DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 23

TECHNICAL CONTROL OF THE COLLOIDAL MATTER OF CLAYS

BY

H. E. ASHLEY, Associate Ceramic Chemist

Bureau of Standards

[NOVEMBER, 1911]

WASHINGTON
GOVERNMENT PRINTING OFFICE
1913

EDITORIAL NOTE

This paper, on Technical Control of the Colloidal Matter of Clays, was written by Mr. H. E. Ashley, but it had not been put into final shape suitable for publication. After the untimely death of Mr. Ashley, in 1910, Dr. John Johnston, of the Geophysical Laboratory of the Carnegie Institution, was asked to edit this paper. It seems advisable to state that Part I has been entirely rewritten, Part II has been rearranged and largely rewritten, while Part III is essentially as Mr. Ashley left it; but in all of this the editor has endeavored to correlate and elucidate the ideas expressed by Mr. Ashley in the original draft. Practically everything in this draft has been retained, for the editor did not, in the circumstances, feel justified in excluding any matter which might have a bearing on the subject in hand, and thus in some instances he has not been able to coordinate fully all the data obtained or cited by Mr. Ashley in the original draft. It might be stated that in order not to delay too long the publication of the results of Mr. Ashley's work it was decided not to take into account the recent literature since 1910.

THE TECHNICAL CONTROL OF THE COLLOIDAL MATTER OF CLAYS

By H. E. Ashley

CONTENTS

Page

Editorial note 2
I. Introduction 5
1. The argument 7
A. Present-day views of the chemistry of colloids 8
2. Classification of disperse systems 9
3. Emulsion and suspension colloids 10
4. Nature of the particles of the disperse phase 11
5. Mechanism of suspension 14
6. Phenomena of flocculation and deflocculation 16
7. Absorption 19
8. Exchange of bases 22
(a) Effect of acid or neutral salt solutions upon silicates 22
(b) Effect of alkaline solutions upon silicates 22
B. Importance of solubility relations in determining the course of a reaction in solution 24
9. Law of mass action 25
10. Solubility product 27
11. Effect of a common ion in diminishing solubility 27
C. Neutrality of aqueous solutions 30
12. Salt hydrolysis 31
II. Chemical reactions of the colloid matter of clays 32
1. Definition of clays 33
2. Origin of clays 34
3. Character of clay substance 35
A. General properties of clays 37
4. Gauging the colloid matter of clay 37
(a) Malachite green test 40
(b) Sodium carbonate test 42
(c) Water storage 42
B. Reactions of the colloidal matter of clays 43
5. Variety of clays and minerals tested 44
6. Time required for the reactions of clays 44
7. Effect of the concentration of the reagent 45
8. Observations on the acidity of clay extracts 46
Table of acidity of water extracts of various clays 47

II. Chemical reactions of the colloid matter of clays—Continued. Page
C. Examination of an insoluble kaolin 48
9. Effect of repeated extraction with water 48
10. Effect of additions of sodium hydroxide 49
D. Examination of a soluble clay 52
11. Nature of the soluble salts 52
12. Effect of additions of sodium hydroxide 53
13. Solvent action of successive portions of water 55
E. Effect of varying the temperature of the water 58
F. General behavior of clays toward reagents 59
14. Concentration of hydroxyl ion a minor factor in promoting the deflocculation of clays 61
15. Deflocculants 63
Bivalent deflocculants 69
Acidic deflocculants 70
Deflocculation by humus, etc. 71
Deflocculation by dyestuffs 72
16. Coagulants 74
17. Addition of soap to clays 75
18. Effect of addition of sodium carbonate and sodium silicate 76
III. Applications 76
A. Improvement of clays 78
1. Weathering 78
2. Effects of salts contained in sliphouse water 79
3. Treating excessively colloidal clays 81
4. Use of colloidal additions 82
5. Increase or decrease of refractoriness 85
6. Use of soluble cobalt stains 85
7. Purifying kaolin 85
B. Mechanical analysis of clays 86
8. Preparation of clays for mechanical analysis 87
9. Extraction with acid, water, and ammonia 87
10. Extraction with ammonia 88
11. Extraction with sodium hydroxide 88
12. Use of alkaline precipitants 89
C. Methods of mechanical analysis 89
D. Determination of the soluble salts in clays 94
13. Proposed method 96
E. Scum on clay wares and its prevention 96
14. Use of barium carbonate to present scum 97
F. Casting process 98
15. Use of alkali to decrease water requirement 99
16. Choice of deflocculant 100
17. Joint use of sodium carbonate and sodium silicate 100
18. Addition of soap to pottery bodies 102
G. Regulation of glazes and engobes 102
19. Shrinkage regulation 104
20. Lack of adhesion 105

III. Applications—Continued. Page
H. Miscellaneous applications 108
21. Water purification 108
(*a*) Use of coagulants to remove clays 109
(*b*) Use of clay to remove bases 110
22. Addition of acid disinfectants to modeling clays 110
23. Use of soap for cleansing 111
24. Cleaning brick fronts 111
25. Polishing plate glass 112
26. Fuller's earth 112
27. Kaolin and fuller's earth as analytical reagents 113
28. Paints 114
I. Acknowledgments 115

I. INTRODUCTION

The applicability of chemistry to the problems of clay working has been seriously limited in scope by the fact that the nature of clay products is dependent more on the physical properties of the raw materials than on their chemical composition. In other words, purely chemical knowledge does not help us here to the extent that it does, for instance, in the manufacture of iron and steel. In this industry the assured place of the chemist is due to the fact that the properties and behavior of the finished product are dependent above all on its chemical composition, and that the physical form in which the raw material reaches the plant is completely destroyed in the furnace, in which it is melted to a homogeneous fluid whose composition and properties may be exactly controlled. The clay worker, on the other hand, retains in his finished products, in large measure, the original physical structure of the raw materials. The grains of the crude kaolin or quartz form the actual skeleton of the finished ware, modified indeed, in the process of manufacture, but nevertheless possessing more or less complete physical identity.[1] The metallurgist establishes by fusion a new uniform basis of operations; the clay worker, with nice adjustment, utilizes the peculiarities of existing physical forms and perpetuates them. A definite chemical analysis tells the metallurgist what the capacities of his material are. Long and tedious experimentation, conscious planning, and more or less subconscious instinct enable the clay worker to adapt his material to the desired production.

