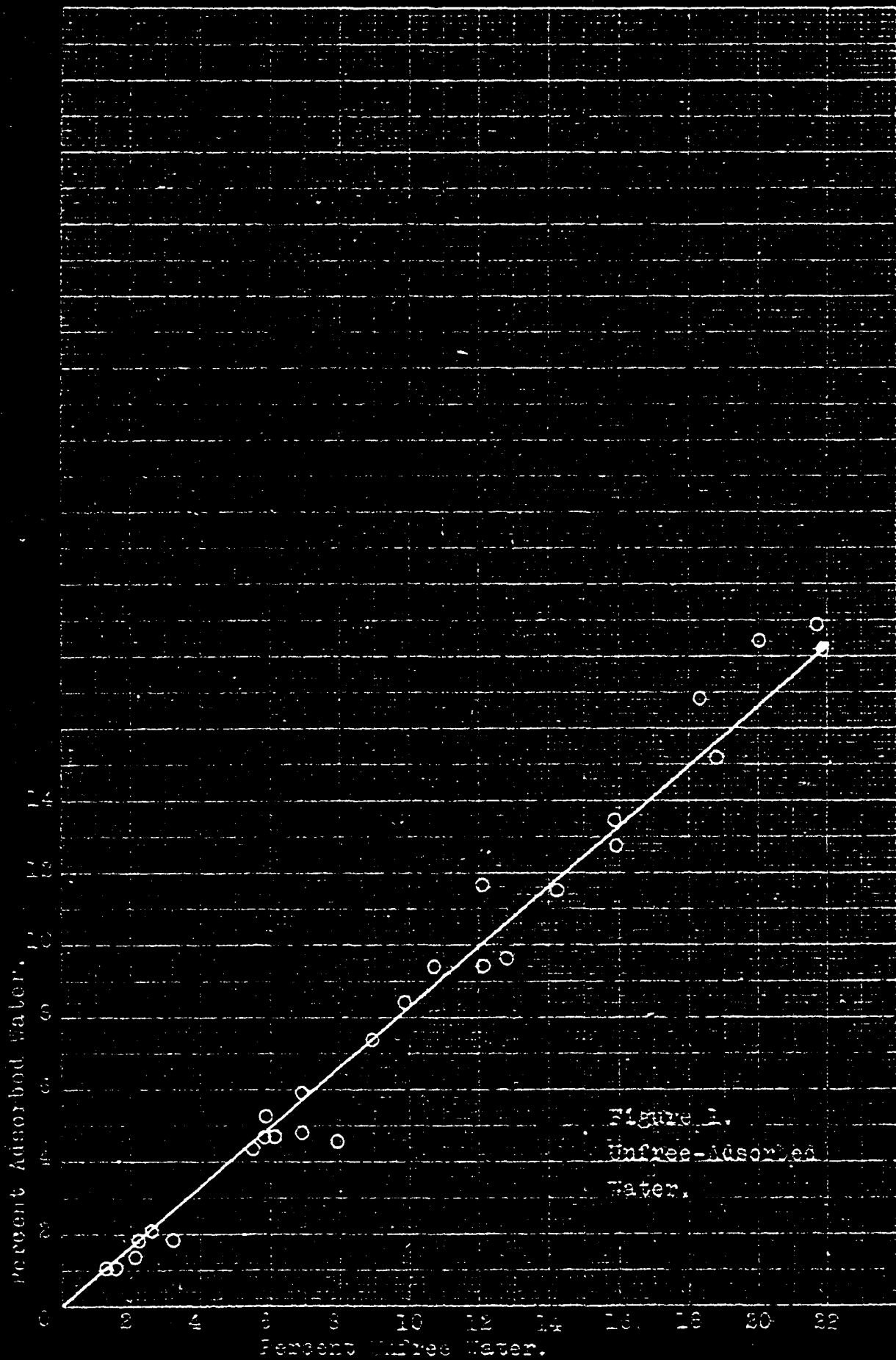


Figure 1.
Unfree-Adsorbed
Water.

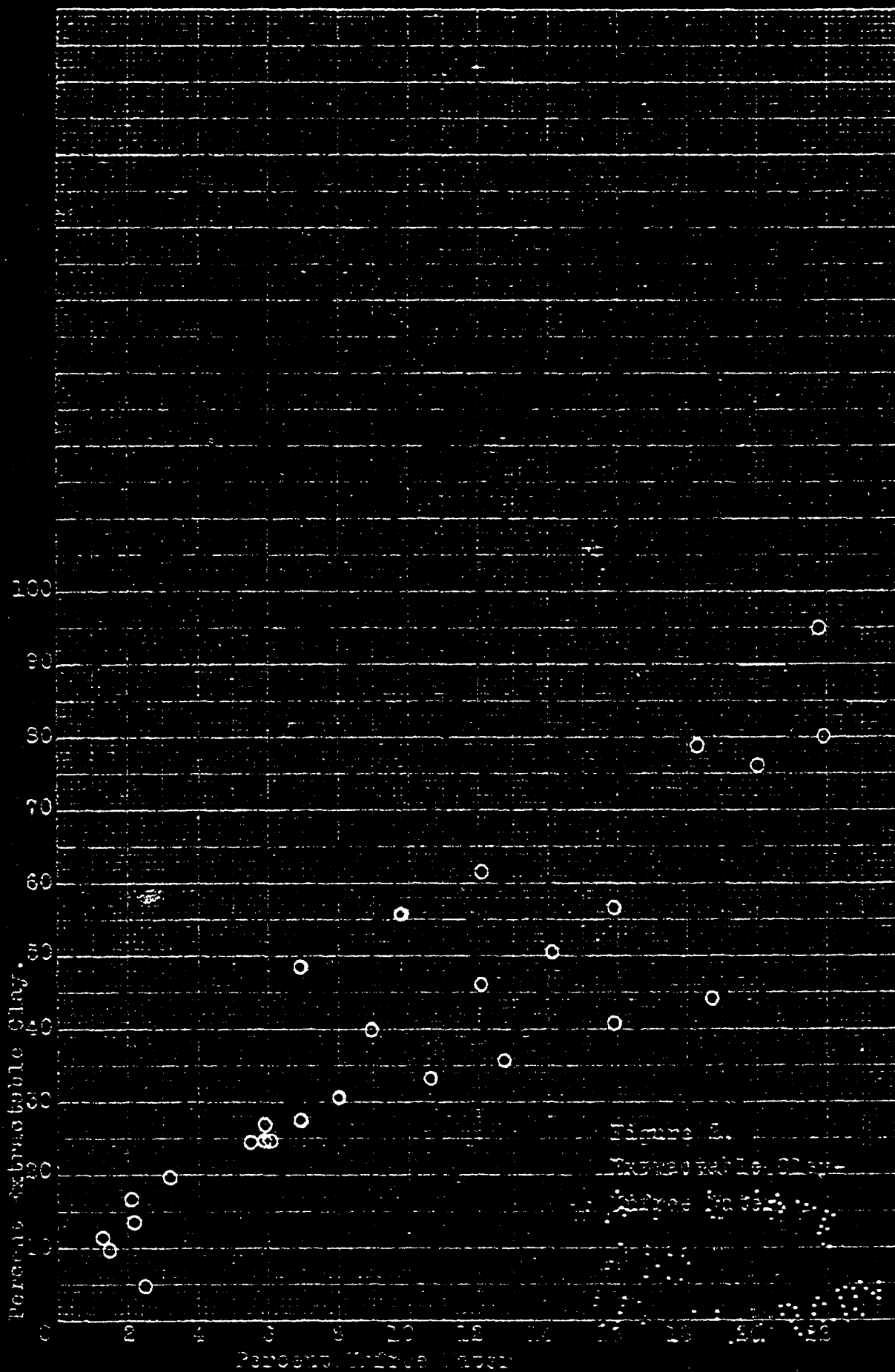
The correlation of the extractable clay by the Bureau of Roads method of mechanical analysis and of unfree water is shown in Figure (2). This indicates a tendency toward a relation but the gradation of particles evidently is quite different in the different earths causing variation of the mass-adsorption ratio. The reason for the points apparently forming three curves instead of grouping about a single one is not apparent.

