

**THE CHEMICAL
NATURE OF A
COLLOIDAL CLAY**

Published @ 2017 Trieste Publishing Pty Ltd

ISBN 9780649305223

The Chemical Nature of a Colloidal Clay by Richard Bradfield

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RICHARD BRADFIELD

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92

DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE
SCHOOL OF THE OHIO STATE UNIVERSITY

By
RICHARD BRADFIELD

The Ohio State University
1922

CONTENTS

	Page
Introduction; Statement of General Problem Involved	5
Methods of Separating Colloidal Matter from Soils	6
Review of Literature	6
Effect of air drying on soil colloids	8
Experimental	9
Effect of air drying on the amount of colloidal matter readily obtained from soils	9
Method of sampling and of storing samples	11
Effect of the soil-water ration on the rate of sedimentation	11
Rate of settling by gravity	12
Separation by means of the supercentrifuge	15
Comparison of Missouri method with the Bureau of Soils method	17
Physical and Chemical Properties of the Separates Obtained	18
Physical Properties	18
Relative amounts of each separate in the soil	18
Water content of separates	18
Linear shrinkage of separates	19
Size of particles	19
Viscosity	19
Reaction and nature of charge	19
Chemical Properties	20
Chemical composition	20
Possible chemical nature of the emulsoid	21
The occurrence of soluble iron and aluminum in soils	21
Detailed Statement of Problem	23
The Preparation of a Synthetic Colloidal Mixture Similar to the	
Natural Colloid Under Study	23
Preparation of Constituent Sols	23
Standardization of concentration of sols	24
Method of Mixing Sols	24
The Velocity of Migration of the Sols in an Electric Field	26
Review of Literature	26
Experimental	26
Methods used	26
Sources of error	27
Results obtained	27
Discussion of results	28
The Effect of the Hydrogen Ion Concentration upon the	
Cataphoresis of the Sols	31
Review of Literature	31
Experimental results	32
Natural emulsoid	32
Silicic acid	34
Ferric hydroxide	35
Aluminum hydroxide	35
Synthetic mixture	35
Conclusion to be Drawn From the Cataphoresis Studies	36

Ohio State Univ. Lib.
4-23-1924

The Buffer Action of the Soils	36
Review of Literature	36
Experimental	37
Titration curves obtained by the Gillespie colorimetric method	37
Titration curves obtained by the electrometric method	39
Conclusions to be Drawn From the Studies of Buffer Action	41
Studies on Coagulation	42
Review of Literature	42
Principles involved	42
Non-precipitation zones	43
The flocculation of soils	43
Protective action	44
Conclusion to be drawn from the literature	45
Experimental	45
Effect of concentration of sol on rate of settling after flocculation	45
Comparative electrolyte requirements of the 0.1% sols	46
Effect of reaction on the electrolyte requirement	47
Effect of reaction on the rate of settling	48
Conclusions to be Drawn from the Flocculation Studies	51
Comparative Analyses of the Fractions of the Soils Soluble in Dilute Solvents	51
Review of literature	51
Experimental	52
Results of Analysis	53
Conclusions to be Drawn from the Analyses	53
General Discussion of Results	55
Summary	56
Bibliography	58

65
911
13177

ACKNOWLEDGMENTS

The author is indebted to Prof. M. F. Miller, Dr. W. A. Albrecht and Dr. F. L. Duley of the Soils Department of the University of Missouri and to Dr. F. E. Bear of the Department of Soils, Dr. Edward Mack of the Department of Chemistry and Dr. E. N. Transeau of the Department of Botany of the Ohio State University for suggestions and constructive criticisms received during the progress of this investigation.

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RICHARD BRADFIELD

Abstract—The fresh subsoil of Putnam silt loam, predominating prairie soil of Northeast Missouri, was suspended in five parts of water by churning, the coarser material settled by gravity and the finest colloidal material separated by means of a centrifugal force of about 30,000 times gravity. This fraction was unusually high in Al_2O_3 and Fe_2O_3 , almost all of which was soluble in hot HCl. This indicated that the colloidal fraction might be made up largely of the completely broken down end products of weathering; colloidal Al_2O_3 , Fe_2O_3 and SiO_2 . A synthetic mixture of these colloids having a chemical composition similar to the natural colloid was prepared and their physico-chemical properties compared. Cataphoresis studies showed that the natural colloid was negative and that the synthetic mixture was positive. The migration velocity of the natural colloid was decreased by traces of acids and increased by traces of alkali; larger amounts of alkali caused flocculation. In no case was the direction of migration reversed. The synthetic colloid had a much stronger buffer action than the natural colloid due apparently to its high content of free Al_2O_3 . The natural colloid was flocculated most readily by polyvalent cations in an acid medium. The synthetic mixture was more sensitive to polyvalent anions and to alkalis. Analyses were made of the fractions of each colloid soluble in dilute acid, and in dilute alkali. The differences were marked throughout. All data obtained indicated that the natural colloid was a complex aluminosilicate, rather than a mixture of the separate colloidal oxides.