[1] Zoellner: Sprechsaal, 41, pp. 471, 490, 504, 519, 533; 1908; C. A., 2, 3271. Mellor and Austin: Trans. Eng. Ceram. Soc., 6, pp. 129–141; C. A., 2, 3132; 1908.

In the clay-working industry the possibility and extent of replacing empirical by exact knowledge has been enormously increased by our greatly widened and improved knowledge of the nature and behavior of colloids; this has been gained, mainly in the last few years, as the result of a very large number of investigations, nearly all of which were made directly because of the enormous practical importance of colloids, especially, perhaps, in connection with the science of agriculture.

These researches indicated that many of the problems of clay working are very intimately connected with the nature and amount of the colloid matter in the clay. Consequently the first investigation begun by the clay-products section was upon the behavior of the colloid matter in clays; this occupied the year 1909.

Amongst the problems on which it was hoped that light would be thrown by such an investigation are: The control of the plasticity of clays, the control of the casting process for making clay wares, the securing of maximum density and strength in clay wares, the analytical separation of colloid and crystal matter in clays, the determination of the sizes of the grains of clay down to 0.01 mm, the prevention of excessive loss from the cracking of clay wares in drying, the prevention of white scum on brick, etc. A preliminary account of part of this work has already been the subject of a paper,[2] in the preface to which A. V. Bleininger writes:

> The most characteristic property of clays is their plasticity, on which depends their use in the arts. Yet this peculiar function of clay has been the most difficult to explain and to measure. Heretofore no criterion has been found which would enable the clay worker to compare with any degree of accuracy the varying degrees of plasticity found in the clays employed in industry. In this paper Mr. Ashley has made an attempt to explain the character of the plastic constituents of clay in the light of recent researches in the field of colloids, and also to offer a method for the comparison of the different clays with respect to this property. He is dealing, therefore, with a subject which is of fundamental importance not only to the scientific investigator but also to the manufacturer, for the success of the practical operations of shaping and drying hinges largely on the character and amount of the plastic matter present in clays.

In the present paper the questions treated in the bulletin just cited are discussed more fully on the basis of further experimental work and of a wider study of the literature pertaining to the subject in hand and to the chemistry of colloids.

---

[2] U. S. Geological Survey, Bull. 388, 1909: The Colloid Matter of Clay and its Measurement, by Harrison Everett Ashley.

1. THE ARGUMENT

In its briefest terms the argument pursued in this paper is: That the plasticity of a clay is directly determined by the character and amount of the colloid matter in the clay; consequently, by measuring and controlling the colloid matter present, we shall be able to control the plasticity of the clay and to obtain the great advantages incident to such control. The first statement above—that the plasticity of a clay is a function of the character and amount of the colloid matter present—is, we believe, generally accepted; we shall, however, bring forward additional evidence in support of it. To justify the second statement is the main aim of the present paper.

Before proceeding further it seemed advisable to give a short sketch of the present status of the chemistry of colloids in as far as it pertains to the subject in hand, and to define and discuss briefly certain of the physicochemical concepts which are introduced in the subsequent discussion. This has been included for the reason that some of the technical workers—to whom this paper is specially addressed—may not be familiar with the exact significance of the ideas and terms in question.[3]

Following this introduction and the brief exposition of some of the terms used there is a general discussion of the subject in hand supported by experimental work on clays, concluding with some applications of the work to specific problems. This order is, however, not rigidly adhered to. The references to the work of other investigators are not assembled in any particular portion of the paper. In some places they are inserted as confirmatory of results obtained; in others they are wholly depended on for essential information. As the literature of the subject is very voluminous, it has doubtless happened that credit has not always been given to the original investigator of some principle, though the effort has been made to do so.

---

[3] For fuller information, the reader is referred especially to Wolfgang Ostwald, Grundriss der Kolloidchemie (referred to hereafter as Wo. Ostwald, Kolloidchemie; a second edition of this book is now appearing) or to H. Freundlich, Kapillarchemie. These books represent the latest and most thorough treatment of the subject of colloid chemistry, and will be referred to in the text. Also Richard Zsigmondy, Colloids and the Ultra-Microscope, translated by Jerome Alexander, published by John Wiley & Sons, 1909 (referred to in the text as Zsigmondy, p. —). An excellent brief account is given by Viktor Pöschl, Einführung in die Kolloidchemie. The physicochemical concepts are treated of in practically all books on physical chemistry, of which James Walker's Introduction to Physical Chemistry (Macmillan's) may be recommended for clearness and accuracy of statement.

A. PRESENT-DAY VIEWS OF THE CHEMISTRY OF COLLOIDS[4]

From his classical experiments (1861–1864) on diffusion and dialysis (diffusion through a membrane, e. g., parchment paper, bladder, etc.) Graham was led to divide substances into two groups, according as the rate of diffusion is comparatively large or exceedingly small. Substances belonging to the latter group he termed "colloids," in contradistinction to the rapidly diffusing group of crystalloids, which, as its name implies, comprised for Graham substances which crystallize well from (and are therefore fairly soluble in) water; the chief examples of this class are salts generally and soluble organic substances (e. g., sugar) of comparatively simple structure. The colloids, on the other hand, were in general substances of very slight solubility in water, and in many cases of complex structure; the typical examples of this class are gelatin, gums, starch, etc.

On this theory then—the so-called chemical theory of colloids—the two classes of substances are chemically distinct; consequently substances belonging to one group should always exhibit the properties characteristic of that group. But there is now overwhelming evidence that this distinction does not hold—that typical crystalloids may under certain conditions behave as colloids, and conversely. For instance, sodium chloride has been obtained in colloidal form by von Veimarn,[5] while, on the other hand, it was found by Paterno[6] that tannin and gallic acid, which in aqueous solutions are typical colloids, give, when dissolved in glacial acetic acid, freezing-point depressions which correspond to normal molecular weights; consequently solutions of these substances in acetic acid are to be regarded as "true" solutions. Moreover, we are now in possession of ample evidence, obtained largely by means of the ultramicroscope, that there is a perfectly continuous progression as we pass from coarse visible suspensions through colloidal solutions to "true" solutions,[7] and one

[4] This section purports only to be a very brief sketch of that portion of the subject which is especially connected with the behavior of clays. This remark applies, mutatis mutandis, to all of the definitions and theoretical discussion presented in this paper.

[5] Zs. Chem. Ind. Kolloide, 7, p. 92; C. A., 5, p. 621; 1911.

[6] Zs. Physik. Chem., 4, p. 457; 1889.