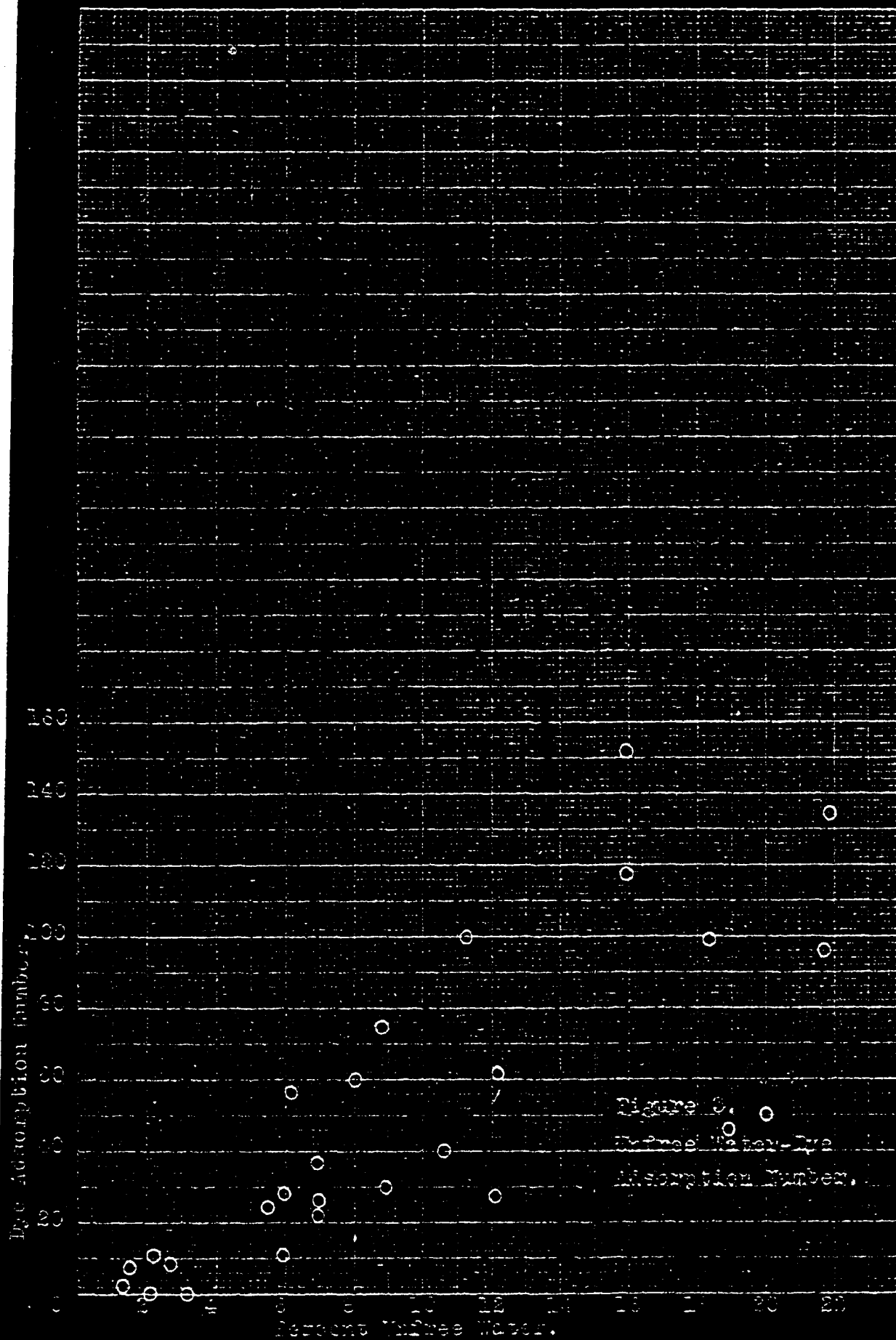
Figure (3) shows that there is little or no relation between the dye adsorption and the unfree water. Indications are that a secondary reaction of some sort caused the dye to show the sum of two or more effects rather than a physical adsorption.

EXTRACTED COLLOIDAL MATERIAL.

In the line of further investigation it was decided to note the unfree water which could be held by the pure colloid. Three samples were procured from the Bureau of Soils and one prepared in this laboratory by the method prescribed by the Bureau.
(13)

Because of the small amount of material available a dilatometer of the usual sealed form was used but was extremely inconvenient. Later dilatometers of the same sort as those used for earths themselves were made using $\frac{3}{8}$ inch test tubes for the bulbs and calibrated capillary tubes in place of





pipettes. Runs were made in the same manner as with the earths.

TABLE 2.