The Putnam silt loam, which is the predominating soil type on the level prairies of northeastern Missouri, is underlaid at a depth of 12 to 20 inches with a very heavy clay layer. This heavy layer is so compact that there is practically no water or air movement through it, except when it is cracked by drought. For this reason crops growing on it suffer severely in periods of wet weather, for the surface soil is kept saturated until the excess of water is removed by surface evaporation. Crop yields are probably reduced even more by the drought periods in the summer, because the supply of moisture stored in the surface and subsurface layers is soon exhausted, and there is little available from beneath.

The imperviousness of the heavy layer is due to the fact that a large proportion of the particles are so extremely small and consequently fit so closely together that there is not enough effective pore space to allow any appreciable passage of either air or water. Tile drains laid in the heavy layer function very poorly.

The object of this investigation was to isolate the colloidal

material found in this subsoil and to study its principal physical and chemical properties with the hope that such studies might furnish some information that would be of value as a basis for field experiments of a more practical nature. This study includes the following: (1) A centrifugal method for separating the colloidal material from the soil. (2) The preparation of a synthetic mixture of colloidal $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$ and H_4SiO_4 , having the same total analysis as the natural colloid. (3) A comparative study of some of the physico-chemical properties of the natural colloid and the synthetic mixture. (4) An interpretation of the comparative physico-chemical studies showing the probable chemical combinations existing in the natural colloid.

METHODS OF SEPARATING COLLOIDAL MATERIAL FROM SOILS

Review of Literature.—The term "colloid" as applied to soils by different investigators has been used to cover a considerable range in size of particles. Hilgard^{22*} regards as colloidal all material which will remain in suspension for 24 hours in a column 8 inches high. In the recent work done by the Bureau of Soils²⁴ 1 micron has been considered the upper limit for colloidal clay. In this study the term is applied to that portion of the soil whose particles are invisible under the high-power direct-vision microscope, which show no tendency to settle out, and which are less than 0.1 micron in diameter. Most of the studies are made only on that fraction of the colloidal material which was physically homogeneous.

Because of the effect of colloidal material on the physical properties of soils, considerable work has been done on the development of some fairly accurate means of estimating the quantity of colloidal material present. Mitscherlich²¹ devised a method based upon the water vapor adsorption of the dry soil. Ashley² devised a method based upon the adsorption of certain dyes. Rhoads⁵⁰ pointed out that the different dyes were specific in their action; that is, some were adsorbed more strongly by one colloid, others by another.

While the above methods give results which are good indications of the quantity of colloidal material present they leave much to be desired when one wishes to make a more thorough study involving the physico-chemical properties of the colloids themselves.

*Refers to Bibliography, page 58.

For this purpose the separation of the colloidal material from the rest of the soil is desirable. Several such methods have been proposed, separation being brought about by differences in (1) solubility, (2) electrical charge, and in (3) size and specific gravity of the particles.

Horvath⁸³ found that the colloidal SiO_2 in soils was dissolved by heating the soil with 1% NaCO_3 for 15 minutes. Fraps²⁸ proposed a method for determining the inorganic colloid content of a soil based upon its solubility in 4% NH_4OH . The soluble colloid content of the soils studied varied from 0.0% to 6%. It contained from 47 to 60% SiO_2 , from 11 to 24% Fe_2O_3 , and from 8 to 37% Al_2O_3 . In the soils containing the larger amounts of soluble colloidal material, the percentage of Al_2O_3 was much higher. While such solubility methods may give an indication of the amount of colloidal material and of its chemical composition, they are without value for the isolation of colloidal material for physico-chemical studies, because the properties of the colloid are changed during the solution process and it would be difficult if not impossible to restore them to their original colloidal condition after they had once been brought into true solution.

For the separation of finely divided suspensions Ormondy⁴⁸ devised a machine utilizing the negative charge of the clay particles. A drum of a non-corroding metal, which served as an anode, was revolved inside strips of copper placed around the anode at a distance of $\frac{3}{4}$ inch. The clay particles are drawn to the anode, water is driven off, impurities settle to the bottom, and the clay in a relatively pure condition may be scraped from the anode. Such a device is not suited to the present work, because considerable material not truly colloidal would be deposited along with the colloids. In addition, part of the colloidal material would give up its negative charge when it came in contact with the anode and would consequently have properties different from the natural colloid.

There remains the possibility of utilizing the difference in size of particle and specific gravity for effecting a separation. Schloesing²⁵ allowed suspensions of clays to stand undisturbed for long periods. Several distinct strata developed. The upper stratum, which never settled, was found to be made up of particles invisible under the highest-powered microscope. When removed and dried, this material formed a translucent, horny mass. The lower layers he considered to be made up of mixtures increasing in complexity as the bottom of the vessel was approached. While this method