[7] Cf., p. 11, postea.

substance may under proper conditions appear in any of these forms.

Therefore, it is now generally concluded that it is not advisable to distinguish between colloid and crystalloid substances; that the term "colloid" is not descriptive of an inherent property of a substance, but of its properties in relation to another substance. In other words, "the theories of colloid chemistry do not deal with colloidal substances, but with the colloidal state of substances." Similarly, "colloid phenomena are not, strictly speaking, the properties of colloidal substances, but are the peculiarities which are exhibited as a first approximation by a given substance, when it is observed in the colloidal state."[8]

This change of viewpoint has resulted in a change in nomenclature, so that it is now usual to speak of the "disperse phase" and the "dispersive medium," the former for the "colloid," the latter to designate the second constituent of the "colloidal solution." The newer terms are preferable because they imply nothing except the obvious fact that the colloidal state is not a strictly homogeneous state of matter;[9] in other words, in the colloidal state more than one phase [10] is present.

According to the newer views, the phenomena peculiar to the colloidal state are conditioned largely, or entirely, by factors due to the fineness of grain of the disperse phase and the consequent relative increase in extent of the aggregate surface of separation between the disperse phase and the dispersive medium. In general the surfaces of the individual particles of the disperse phase will be convex; that of the dispersive medium will be concave.

2. CLASSIFICATION OF DISPERSE SYSTEMS

Many schemes of classification have been proposed, all more or less arbitrary; the most useful are those in which the classification depends on the nature of the surface of separation of the two

---

[8] Wo. Ostwald, Kolloidchemie, p. 145.

[9] In the main part of this paper, however, the term "colloid matter of clay" is used throughout for the sake of convenience; but since in this special case the presence of water as the dispersive medium is always understood, this usage will lead to no confusion.

[10] A phase, in physicochemical usage, is defined as a mass chemically and physically homogeneous, or a mass of uniform concentration. (See Bancroft's The Phase Rule.)

components of the system. The most general scheme is that given by Wo. Ostwald,[11] as follows:

Dispersive medium	Disperse phase		
	Gaseous	Liquid	Solid
Gaseous.....	Class 9: G+G—No real example, as gases always are completely miscible	Class 8: G+L—Fog, e. g., at the point of liquefaction of gases, atmospheric fog, etc.	Class 7: G+S—Smoke, cooled ammonium chloride vapor, etc.
Liquid.....	Class 6: L+G—Foams.....	Class 5: L+L—Emulsions...	Class 4: L+S—Suspensions; gels.
Solid.....	Class 3: S+G—Gas inclusions in minerals (e. g., pumice) or in metals	Class 2: S+L—Liquid inclusions in minerals; occluded water; water of crystallization	Class 1: S+S—Inclusions of solid particles in minerals; solid solutions

It is, of course, obvious that no hard and fast distinction can be drawn, for there is a continuous change of properties as we pass from one class to another. The above classification is given merely to show the generality of the phenomenon of dispersion and because such a scheme may aid us in applying the results and conclusions obtained with one class to any other.

3. EMULSION AND SUSPENSION COLLOIDS (EMULSOIDS AND SUSPENSOIDS)

These two groups make up what has been termed "colloid chemistry," and are by far the most important of all the groups. The properties of typical examples of each group show marked divergences, and accordingly they have been distinguished by various names. Thus, A. A. Noyes [12] calls them "colloidal solutions" and "colloidal suspensions," respectively; the former characterized as "viscous, gelatinizing, colloidal mixtures, not (easily) coagulated by salts," the latter as "nonviscous, nongelatinizing, but readily coagulable mixtures." They have also been termed "lyophile" and "lyophobe."

Practically the same distinction is made in the two terms "sol" and "gel," which, however, are often more loosely used. In this

[11] Kolloidchemie, pp. 94–97. This classification was also made independently and about the same time by E. E. Free (J. Franklin Inst., 169, p. 424; 1910).

[12] J. Am. Chem. Soc., 27, p. 85, 1905. For a fuller discussion, see Wo. Ostwald, Kolloidchemie, pp. 97 et seq.; Freundlich, Kapillarchemie, p. 309 et seq.

paper the word "sol" is used to denote colloid conditions similar to the typical gold sols or sols of other metals; gel to denote gelatinous or jellylike colloids.

No definite distinction can be made between these two; thus colloidal alumina and silica—constituents of the colloid matter of clays—may appear in either form or change from one form to another, according to the conditions. Moreover, there is no absolutely sharp line of demarcation between emulsoids and "true" solutions, on the one hand, and between suspensoids and coarse visible suspensions, on the other. This is equivalent to the statement that the properties of such disperse systems [13] vary continuously with the degree of fineness of the particles of the disperse phase, or with the aggregate extent of its surface per unit of weight; in other words, the properties vary with the degree of dispersion.

Of this there is ample proof. Perhaps the best illustration is some work of P. P. von Veimarn [14] on the form in which barium sulphate appears when it is precipitated by mixing equivalent solutions of barium thiocyanate and manganese sulphate in progressively increasing concentrations. These experiments showed that from the most dilute solutions were formed crystals of measurable size, which with increasing concentration diminished progressively through the microscopic to the ultramicroscopic; while from the concentrated solutions (about 0.1–10 *N*) colloidal sols and finally gels of gradually increasing permanence were obtained.

4. NATURE OF THE PARTICLES OF THE DISPERSE PHASE

On the basis of these observations von Veimarn has propounded the theory that matter always has the crystalline form, the size of the crystals varying from microscopic down to molecular size. He considers the molecules in the interior of the close-packed crystal to be very rigidly restricted as to freedom of motion, while those at the surface have a much greater degree of freedom, approaching that of the liquid state, and even capable of dissolving substances (adsorption). If, then, the crystals of a substance are

[13] Including "true" solutions as a limiting case.

[14] This work and the deductions von Veimarn has made from it form the basis of the numerous papers which he has published during the last few years in Z. Chem. Ind. Kolloide. It is more fully summarized by Johnston and Adams, J. Am. Chem. Soc., 33, pp. 837–839, 1911.

of smaller and smaller size, there will be a larger and larger proportion of incompletely oriented molecules until finally the substance as a whole possesses those properties that we call colloidal. These views are in harmony with a large number of diverse observations.[15] For instance, Mellor,[16] from mathematical considerations and from observations on melting behavior, concluded that the smaller the particles the lower the temperature at which the surface of the particle will begin to show signs of its diminishing viscosity; in other words, the smaller the particles the lower the observed softening temperature. Mayer [17] also practically demonstrated that feldspar in fine powder shows an earlier softening point than when coarse ground.