Material	Soil Extracted From	Adsorbed Water %	Unfree Water %
Colloid	Sharkey	27.42	29.80
Colloid	Sassafras	26.76	33.20
Colloid	Wabash	30.65	37.90
Colloid	Carrington Sub-soil	28.63	36.60

The colloidal extracts behave in exactly the same manner as the whole sample and the ratio of adsorbed water to unfree water is nearly the same. It would be possible to use the same scheme in calculating colloids as that made use of by the Bureau of Soils workers in calculating percentage colloids by the adsorption ratio, namely

$$\frac{\text{Adsorption per gram of soil}}{\text{Adsorption per gram of colloid}} \times 100$$

It is possible to use unfree water in a similar calculation, but because of the difficulty of obtaining a truly representative sample of the colloid, the value of such a method is doubtful.

From the results in Tables (1) and (2) it is evident that the unfree water method holds over a range of texture from extremely sandy earths to purely colloidal material, and bears a constant relation to the adsorbed water for this range. The indication is that both methods measure the purely adsorptive function in different manners.

SUMMARY.

A review of the literature shows a wide variation of the properties measured in the estimation of colloidal content. Various procedures are more or less complicated and require the services of a trained laboratory technician. The unfree water method makes use of a large sample and requires no extremely close work, standard solutions or expensive apparatus. It is designed for the use of engineers and others interested in colloidal investigations of earths. Correlations with various methods in use at the present time are shown for a wide variation of earths.

CONCLUSIONS.

1. Unfree water in earth materials may be readily measured with simple apparatus.
2. Unfree water is a measure of total surface in earth materials.
3. The unfree water method is applicable to earths having

a wide variation of texture.

4. Unfree water and adsorbed water by the Bureau of Soils method bear a definite relation to each other.

5. There is some relation between unfree water and extractable clay by the Bureau of Public Roads method.

6. There is little or no correlation between dye adsorption by the Lord method and the amount of unfree water.

LITERATURE CITED.

- (1) U.S. Bureau of Public Roads. Unpublished Data. (Tests, adsorption and others, applied to subgrade materials.)
- (2) Iowa Engineering Experiment Station. Unpublished Data. (Physical properties of earths and effects of colloidal content upon them.)
- (3) Schloesing, T. Sur la precipitation des limons par des solutions salines tres etendues. Compt. Rend. 70:1345-48, 1870. (Quoted from Bul. 1193 U.S. Dept. of Ag.)
- (4) Schloesing, T. Determination de l'argile dans la terre arable. Compt. Rend. 78:1276-79, 1874. (Quoted from Bul. 1193 U.S. Dept. of Ag.)
- (5) Hilgard, E.W. Soils, McMillan Co. New York. P 1-389, 1921.
- (6) Bureau of Soils. Estimation of colloidal material in soils by adsorption. U.S. Dept. of Ag. Bul. 1193, 1-41, 1924. (Results obtained by water vapor, dye and ammonia adsorption on various soils and soil separates.)
- (7) Goldbeck, A.T. and Jackson, F.H. Tests for soils in relation to their use in the subgrade of highways. Trans. Am Soc. Civil Eng., 21:1057, 1921. (Description of various tests used in the U.S. Bureau of Public Roads Laboratory.)

- (8) Surecht, H.G. Sedimentation as a means of classifying extremely fine clay particles. J. Am. Cer. Soc. 4:812-21, 1921.
- (9) Wiley, H.W. Analysis of Agricultural Materials Vol. II. Soils. The Chemical Publishing Co., Easton, Pa. (A collection of test and analysis methods.)
- (10) Oden, Sven. On clays as disperse systems. Trans. Faraday Soc. 17:327-48, 1922. (Description of a method of sedimentation which gives fineness as a continuous function. Describes an ingenious automatic apparatus for performing the test.)
- (11) Fry, W.H. The microscopic estimation of colloids in soil separates. J. Ag. Res., 24:789-883, 1923. (Gives a method and shows results on extracts, soils and minerals. Shows inability of mechanical analysis methods to remove colloid completely.)
- (12) Ashley, H.E. The colloidal matter of clay and its measurement. U.S. Geol. Survey Bul. 388, 1-65, 1909. (Proposes relative measurement of colloids by dye adsorption.)
- (13) Moore, C.J., Fry, W.H. and Middleton, H.E. Methods for determining the amount of colloidal material in soils. J. Ind. & Eng. Chem., 13:527-30, 1921. (Description of water vapor, ammonia and dye adsorption methods with results on some soils. Some properties of the extracted colloid are discussed.)
- (14) Bergues Y Escudor, D. Casmiro. Colloidal clay. Mem. Acad. ciene artes. 17:14, 1922. Original not seen. (Adsorption of a clay for different dyes was found to be different. Dye adsorption not a simple measure of colloidalilty.)
- (15) Wilhem, Graf. zu Lermugen. The adsorption of organic dyes by colloidal clay. Kolloid z. 19:165. J. Chem. Soc. 112:112. (Methylene blue is found to be the best of a series of dyes tested. Concludes that dye adsorption bears no simple relation to colloidalilty.)
- (16) Hoff, Wilber and Wilkinson, J.A. Adsorption of dyes by soils. J. Phys. Chem., 27:808, 1925. (Effect of salts, bases and acids on adsorption of various dyestuffs. Calcium is displaced by the dye giving evidence of a chemical reaction.)

- (17) Mitscherlich, E.A. and Floess, R. Ein betrag zur bestimmung der hydroskopizität und zur bewertung der phisickalischen bodenanalyse. Intern. M.H.Bodenk, Bd. (Quoted from Bul. 1193, U.S.Dept. of Ag.)
- (18) Endell, K. Quantitative determination of colloids in clay. Chem. Ind. Kolloide. 5:244. (Smooth surface of dry powdered clay in Canada balsam immersed in cold conc. solution of fuchsin for 12 hrs and washed. Photographed under 280 power microscope. It is possible to cut out and weigh the stained portions.)
- (19) Bouyoucos, G.J. Heat of wetting as a new means of estimating colloidal material in soils. Soil Science. 119:153, 1925. (Method and some results on soils.)
- (20) Anderson, M.S. Heat of wetting of soil colloids. J. Ag. Res. 28:927, 1924. (Method correlated with water vapor, dye and ammonia for entire soil and fractions.)
- (21) Stremme, H. and Marino B. Die bestimmung des gehaltes anorganischer kolloide in zersetzten gesteinen und deren tonigan umlagerungs producten. Zeitschrift f Prak Geol. Bd. 19:325-49, 1911. (Original not seen.)
- (22) Tempary, H.A. The shrinkage of soils. J. Ag. Sci. 8:312-30, 1916. (Attributes shrinkage to colloidal material and proposes it as a measure.)
- (23) Foote, H.W. and Saxton, Blair. Effect of freezing on certain inorganic hydrogels. J. Am. Chem. Soc., 38:538-609, 1916. (Some water is kept from freezing, the amount depending on the nature, age and method of preparation of the gel. Use is made of the dilatometer in measuring the frozen water by expansion.)
- (24) Foote, H.W. and Saxton, Blair. Freezing of water adsorbed in lampblack. J. Am. Chem. Soc., 39:1103-25, 1917. (Some water remains unfrozen in lampblack at a temperature far below its normal freezing temperature. Expansion of one gram of water when frozen is found to be 0.0932 cc.)
- (25) Foote, H.W. and Saxton, Blair. Effect of freezing on certain hydrogels. J. Am. Chem. Soc. 38:588-609, 1916. (Studies effect of continued freezing, long standing, etc. on artificially prepared colloids.)

- (26) Bouyoucos, G.J. Degree of temperature to which soils may be cooled without freezing. J. Ag. Res. 20:267-69, 1920. (All moisture in soils is not frozen at -70 C.)
- (27) Bouyoucos, G.J. and McCool, H. Further studies on the freezing point lowering of soils. Mich. Ag. Exp. Sta. Tech. Bul. 51, 1916. (Effect of soluble salts does not explain reluctance of some water to freeze.)
- (28) Bouyoucos, G.J. Measurement of inactive or unfree moisture in soil by means of the dilatometer method. J. Ag. Res. 8:195, 1917. (Method and results on various soils.)
- (29) Robinson, W.O. The adsorption of water vapor by soil colloids. J. Phys. Chem. 26:647-53, 1922. (Adsorptions on a large number of different colloidal extracts gave fairly close agreement. The average was very close to 0.5 gram of water per gram of colloid.)

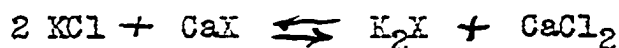
II. SOME FACTORS AFFECTING BASE EXCHANGE IN SOIL
AND SUBSOIL.

INTRODUCTION

The retention and release of plant food by soil is one of Nature's most important phenomena. Without the great reservoir of the soil and subsoil the immediate supply of plant food of an inorganic nature would be dependent upon the decomposition of minerals a slow and uncertain process. Leaching would take place without hinderance and the ocean instead of the plant would receive the major supply of those elements necessary for growth. For the proper treatment of the soil it is necessary to understand the nature of the fixation of the plant food elements. Potassium is one of these elements and while the problem of its supply is not as pressing in most localities at the present time as that of some others, the application of various forms of fertilizers and the effect of liming need a better understanding.

THEORETICAL.

The process whereby potassium is fixed in soil seems to be similar to the one which occurs in commercial zeolite water softeners. It may be represented by the equation:



where X represents some combination of hydrated double silicates the salts of which, both alkali and alkaline earth, are insoluble. The process is readily reversible and extremely rapid. The fixation of one base is always accompanied by the

release of an equivalent amount of another or of several others and vice versa. This apparent double decomposition reaction is commonly called base exchange.

The capacity to undergo base exchange is evidently not limited to a few definite mineral forms but is a property common to many hydrated double silicates. Some investigators have searched the soil for natural zeolitic silicates and finding none, have concluded that base exchange does not take place. It has been found, however, that the major portion, if not all the material which enters into a base exchange, is found in the colloidal and near colloidal portion of the soil. Fairly satisfactory water softeners have been made in this laboratory by concentrating these fractions of a clay subsoil and stabilizing them. These fine fractions may or may not be crystalline but are beyond the scope of present methods of geological identification and may consist to a great extent of natural zeolites. The capacity of artificially prepared double silicates of no particular structure to undergo base exchange precludes the necessity of the zeolitic form being present.

There is some disagreement among investigators regarding the nature of the fixation process. Its rapidity and the fact that it follows the usual adsorption curve for varying concentrations suggests that the process is a physical adsorption, but adsorptions do not give the strict equivalence found in the fixation and release by base exchange.

It seems possible that the fixation process includes both an adsorption and a chemical reaction. The rapidity of the reaction suggests that the salt or one of its ions is adsorbed on the surface of the particle and because of the close contact an immediate reaction with the double silicate takes place. If the process were entirely chemical it would proceed much more slowly. The equivalence of the process is probably governed by the chemical reaction between the silicate and the adsorbed material. The fact that the curve between concentration and amount of base fixed has the usual form of an adsorption curve suggests that the adsorption is the limiting factor. It would seem that the adsorbed portion of the salt or its ions would prevent the equivalence commonly found in the exchange but the amount adsorbed is probably very small and beyond ordinary analytical detection. The amount of a neutral salt removed from solution during coagulation of a soil or even a quite highly colloidal clay is very small. Negative adsorption^(a) of the soil for the salt might also have some bearing on the inability to detect loss of salt from solution.

CONDITIONS AFFECTING BASE EXCHANGE IN SOILS.

The more important conditions affecting exchange in soils may be given as follows: (1) Concentration of replacing base;

- (a) Negative adsorption is understood to refer to adsorption of the water or of a more dilute solution than the surrounding medium, causing increased concentration.

(2) concentration of replaced base or bases; (3) temperature; (4) time; (5) presence of acid; (6) presence of basic material. These effects have been studied upon a typical fertile soil and subsoil and the results given in the following paragraphs. In addition, the manner of fixation of an alkaline material has been investigated and a method given for determining the replaceable potassium.

EXPERIMENTAL.

Treatment of Sample.

The samples used were a Carrington loam and the yellow clay underlying it. The air dried soil was broken up to 40 mesh and washed with distilled water in a Chamberlain filter until no soluble salts could be detected upon evaporation of a liter of the washings. ^(a) The washed sample was air dried and again broken up.

The Effect of Concentration.