On the other hand, Freundlich concludes from a review of the matter,[18] "The suspensoids contain in general particles, whose diameter lies between 250$\mu\mu$ [19] and 6$\mu\mu$; sometimes also particles less than 6$\mu\mu$ in diameter. The particles are probably approximately spherical and amorphous."

It seems inadvisable, therefore, in the present state of our knowledge to state that disperse particles are always crystalline, though in many cases they doubtless are. It may be well to observe here that "colloid" and "amorphous" should not be used as synonymous terms. Many substances, and amongst them the most familiar typical colloids, when dispersed in water, are apparently amorphous; yet this may easily be due to their vanishingly small real solubility in water, which would tend to cause the formation of masses of exceedingly small crystals. The probability of this is indicated by the following considerations.

In the course of the experiments quoted above von Veimarn has shown that the size of the particles of any specified precipitate diminishes progressively as we increase the degree of supersaturation of that precipitate with reference to the medium in which it is being formed. The degree of supersaturation is defined as the ratio of the total[20] concentration of substance to the concentra-

---

[15] See Wo. Ostwald, Kolloidchemie, pp. 118 et seq.; 137.

[16] Pottery Gazette, **35**, pp. 1032–1038, 1910; Trans. Eng. Ceram. Soc., **9**, p. 126, 1910.

[17] Trans. Am. Ceram. Soc., **4**, p. 30, 1902.

[18] Kapillarchemie, pp. 318–321.

[19] 1$\mu\mu$ is the one-millionth part of a millimeter. The above dimensions (250 and 6$\mu\mu$) represent the limits of the ultramicroscope. Particles larger than 250$\mu\mu$ are visible in the ordinary microscope.

[20] That is, the aggregate weight of substance as precipitate and remaining in solution divided by the total volume of the medium in which the reaction took place: cf. C. A., **5**, p. 621.

tion of its saturated solution in the particular medium employed. The physical form of the products of a chemical reaction therefore depends wholly on the conditions under which it is carried on and can be varied at will from amorphous to coarsely crystalline. For gel formation the reaction must be as rapid as possible, therefore, by the interaction of concentrated solutions in solvents in which the reaction product is very sparingly soluble.

Conversely, even substances of such pronounced gelatinous character as aluminum hydroxide may be obtained in the crystalline condition if they are formed very slowly from dilute solutions. The number of centers of crystallization must be kept small, the total volume of the reacting solutions must be very great, a long time may be necessary, and a solvent must be used giving as large a solubility as possible. Crystallization is also promoted by means that artificially increase the solubility, namely, increase of temperature and pressure, introduction of foreign substances, etc. The principal and absolutely essential condition for the formation of stable fine suspensions is the exceedingly small solvent power of the medium for that particular material. Subsidiary conditions are that the velocity of formation of the substance whose suspension is desired must be considerable, and the concentrations of the reacting solutions must lie within definite limits. If these conditions can be fulfilled, a stable sol of any substance may be obtained. Moreover, since a very slight solubility is the most likely to be accompanied by a high degree of supersaturation, we should expect to get the finest particles with those substances which have the slightest solubility in the particular medium. In other words, substances which readily assume the colloidal state in water tend to be complex substances of high molecular weight—qualities which are usually associated with very slight solubility in water. Thus this serves to account for the old distinction between colloids and crystalloids.

On this view it should be possible to obtain any substance in the colloidal state if we can precipitate it rapidly in a medium in which it is very slightly soluble. The exact character of the disperse system thus produced will depend on the solubility and on the relative rapidity of precipitation. And this is in complete harmony with experience. Moreover, if we vary the medium in

such a way that the solubility of a given substance is decreased, but keep other conditions constant, we may change a sol into a gel. Therefore, if we add to a sol a reagent which by interaction with the disperse phase produces a phase less soluble in the particular medium than the original disperse phase, we shall by this means apparently coagulate the sol. What we have really done is to change the constitution of the disperse phase in such a way that the sol has been transformed into a gel. This is important, for, as we shall see later, this transformation is of very frequent occurrence with clays.

5. MECHANISM OF SUSPENSION

According to Stokes's formula the limiting velocity of fall v of a spherical particle of radius r through a fluid is given by the expression

$$v=\frac{2r^2g}{9k}\left(d-d^1\right)$$

where k is the viscosity of the fluid, d and d^1 the density of fluid and particle, respectively, and g the acceleration of gravity. From this it is evident that for a given fluid and for particles of given material the limiting rate depends directly on the size of the particle.[21]

It is evident, first, that for a finite size of particle the velocity of fall can never become zero. Theoretically, therefore, permanent suspension can not occur with particles the density of which differs from that of the surrounding medium. Practically, however, since the velocity of fall varies with the square of the radius, it is easily possible to find particles so small that their fall is almost infinitely slow, so slow in fact as to be entirely counteracted by convectional and other circulations which it is impossible entirely to eliminate from the medium itself. Practically permanent suspension is therefore possible by the action of well-known physical factors, even without the necessity of invoking those chemical combinations and electrical and molecular-kinetic actions which seem to come into play in the finer grained of the disperse systems.[22]

This view has received striking confirmation from recent work, especially by Perrin,[23] who, by counting the number of particles

[21] The particle is assumed to be spherical; deviations from spherical form would necessitate correction terms in the above formula, but do not invalidate the present argument. Incidentally, it may be observed that "true" solutions exhibit an entirely analagous behavior, for in a solution containing particles (ions) of different relative weights, the heavier particles tend to concentrate at the bottom of the solution under the action of gravity or, when the solution is centrifuged, away from the center of rotation. This has been definitely proved by R. C. Tolman (Proc. Am. Acad., **46**, pp. 109–146, 1910; C. A., **5**, p. 15, 1911).

[22] E. E. Free: J. Franklin Inst., **169**, p. 427, 1910.