Five hundred cc. portions of KCl solution of various concentrations were added to 100 grams samples of the air dried soil and shaken vigorously at intervals during 24 hours. After settling, a 100 cc. portion was drawn off and the calcium and magnesium determined. In certain cases noted, the

- (a) This precaution which was to insure against soluble salts interfering with the equivalence of the reaction was not entirely successful, for in some later treatments, small amounts of calcium were extracted by treatment with pure water.

potassium remaining in solution was also determined by precipitating magnesium with $\text{Ba}(\text{OH})_2$ and the barium and calcium with $(\text{NH}_4)_2\text{CO}_3$ and NH_4OH , and weighing the potassium as sulfate. Treatment of the sulfates with chloroplatinate and calculation of equivalents established the absence of sodium. The amount of potassium was checked in the original solution also. A moisture sample dried at 110 C. gave the moisture content on the air dried samples. Chlorides were determined by precipitation on aliquot portions of the original and final solutions as noted. Results are shown in Table I and are expressed in grams per 100 grams of dry soil.

TABLE I.

Conc. of Added KCl	Ca. in Solution	Mg. in Solution	Equivalent K Fixed. Calculated	K Remaining in Solution Calculated.
TOP SOIL.				
0.0000 M	0.0011 gm.	0.0000 gm.	0.0000 gm.	0.0000 gm.
0.0100	0.0243	0.0000	0.0474	0.1476
0.0250	0.0314	0.0000	0.0612	0.4263
0.0500	0.0339	0.0000	0.0661	0.9089
0.1000	0.0602	0.0000	0.1154 (a)	1.8346 (a)
0.2000	0.0634	0.0000	0.1237	3.7764
0.5000	0.0761	0.0000	0.1484	9.6016
1.0000	0.0960	0.0000	0.1872	19.5128
2.0000	0.1070	0.0000	0.2086	38.7914
3.0000	0.1152	0.0000	0.2246	58.2754

TABLE I (Contd)

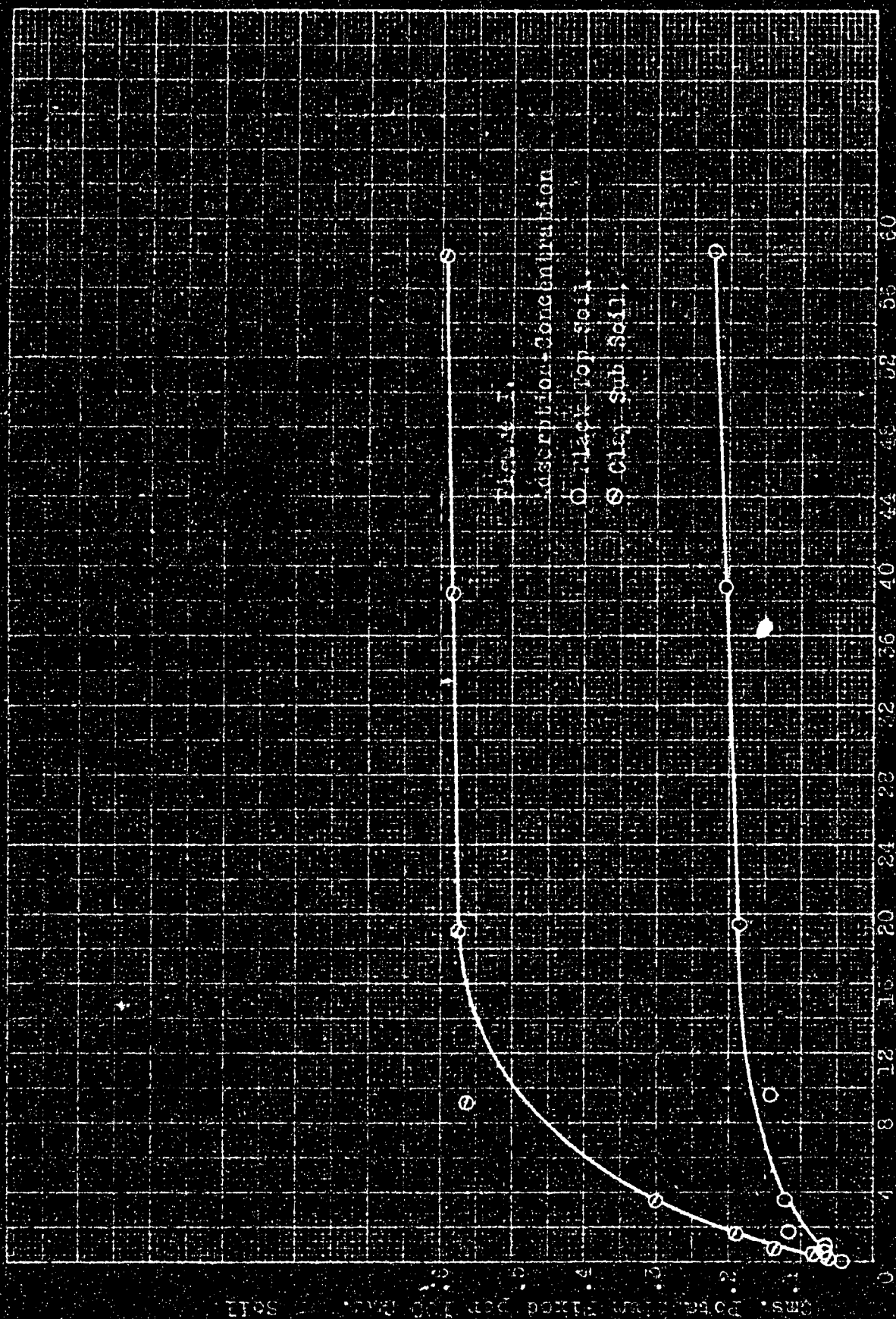
Conc. of Added KCl	Cc. in Solution	Mg. in Solution	Equivalent K Fixed. Calculated	K Remaining in Solution Calculated
SUB SOIL.				
0.0000 M.	0.0008gm.	0.0000gm.	0.0000 gm.	0.0000 gm.
0.0100	0.0288	0.0000	0.0562	0.1388
0.0250	0.0412	0.0000	0.0803	0.4072
0.0500	0.0678	0.0020	0.1386	0.8364
0.1000	0.0945	0.0041	0.1950 (a)	1.7550 (a)
0.2000	0.1458	0.0052	0.3009	3.5991
0.5000	0.2804	0.0062	0.5668	9.1832
1.0000	0.2804	0.0093	0.5767	18.9233
2.0000	0.2808	0.0110	0.5829	38.4171
3.0000	0.2815	0.0145	0.5954	57.9046

(a) The potassium fixed was determined by analyzing the original and final solutions. In the case of the other concentrations, the value was calculated. The chloride in 5 cc. of the original solution was found to be 0.0176 gm. and in 5 cc. of the final solution 0.0180 gm. for the top soil, and 0.0177 gm. for the black soil.