[23] Perrin: Compt. rend., **147**, pp. 475, 530; **149**, pp. 477, 549; summarized by Perrin (Le Radium, **6**, p. 353, 1909; **7**, p. 247, 1910; and in the newer books on colloid chemistry).

at different levels in thin films of certain suspensions, has calculated values of the Avogadro constant N (the number of molecules in 1 gram-mol), which are in excellent agreement with values of this same constant obtained by totally distinct methods.[24] In one of these N is calculated from measurements of the amplitude of the Brownian movement by means of a formula deduced by Einstein [25] from kinetic-theory considerations. This also serves to show that the kinetic theory is sufficient to account for the phenomenon of the suspension of fine particles. The characteristic darting motion, known as the Brownian movement, is shown by all suspensions containing particles less than 0.004 mm (4μ) in diameter; it is shown strongly by clay suspensions. Indeed, Atterberg [26] defines clay as particles under 0.002 mm diameter, which show Brownian movement strongly (0.003 mm show it only weakly).

W. H. Brewer [27] noted that "Those substances which retard the 'Brownian movements' hasten the 'precipitation' of fine-grained sand, flocculant clays, and pulverized charcoal when suspended in water." This, which has been confirmed by Duclaux,[28] is in harmony with the preceding statements.

The conclusions to be drawn from the foregoing discussion may be summed up: To say that a substance is in the colloid state (with reference to another substance, water in practically every case) is equivalent to the statement that the substance is dispersed throughout the water to form particles of which the diameter may range all the way from molecular up to microscopic and macroscopic dimensions. The size of the particles is determined by the method of formation of the disperse system (as it is now generally termed). The properties exhibited by the system vary with the fineness of the particles (the degree of dispersion); consequently the phenomena produced in disperse systems by variation of external conditions or by addition of reagents—apart from purely chemical effects, such as the ordinary solvent effect of hydrochloric acid upon colloidal ferric hydroxide—are due to variation in the degree of dispersion produced by the change of circumstances.

---

[24] The most probable value of N from all the determinations is, according to Perrin, 68.5×10^{22}.

[25] Ann. Phys., **17**, p. 549, 1905; Zs. Elektrochem., **13**, p. 41; **14**, p. 235.

[26] Landw. Vers. Sta., **69**, p. 135, 1908.

[27] Mem. Nat. Acad. Sciences, **2**, p. 165, 1883.

[28] J. chim. phys., **5**, pp. 29–56, 1907; Z. Chem. Ind. Kolloide, **3**, p. 161, 1908.

93329°—13——2

6. PHENOMENA OF FLOCCULATION AND DEFLOCCULATION [29]

The process of coarsening or sedimentation of the particles is now commonly termed *flocculation;* the opposite process *deflocculation.* The latter term especially has come to mean a decrease in the rate of clearing, and suspensions are said to be *deflocculated* when they settle slowly or not at all. These terms are relative only, for we have no direct measure of the extent of flocculation. It is, however, convenient to speak of the *degree of flocculation.* Thus, when we say that addition of an alkali decreases the degree of flocculation, we understand that an alkali tends to deflocculate the system; or, in other words, to decrease the size of the disperse particles and so to render the suspension more permanent.

The degree of flocculation depends upon the surroundings of the system; but the influence of these external circumstances is by no means clearly made out, except that rise in temperature causes practically always an increase in the degree of flocculation. As compared with these external effects the addition of many material agents, sometimes in very small amount, has a great, and more thoroughly investigated, effect.

Indeed, this is the main way in which changes in flocculation are brought about in practice, and here lie the main technical applications of the phenomenon. Of the bodies which have large influences the main are the stronger alkalies and the organic colloids which decrease the degree of flocculation, and neutral salts and acids which increase it. The former are the "deflocculators," the latter the "flocculators." [30]

Turning first to the action of the flocculating agents—the acids and neutral salts—and considering the effect of varying concentrations of these bodies, the most noticeable fact is that a certain minimum concentration of the salt in the solution is necessary before there is any apparent action on the suspension. The absolute value of this initial active concentration (the so-called threshold concentration) varies with the different salts, but once attained the flocculating action on the suspension begins suddenly and continues rapidly * * *.

Next in importance to the effect of concentration is the effect of the chemical nature of the salt, and here we have two general rules. The first is due to Hardy [31] and states that a suspension (or colloid) will be flocculated only by a solution or another suspension whose ions or particles are of opposing electrical sign.[32] That is, a suspension the particles of which carry negative charges will be flocculated only by a solution containing positive ions, and vice versa. * * * The second rule is that of Schulze,[33] and says that the flocculating power of an ion increases very rapidly with its valence.[34]

---

[29] For much of the contents of this section the writer (J. J.) is indebted to the admirable presentation given by E. E. Free: The Phenomena of Flocculation and Deflocculation (J. Franklin Inst., **169**, pp. 421–438; **170**, pp. 46–57, 1910).

[30] Free, loc. cit., p. 429.

[31] Proc. Roy. Soc. London, **66**, p. 115; 1899.

[32] Cf., p. 17.

[33] J. prakt. Chem. 2, **25**, pp. 445–446; 1882.

[34] Free, loc. cit., pp. 430–431.

The deflocculators, which comprise only the hydroxides, carbonates, and other highly hydrolyzed salts of the alkali metals (all of which therefore have a strong alkaline reaction), also show the "threshold concentration" effect. Their behavior will be more fully discussed in their application to the specific case of clay.[35]

The flocculating action of acids and salts is probably the resultant of a number of factors, but there is little doubt that the most important primary factors are the effect of the salt or acid on the solubility relations and on the electric charges of the system.

For an understanding of the first of these it is necessary first to recognize that the separation between each suspended particle and the medium surrounding it is seldom a sharp one. The best instances are the emulsions. An emulsion of, say, chloroform and water really consists of a solution of chloroform in water in which are suspended droplets of a solution of water in chloroform. This mutual solubility of the two bodies probably has a great effect on the character of the surface of the particles, and since the nature of this surface is known to be active in controlling sedimentation and flocculation, it is to be expected that the amount of the mutual solubility will importantly influence the latter phenomena. But soluble bodies are likely to influence the solution equilibria of systems to which they are added, and it is therefore probable that their addition to emulsions will have noticeable effects on the mutual solubility of the particle and the medium, hence on the surface of the particle, and finally on the degree of flocculation. In the chloroform-water emulsion, above mentioned, the addition of a salt to the chloroform-in-water solution (the medium) will usually influence the solubility equilibrium between this and the water-in-chloroform solution (the particle); the quantities of water dissolved in the particles and of chloroform dissolved in the medium will change; and the surfaces of the particles, the degree of flocculation, and the other properties may change in turn. These relations are most obvious in the case of emulsions, but they apply, changed only in degree, to the solid-particle suspensions. * * *

The second way in which dissolved salts may act on suspensions is by changing the charges of electricity which are known to be resident on the surfaces of the particles. The action of these charges on flocculation might be either direct or indirect. In the first case the mechanism would be ordinary electrostatic repulsion. When the particles were all charged and of the same sign, there would be a repulsive force tending to prevent flocculation. The addition of salt solutions furnishes a means of changing the charges[36] on the particles, and hence of modifying this electrostatic resistance to flocculation. If the charges on the particles be reduced to zero, this resistance to flocculation will disappear, and flocculation may take place. There are, in fact, certain colloids and suspensions for which the point of zero electric charge (the "isoelectric point") corresponds to the greatest degree of flocculation. * * * These actions may be used to explain the rules of Hardy and Schulze, above mentioned. The action of suspensions of opposing charge in precipitating each other

[35] See p. 63 et seq.

[36] In terms of the most generally accepted theory of solution, this action is to be ascribed to the charges carried by the ions.

may obviously be ascribed to neutralization and the destruction of the electrostatic resistance to flocculation. The increase in the flocculating activity with increase of valence of the active ion is explainable on the supposition (already reached on electrochemical grounds) that the charge carried by an ion increases with its valence.[37] * * * Moreover, the sudden action at the "threshold" concentration (which shows practically no variation with increase of concentration thereafter) is exactly the course of events to be expected if the action is due mainly to the neutralization of electric charge, for this would be completed by the addition of a definite amount of the neutralizing material.[38]

With respect to secondary actions, definite knowledge is lacking. For instance, electric charges may produce indirect effects in opposing or assisting the surface tensions or other forms of energy resident on the surface of suspended particles; but the nature and action of these forms of energy is as yet very little understood.

It seems probable, therefore, that two of the ways in which dissolved bodies influence the phenomena of flocculation are by acting on the mutual solubility of the particle and the medium and by changing the electric potential at the surface of the two. Assuming that these actions can go on side by side and in varying degree, with the predominance now of one and now of the other, we have a reasonable explanation of the almost infinite complexity of the resultant actions which we actually observe. Add to this the known existence of still other factors of which we have as yet no understanding, and the existing confusion of knowledge does not seem surprising.[39]

These arguments and conclusions have been quoted at considerable length, because it seems to the writer that we can not hope to correlate the phenomena actually observed in the case of clays except with the aid of considerations analogous to those just advanced, and in addition of special ones which may seem to apply to the particular case, e. g., the effect of interchange of bases. (See p. 22.) And it is surely preferable to refer the observed effects to some phenomenon concerning which we have some positive knowledge rather than to some cause—for instance, to absorption, to which the reactions of clays have frequently been attributed—about which our knowledge is partly contradictory and largely uncertain. Yet it seems advisable to say a few words about absorption in general before passing on to the considera-

[37] In this connection it may be pointed out that is is possible that the Schulze rule may be accounted for in certain cases as follows: That this behavior is due to the smaller solubility of many salts of metals of higher valence (as compared to that of the corresponding salts of metals of lower valence); and this in turn would tend to promote the metathetical reaction which occurs in certain cases on addition of a salt to a colloid, e. g., clay. (Cf., p. 74.)

[38] Free, loc. cit., pp. 434–437.

[39] Free, loc. cit., p. 436.

tion of the "absorption" by clays, which, as we believe, is due in large part to chemical reaction—a double decomposition—between the clay and the "absorbed" salt.

7. ABSORPTION

It is somewhat difficult to give a brief definition of the term "absorption" which shall be free from objection. Consequently we shall limit ourselves to stating that we use the term in its broadest sense, without theoretical implication. To take examples at random, the dyeing of fibers, the taking up by charcoal of gases and vapors, are cases of absorption.

Now, it is generally thought that absorption is a surface action, and hence purely physical in character; and so it doubtless is in many cases. But in other cases there is good evidence that a part is also played by purely chemical effects which sometimes may predominate to such an extent that the effect of the purely physical factors may be neglected entirely. For instance, the typical case of absorption by charcoal is generally referred to the physical surface effect, yet there are experimental data which indicate that purely chemical factors ought to be taken into account, at least in the absorption by charcoal of certain substances.

Thus, Glassner and Suida [40] found that benzine will extract from soot a substance which takes up dyes from aqueous solution. The soots, sugar charcoal, and wood charcoal contain hydrogen and oxygen; those which are the most active absorbents contain the most oxygen. Further, the same amount of one and the same charcoal always, under equal conditions, from concentrated or dilute solutions will take up very nearly the same amount of dye.

Knecht [41] has shown that the affinity of animal charcoal for acid dyestuffs like crystal scarlet varies with the percentage of nitrogen in the charcoal. Also that the affinity for basic dyes like methylene blue may be decreased by heating the charcoal with aluminum powder or zinc dust, and then treating successively with hydrochloric and hydrofluoric acids. The opinion expressed by Paterson and by Glassner and Suida that animal charcoal owes its decolorizing action to the presence of organic compounds

---

[40] Annalen, **361**, p. 353; 1908.

[41] E. Knecht: J. Soc. Chem. Ind., **27**, p. 949; **28**, p. 700; C. A., **4**, p. 1382, 1910.

stable at red heat is upheld by Knecht. He also discusses the decolorizing action of other forms of charcoal, such as coconut charcoal, lampblack, acetylene black, and naphthalene black, and shows that the more closely the substance approaches pure carbon in composition the less is its decolorizing property. He thinks it probable that absolutely pure amorphous carbon, however fine its state of division, would be found to be devoid of any decolorizing power on either acid or basic dyestuffs.

This behavior indicates chemical action, yet it must be recognized that the absorption by charcoal of such neutral and inert gases as argon, nitrogen, methane, ethylene, carbon monoxide, and carbon dioxide can hardly be attributed to chemical action. This question was investigated by Miss I. F. Homfray,[42] who came to the conclusion that the absorption of gases by charcoal can best be explained by the solution hypothesis, wherein the charcoal is considered as a strongly undercooled liquid (in the same sense that glasses are undercooled liquids). On the other hand, the work of Walker and Appleyard [43] on the distribution of a dye between water and silk indicates that the absorption of dyestuffs by silk is not a case of solution.

Hence absorption by charcoal, of certain substances at least, may be accounted for without the necessity of assuming the existence of surface films of extraordinary pressure and of remarkable solvent power. This, of course, by no means excludes the possibility that in many cases the purely physical effect is the predominating factor.