The results indicate that an increase of concentration increases the fixation of potassium as would be expected. Figure 1 illustrates the results graphically. The curves follow the usual form for adsorptions at varying concentrations:

$$\frac{Y}{M} = \frac{k}{C^p}$$

where Y is the weight of adsorbed material, M the weight of the adsorbing medium, C the final concentration and k and p constants. Due to some sort of a saturation, the values obtained for the clay soil with concentrations greater than



0.5 M solutions do not follow the above form.

THE EFFECT OF REMOVING THE REPLACED BASE.

One hundred grams of soil were placed in a section of glass tubing of one inch inside diameter and both ends of the tube plugged with single hole rubber stoppers covered with small disks of filter cloth. This apparatus was placed in an upright position and the lower end connected to an elevated tank of 0.1 M KCl by means of appropriate glass and rubber connections. The upper end was similarly connected to a 500 cc. flask. Flow of the solution through the sample was started and regulated by screw clamps to about 100 cc. an hour. Calcium and magnesium were determined in each 500 cc portion of the solution as it came through. Results are shown in Table II and are on the basis of grams per 100 grams of dry soil

TABLE II.

TOP SOIL			
500 cc. Portion	Ca. in Solution	Mg. in Solution	Equivalent %
1st	0.0576 gm.	0.0000 gm.	0.1123 gm.
2nd	0.0834	0.0000	0.0749
3rd	0.0179	0.0000	0.0349
4th	0.0043	0.0000	0.0084
5th	0.0005	0.0000	0.0009
Total	0.1187	0.0000	0.2315

TABLE II (Contd)

SUB SOIL			
500 cc. Portion	Ca. in Solution	Mg. in Solution	Equivalent K Calculated
1st	0.1940 gm.	0.0040 gm.	0.3911 gm.
2nd	0.0627	0.0046	0.1570
3rd	0.0216	0.0040	0.0424
4th	0.0040	0.0016	0.0129
5th	0.0000	0.0000	0.0000
Total	0.2825	0.0134	0.5854

It is evident that replacement is much retarded by the presence of the released base. From Table I it may be seen that only 0.1154 grams of potassium were fixed by the black soil and 0.1950 grams were fixed by the clay when samples of the two were treated with 0.1 M KCl solution and the products allowed to remain. By removing the released base, the fixation was increased to 0.1187 grams for the black soil and 0.2823 grams for the clay soil. These values are higher than were obtained with 3 M KCl solution with the released base present. The reaction was evidently carried practically to completion by removing the released base.

THE EFFECT OF TEMPERATURE UPON BASE EXCHANGE.

Samples of 100 grams of soil were treated at 21 C and 88 C. in order to ascertain the effect of temperature upon the fixation process. Five hundred cc. of 0.1 molar KCl was used

and the samples were allowed to stand 24 hours with occasional shaking. For the higher temperature, the 0.1 M solution was made from hot water at 88 C. and the aliquot samples were drawn off at the same temperature in order to correct for expansion of the liquid. Corrections were also made for the expansion of the glassware used.

TABLE III.

Temperature	Replaced Ca.	Replaced Mg.	Equivalent K.
TOP SOIL			
21 C.	0.0602gm.	0.0000gm.	0.1174 gm.
88 C.	0.0578	0.0000	0.1127
SUB SOIL			
21 C.	0.0945gm.	0.0041gm.	0.1974 gm.
88 C.	0.0890	0.0043	0.1873

Temperature has some effect upon the process as would be expected but the influence is slight.

THE EFFECT OF TIME.

The effect of time upon the exchange was studied by drawing off aliquot parts at the end of hourly intervals. One hundred gram samples were used and were treated with 0.1 M

KCl solution. Results indicated that with frequent agitation the equilibrium was reached in somewhat less than one hour. For intervals equal to or greater than one hour no difference could be noted for 24 hours. Attempts to measure the replacement at intervals less than one hour gave widely varying results. For the shorter reaction periods the solution could not be drawn off free from suspended material and it was necessary to filter it. Care was taken to discard the first 50 cc. of the filtrate but despite this precaution erratic results were obtained. It is believed that the difficulty was due to the fact that the thin layer of material remaining upon the filter was subjected to a percolation treatment by the liquid passing through and entered into a further replacement.

THE EFFECT OF THE PRESENCE OF AN ALKALINE
MATERIAL UPON BASE EXCHANGE.

One hundred grams of soil were treated for 24 hours with 500 cc. of 0.1 M KCl in conductivity water containing various concentrations of KOH. Conductivity water was used in the solutions in order to avoid precipitation of the calcium by carbon dioxide. Results are shown in Table IV.

TABLE IV.

Conc. of KCl	Conc. of KOH	Ca. in Solution	Mg. in Solution	Equivalent K Calculated.
TOP SOIL				
0.1000 M	0.0000 N.	0.0602gm.	0.0000gm.	0.1174 gm.
0.1000	0.0050	0.0371	0.0000	0.0723
0.1000	0.0100	0.0242	0.0000	0.0472
0.1000	0.0250	0.0000	0.0000	0.0000
0.1000	0.0500	0.0000	0.0000	0.0000
0.1000	0.1000	0.0000	0.0000	0.0000
SUB SOIL				
0.1000	0.0000	0.0945	0.0041	0.1974
0.1000	0.0050	0.0940	0.0020	0.1897
0.1000	0.0100	0.0942	0.0000	0.1837
0.1000	0.0250	0.0939	0.0000	0.1851
0.1000	0.0500	0.0640	0.0000	0.1248 (a)
0.1000	0.1000	0.0010	0.0000	0.0019 (b)

(a) Final alkalinity approximately 0.006 N.

(b) Final alkalinity approximately 0.040 N.

It is evident that the alkalinity interfered with the base exchange. A very low concentration entirely prevented the exchange from taking place in the black soil but the clay sub soil was not so sensitive. The reason for this difference is not apparent but it is believed to be due to the organic material in the top soil.

THE EFFECT OF ACIDITY UPON REPLACEMENT.

One hundred grams of soil were treated with 0.1 M KCl solution containing various concentrations of HCl for 24 hours and calcium and magnesium determined. The final acidity of the solution was also determined. Results in Table V are on the basis of 100 grams of dry soil.

TABLE V.