Incidentally it may be remarked that we can not deduce anything as to the mechanism of the process of absorption from the fact that the experimental results can be expressed by the so-called absorption equation or absorption isotherm. According to this equation

$$x/a = k\,c^{m}$$

where x is the absorbed amount, a the absorbing surface (usually measured by the weight of absorbent), c the initial concentration of the solution, and k and m constants, derived by calculation or by a graphical method from the experimental results themselves.

---

[42] Zs. Physik. Chem., 74, pp. 129–201, 1910; C. A., 4, p. 2896.

[43] J. Chem. Soc., 69, p. 1334, 1896.

The reason that no conclusion as to mechanism can be drawn from agreement of experiment with the absorption equation is that, since no theoretical explanation is implicit in the derivation of the equation, it is possible by means of such an exponential equation with properly chosen constants to fit with fair accuracy any series of observations, provided only that the quantities in question change continuously in one direction only,[44] a condition which is fulfilled in a very large number of series of experimental results.

As stated above, there is evidence that absorption by charcoal may be a chemical reaction. When we study the "absorption" by minerals of salts in solution, there is a much greater weight of evidence in favor of the view that the phenomena in question are to be ascribed to an exchange of bases between the mineral and the salt.

This matter has been very fully treated by E. C. Sullivan,[45] who from a discussion of previous investigations and from his own experimental work concludes:

> The natural silicates precipitate the metals from solutions of salts, while at the same time the bases of the silicates are dissolved in quantities nearly equivalent to the precipitated metals. The bases most commonly replacing the metals in these processes are potassium, sodium, magnesium, and calcium. When exact equivalence is wanting, it is attributable either to solubility of the mineral in pure water or to the precipitation of basic salts. The metals are precipitated as hydroxides or basic salts with more or less silicate * * *. Adsorption, a mechanical surface action, plays a comparatively insignificant part, if any, in the retention of copper by kaolin. If adsorption is lacking in the case of kaolin, it seems reasonable to assume that it is lacking in the case of other silicates also.[46]

This makes it evident that in the case of clays, effects due to absorption will in general be unimportant as compared with those caused by the exchange of bases. Accordingly, this question will be considered somewhat more in detail, as it is important in connection with the reactions of clays.

---

[44] This is equivalent to the statements (1) that the first derivative (the differential coefficient) shall not change sign; (2) that there shall be no maxima or minima in the curve.

[45] The Interaction between Minerals and Water Solutions, U. S. Geological Survey, Bull. 312, 1907, which contains copious references to the previous literature of the subject. Later references are: F. W. Clarke: U. S. Geol. Survey, Bull. 330, p. 425, 1908. A. Reychler: J. Chim. Phys., 7, pp. 362–368; C. A., 3, p. 2644, 1909. F. Cornu: Min. pet. Mitt., 25, pp. 453–455. E. Jordis: Z. Elektrochem., 13, p. 525, 1907. E. Jordis: Z. Chem. Ind. Kolloide, 3, pp. 22, 24, 1908. P. Ehrenberg: Landw. Jahrb., 38, pp. 857–861, 1909; C. A., 4, p. 1521, 1910. Fred W. Morse and Bert E. Curry: A Study of the Reactions between the Manurial Salts and Clays, Mucks, and Soils, 19th and 20th annual reports of the N. H. Agr. Exp. Sta., pp. 271–310, 1908. Hall and Gimmingham: J. Chem. Soc., 91, p. 667, 1907. Hopkins: U. S. Dept. Agr., Bur. Chem., Bull., 73, p. 14.

[46] Sullivan, loc. cit., p. 64.

8. EXCHANGE OF BASES

(a) EFFECT OF ACID OR NEUTRAL SALT SOLUTIONS UPON SILICATES

To quote again from Sullivan's discussion:

So far as the evidence goes, then, the action of silicates, clay, and other constituents of the earth's crust on solutions of such salts as do not dissolve in water with alkaline reaction consists in an equivalent exchange of bases. Any absorption of the salt as a whole by the solids mentioned is so small as to have escaped detection. As bearing on the latter point it should be said that certain colloid substances do take from solution both the acid and base of the salts mentioned. Ferric and aluminum oxides and metastannic and stannic acids, for instance, take potassium sulphate from solution, while hydrated manganese dioxide takes up sulphate, chloride, and nitrate of potassium. This of course does not necessarily imply absorption. It is not at all impossible, as van Bemmelen suggests, that chemical reaction takes place. Manganese dioxide takes up more base than acid from a neutral salt solution, and thus imparts to the solution acid reaction. Cupric oxide takes more of the acid and alkalinity results. These and other similar reactions suggest the reaction between mercuric oxide and potassium chloride, where potassium hydroxide forms owing to the slight electrolytic dissociation of mercuric chloride, and they may be due to similar causes. The solids capable of absorbing both acid and base from a neutral salt solution are in the main those which themselves exercise both basic and acidic functions.[47]

Now, the metallic salts, the aqueous solutions of which are neutral or acid, comprise for practical purposes the salts of the strong acids—the chlorides, nitrates, and sulphates; hence, the reaction consists in an interchange of bases between the silicate and salt, resulting in the formation of a slightly different (insoluble) silicate and of a soluble salt.[48, 49]

(b) EFFECT OF ALKALINE SOLUTIONS UPON SILICATES

Alkaline solutions comprise, in addition to the solutions of the free alkalies, solutions of those salts which are formed by the union of a strong base with a weak acid, and consequently undergo hydrolysis. Now the weak acids commonly met with—for instance, carbonates, phosphates, sulphides (also silicates themselves)—are precisely those acids which form slightly soluble salts with the bases most commonly present in silicates, e. g., calcium, iron, magnesium. Therefore, with alkaline solutions the final

[47] Sullivan, loc. cit., pp. 27–28.

[48] If silicates containing barium or strontium were brought in contact with sulphate solutions, probably only an inappreciable quantity of the slightly soluble sulphate would be formed on account of the very slight solubility of the silicates of these metals, a solubility which is probably much less than that of their sulphates. Of course some sulphate would be formed, the amount of which could be calculated from the principle of mass action if the solubilities of the sulphates and silicates were known.