Conc. of KCl	Conc. of Orig. HCl	Final Conc. HCl	Ca. in Solution	Mg. in Solution
BLACK SOIL				
0.1000 M	0.0000 N.	0.0000 N.	0.0602gm.	0.0000 gm.
0.1000	0.0010	0.0000	0.0563	0.0000
0.1000	0.0100	Trace	0.0972	0.0000
0.1000	0.0500	0.0050	0.1408	0.0000
0.1000	0.1000	0.0150	0.1459	0.0000
CLAY SOIL				
0.1000	0.0000	0.0000	0.0946	0.0048
0.1000	0.0010	0.0000	0.0585	0.0096
0.1000	0.0100	Trace	0.1355	0.0411
0.1000	0.0500	0.0320	0.2275	0.0668
0.1000	0.1000	0.0720	0.2475	0.0640

At concentrations greater than 0.001 N there are evidences of decomposition. Some colloidal silica and aluminum salts

appear in the solutions and the amount of base freed becomes very high. A check determination of the potassium removed from solution on the samples treated with HCl of 0.01 N acidity gave 0.0860 grams for the black soil and 0.1021 grams for the clay. Calculating the potassium equivalent to the amount of bases in solution gives 0.1895 grams and 0.4733 grams respectively for the black soil and clay. This shows that the reaction is not equivalent but that the release of bases comes from the decomposition of active material. To note the damage to the exchange medium, the samples from the 0.01 N acid were treated with two portions of CaCl_2 solution, washed free from calcium and treated with 0.1 N KCl. The black soil released only 0.0302 grams of calcium and the clay soil 0.0446 grams showing that approximately half the active material had been destroyed. An interesting point in the table is the fact that the 0.001 N acid retarded the placement in both soils.

THE RETENTION OF ALKALINE MATERIALS BY SOILS.

It became evident in the course of the investigation that hydroxides did not give reactions of the same type as neutral salts when in contact with soils. Consequently it was decided to investigate their action. Color developed by alkalinity prevented the use of the black soil, so observations were confined to the subsoil.

One hundred grams of soil were treated with 500 cc. of various concentrations of KOH in conductivity water, and after 24 hours, the alkalinity of the solution was determined. The results are shown in Table VI, the potassium remaining in solution being calculated from the alkalinity.

TABLE VI.

CLAY SOIL				
Original Conc. of KOH	K Remaining in Solution	K Adsorbed	Ca. in Solution	
0.0100 M.	0.0000 gm.	0.1950 gm.	Faint	
0.0250	0.0877	0.5998	Trace	
0.0500	0.2389 (a)	0.7361	Faint	
0.1000	0.8853	1.0647	Trace	
0.2000	2.6598	1.2402	Faint	
0.5000	7.8312	1.9188	Trace	
			Faint	
			Trace (b)	

(a) Potassium in solution determined.

(b) Some evidence of decomposition of silicates.

It is evident that while there is an extremely large fixation there is no release of replaced bases. By determination of the potassium remaining in one of the solutions it was found that the amounts of potassium and hydroxide were equivalent. This point was checked with a solution of calcium hydroxide and it was found that the calcium and hydroxyl ion remaining in solution were equivalent. It was also noted that

practically all the adsorbed KOH could be removed by washing with pure water. These facts indicate that base exchange does not take place with hydroxides. An observation made with K_2CO_3 showed that this salt behaved in the same manner. Alkaline materials do not enter into base exchange with soils but are adsorbed probably in molecular form.

A METHOD OF DETERMINING COMBINED REPLACABLE
AND SOLUBLE POTASSIUM IN SOILS.

One hundred grams of soil and 500 cc. of 0.5N calcium chloride solution are placed in a liter flask and allowed to stand for six hours with frequent shaking. After settling, the supernatant liquid is siphoned off as closely as possible. Five hundred cc. of fresh solution are added and allowed to stand six hours. The liquid is again siphoned off and the opening to the flask covered with a small disk of filter cloth secured with a rubber band. The flask is inverted and allowed to drain. On colloidal soils it may be found necessary to replace the cloth covering with a disk of filter cloth held in place by a one hole stopper. To this a suction flask is connected by means of a glass tube and draining aided by applying suction. This method of draining is to be preferred over the Chamberlain filter because of the tendency of the porous tubes to adsorb potassium. The portions of solution are mixed and evaporated to small volume. This solution is treated in the same manner as the dissolved portion of the

residue from the J. Lawrence Smith fusion and the potassium determined by standard methods.

In the case of soils containing very high percentages of replacable potassium, a third portion of liquid may be added to insure complete replacement. Over 90 percent of the potassium is removed by the first treatment and it is doubtful if the amount remaining after the second extraction is measurable.

This method showed 0.0421 grams of potassium from 100 grams of the black soil and 0.0538 grams in 100 grams of the clay.

This method is given in the hope that it may aid in the solution of some of the problems connected with plant food supply. It is believed that a knowledge of the amount of potassium in the soluble and replacable forms is of much more importance than the total potassium as obtained by chemical analysis of the soil. Combined with a study of the calcium and magnesium in the soluble and replacable forms, which may be determined in a similar manner, an application of this method should throw some light on the seasonal change of the equilibrium of these substances.

SUMMARY.

Base replacement in soils is probably a combination of a physical adsorption and chemical reaction. At the concentrations encountered by soils in the natural state it is controlled by laws of adsorption. An increase of concentration of a base or the removal of another base from solution results in the fixation of greater quantities of the first base. The reaction is slightly influenced by temperature but this effect for variation encountered in the natural state would be very small. The exchange is very rapid and would probably take place in a natural bed of soil as fast as the solution filtered through it. Alkalinity in high concentrations hinders or entirely prevents the reaction. Acidity in the very small quantities likely to be found in soils retards the reaction and in higher concentrations destroys the active material. Alkaline hydroxides or carbonates do not enter into the replacement but are adsorbed. A method is given for determining the replacable potassium in soils.

CONCLUSIONS.

Base exchange in moderate concentrations follows the laws of adsorption.

The removal of the replaced base carries the reaction practically to completion.

Temperature has a very slight effect.

The fixation process is very rapid.

The presence of alkaline hydroxides retards the fixation process.

Acids retard the process in very low concentrations and in the higher concentrations destroy the active material.

Alkaline hydroxides and carbonates do not enter into replacement but are adsorbed in large quantities by soil.

LITERATURE REVIEWED.

Aberson, J.H. Das absorptions vermogen der ackererde. Zeit. Chem. Ind. Kolloid. 10:13-22. (The adsorption of ammonium chloride by clay follows the form of the curve given by $Y = \frac{M}{bC + e}$ where Y is the adsorbed material, M the adsorbing material, C the final concentration and b and e constants. A rise of temperature decreases the amount of adsorption.) Original not seen.

Bogue, R.H. Absorption of potassium and phosphorus ions by typical soil. J. Phys. Chem. 19:665-95, 1915. (Assumes that the process is entirely physical.)

Erdmann, L.W. Effect of gypsum on Iowa soils. Soil Science. 15:137-55. (Finds treatment with gypsum increases soluble potash.)

Haley, D.B. Availability of orthoclase for plant nutrition. Soil Science. 15:167-80, 1923. (Grew buckwheat in orthoclase sand.)

Hissink, D.J. The adsorption processes in soils. Soil Science, 15:269-76. (Gives replacement theory and method of obtaining exchangeable bases.)

Knight, H.G. Acidimetry and acidimetry of soils. PhD. Thesis, U of Ill., 1917. (Data on the acid and base adsorption.)

Kilbanger, A. What becomes of ammonium sulfate and potassium nitrate in soil. Mittdeut Landw ges. 37:355-4, 1922. (These salts react with the colloidal calcium and magnesium compounds forming calcium sulfate and magnesium sulfate which leach out. May injure soil too much if present in large amounts. Lime will remedy this condition.) Original not seen.

Lipman, C.B. and Gericke, W.F. Does calcium carbonate or calcium sulfate treatment effect the solubility of soil constituents? U. of Cal. Bul. Vol.3, No.10, p 271-82, 1918. (Gives a good review of theory applying to the process. Discusses mass law application. Finds soils behave differently.)

Lyon, T.J. and Briggs, J.A. Calcium, magnesium, potassium and sodium in the drain water of limed and unlimed soils. J. Am. Soc. Agron. 8:81. (Finds increase of bases.)

McCall, A.G. Absorption of potassium by the soil. J. Phys. Chem. 20:51-63, 1916. (Considers problem from the adsorption angle. Gives experimental data.)

Mehring, E. Fertilizing fish ponds; exchange of bases in the soil. Bul. Ag. Intelligence 13:1445-50. (Exchange takes place where there is an active substance in excess. Recognizes the evil of liming too heavily. Gypsum has some effect. Potassium in soil prevents weeds from growing.)

Morse, F.W. and Curry B.E. A study of the reactions between manurial salts and clays, mucks and soils. New Hampshire College Bul. 27, 1908. (Data on removal and fixation of fertilizer substances.)

Nolte, O. Action of salt solutions on soil. Exp. Sta. Record 47:19-20. Trans. from Landw. Vers. Sta. 98:135-53, 1921. (Chloride, sulfate and nitrate of sodium increased permeability but it reverted. These applications also increased the soluble potassium. Sodium carbonate decreased permeability.)

Patten, H.E. and Waggaman, W.H. Absorption by soils. U.S. Dept. Ag. Bul. 52, 1908. (Reviews early literature on replacement and release of the bases.)

Petil, A. Ammonia absorbing capacity of the soil. Bul. Ag. Intelligence, 12:1377-78. (Moor soil gives up ammonia to water but the process is encouraged by potassium chloride, sodium nitrate and lime.)

Prescott, J.A. The phenomena of adsorption in its relation to soils. J. Ag. Res. 8:111-136, 1917. (A very complete and comprehensive review of all literature on the subject of adsorption and base exchange. The chemical and physical viewpoints are discussed and experimental data in support of each are given.)

Robinson, R.H. and Bullis, D.E. Arid soil studies III. Influences of calcium carbonate, calcium oxide and calcium sulfate on soluble materials of arid soils. Soil Science, 13:449-60, 1922. (Treatments with calcium sulfate increased the solubility of potassium and magnesium in all the soils tested.)

Robinson, W.O. and Holmes, R.S. The chemical composition of soil colloids. U.S. Dept. Ag. Bul. 1311. (Introductory paragraph states that zeolites are rarely if ever present in soil. An excellent review of earlier work is given. Gives the analysis of many types of soils and soil colloids.)

Ruprecht, R.W. and Morse, F.W. Effect of sulfate of ammonia on soil. Mass. Ag. Exp. Sta. Bul. 165, 1915. (Tried effect of ammonium sulfate on amount of dye adsorbed but found little effect. Found sodium and potassium removed by the ammonium sulfate.)

Russell, E.J. Soil conditions and plant growth. Longmans Green & Co., p 1-243. (Retentive power of the soil for salts necessary for plant food is due to the colloidal solutions in the clay and humus.)

Schreiner, O. and Failyer, G.E. The absorption of phosphates and potassium by the soil. U.S. Dept. of Ag. Bul. 32, 1906. (Gives mathematical law for the adsorption which is different from the regular adsorption curve, $\frac{dy}{dv} = k(A - Y)$,

where Y is the quantity fixed, A is the maximum quantity which can be fixed, V the volume of solution percolated through and k is the coefficient. Some potassium is continually being leached out by pure water.)

Spurway, C.E. Reactions between soils and various chemical compounds. Mich. Ag. Exp. Sta. Tech. paper 51, 1921. (Gives much valuable data on replacement studies. Finds close equivalence between fixed and replaced bases.)

Thompson, H.S. Reactions of soils with manurial salts. J. Roy. Ag. Soc. 11:68, 1850. (Soils absorb much ammonia from the sulfate or carbonate and liberate calcium. Sulfate gives more than the carbonate.)

Ungerer, E. Einige versuche uber basengustasch mit salzen organische stickstoff verbindungen. Kolloid Zeit. 36:288-335, 1925. (Found that complex organic salts containing nitrogen entered into base exchange. Has rather conclusive proof that the nitrogen supply as well as potassium is dependent upon base exchange.)

Way, J.T. On the power of soils to absorb manure. J. Roy. Ag. Soc. 13, 1852. (Fixation is by a small quantity of the clay material. Prepared artificial double silicates which gave base exchange. Order of replacement given as $\text{Na} \{ \text{K} \{ \text{Ca} \{ \text{Mg} \{ \text{NH}_4 \}$.)

Wiley, R.C. and Gordan, E.E. Adsorption of plant food by colloidal silica. Soil Science. 14:441-48, 1922. (Much adsorption is found with colloidal silica but the results are not correlated with the phenomena encountered in natural soil.)

Zsigmondy, R. and Spear, E.B. Chemistry of Colloids. John Wiley & Sons, New York, p 1-282. (Acid or neutral salts adsorbed. Sodium, potassium or magnesium may be released or dissolved while an equivalent amount of adsorbed base remains with the clay.)