[49] An exception to this statement is afforded by such acid solutions as the solution of calcium carbonate in water containing carbon dioxide; the reason for this is obvious.

effect is slightly more complex than with acid solutions, for in addition we have the following two reactions:[50]

1. The free alkali may react with free (colloidal) silica, thus forming a substitution product. This serves to account for the fact that the absorption of free alkali (potassium hydroxide) by clay is greater after the clay has been extracted by acid, a process which removes some of the bases from the clay and is therefore analogous to, or indeed identical with, exchange of bases. It may be remarked that in general free alkali has a greater action on silicates than a neutral salt has. The reason of this was pointed out by Rümpler,[51] namely, that when potassium hydroxide acts on a silicate the calcium and magnesium which are removed are at once precipitated as hydroxides and therefore do not tend to put a stop to further substitution of potassium by promoting the reverse reaction, as their soluble salts would do.

2. The metal displaced from the silicate combines with the acid in the solution to form a slightly soluble salt, which accordingly is precipitated from solution. This accounts for the "absorption" by soils and clays of a soluble carbonate or phosphate; in reality more or less complete double decomposition takes place with the formation of slightly soluble substances only. The soundness of this explanation is confirmed by some early work of van Bemmelen,[52] who showed that extraction with hydrochloric acid, which dissolved oxides of iron and aluminum and decomposed silicates to such an extent that absorption and substitution would not take place, also did away with precipitation of the carbonate, phosphate, and borate radicals by the soil. Moreover, a soil thus extracted took up half the alkali from sodium carbonate solution, leaving the acid radical in its entirety as bicarbonate. To this it might be objected that extraction with hydrochloric acid destroys the absorbent power by removing the main absorbents—the (colloidal) iron and aluminum hydroxides. But to the writer the explanation given is more convincing; it is based on well-known facts and is in harmony with the observations; further it accounts quantitatively for the phenomena in some cases and would doubtless do so always if the solubility relations involved were accurately known.

---

[50] Whether, and to what extent, they take place, is determined entirely by the solubility of the possible product, or products, relative to that of the substances initially present.

[51] Report International Congress Applied Chemistry, 3, p. 59, 1903.

[52] Landw. Vers. Stat., 23, p. 267; 1879.

B. IMPORTANCE OF SOLUBILITY RELATIONS IN DETERMINING THE COURSE OF A REACTION IN SOLUTION

The importance of the fact that solubility, or perhaps we should rather say lack of solubility, is the predominating factor in determining the products of reaction of any system is not thoroughly appreciated by a very large number of chemists. The appearance of any one product is very often ascribed to the existence of a greater affinity between its component parts than exists between the components of the other compounds which might conceivably be formed by the reaction. In a certain sense this is true, but in the sense in which the term "affinity" is ordinarily employed it is fallacious and misleading. For example, consider the following reactions:

$$2AgNO_3 + BaCl_2 = 2AgCl + Ba(NO_3)_2$$
$$Ba(NO_3)_2 + Ag_2SO_4 = BaSO_4 + 2AgNO_3$$

From the first of these we should, according to the above reasoning, conclude that silver was a stronger base than barium, while from the second we reach the directly opposite conclusion.

As another example, take the statement, which appears in the majority of textbooks on organic chemistry, that tetramethylammonium hydroxide ($N(CH_3)_4OH$) can not be displaced from aqueous solutions of its salts (e. g., the chloride) by potassium hydroxide, because the former is the stronger base. But it has been shown that if we choose a medium (methyl alcohol) in which one of the products (potassium chloride) of the reaction is insoluble, the reaction

$$N(CH_3)_4Cl + KOH = N(CH_3)_4OH + KCl$$

takes place and yields practically the theoretical amount of the tetramethylammonium hydroxide.[53]

These two examples,[54] which are typical of a very large number of similar cases, demonstrate that the relative strength of the competing acids and bases is a negligible factor in determining

[53] Walker and Johnston: J. Chem. Soc., 87, p. 955; 1905.

[54] Another good example is this: If we add hydrochloric acid to a solution of sodium silicate, sodium chloride will be formed and silicic acid liberated, but yet at a very high temperature, as in the process of glazing earthenware, silicic anhydride in presence of water vapor is capable of decomposing sodium chloride w th expulsion of hydrochloric acid. This behavior is not at first sight dependent on solubility relations, but it is perfectly analogous if we consider that volatility may be looked upon as solubility in a vacuum.

the product which separates out following a reaction in aqueous (or other) solution; the important factor is the relative solubility of the original substances and of the possible products of reaction. This behavior is in thorough accordance with the law of mass action and with the currently accepted theory of solution; so that if we know the solubility relations of all possible products (including complex salts, e. g., the double cyanides and oxalates, if such are formed), we can predict quantitatively the course of the reaction.[55]

Since a proper appreciation of mutual solubility relations and their consequences is important for the thorough understanding of the main part of this paper, an outline of the theory involved has been given. In this outline it has not been possible to enter into the practical limitations of this theory; these limitations are, however, generally of minor importance, and are absolutely unimportant here. Their effect is such that a lack of concordance of a few per cent may be found between theory and experiment.[56]

9. LAW OF MASS ACTION

Consider the reversible chemical action

$$A + B = C + D$$

where the letters represent single molecules of the substances, as in ordinary chemical formulæ. Then, according to the law of mass action, the state of equilibrium of the above system is determined by the equation

$$\frac{[A]\,[B]}{[C]\,[D]} = K$$

where the symbols [A], [B], etc., represent the "active masses" of the respective substances when equilibrium has been attained; K is a constant, the value of which depends solely on the external conditions (e. g., temperature). When the reaction takes place in a wholly gaseous system, the "active mass" of each substance is proportional to its molecular concentration; when the system is

[55] This statement is subject to slight limitations, which, however, are not of importance in the present connection, and hence are not discussed here. Compare footnote 56.

[56] The reader desirous of fuller information is referred to recent publications from the laboratory of A. A. Noyes, especially the papers of which W. C. Bray is sole or joint author. (Published in J. Am. Chem. Soc. during the last few years.)

an aqueous solution, the active mass of each reacting molecular species (which are, according to the current views, ions or undissociated molecules) is given by the concentration of that particular species (expressed always in molecular or equivalent concentrations).

As an example, take the reaction

$$KI + I_2 = KI_3$$

Writing the equation for the ions, we obtain

$$K^+ + I' + I_2 = K^+ + I'_3$$

or, eliminating what is common to both members of the equation, $I' + I_2 = I'_3$. Consequently it is the actual concentrations of these three molecular species which determine the equilibrium. The concentration of KI or KI_3 has no effect on the equilibrium, except through its relation to the concentration of I' or I'_3, a relation which in its turn is determined by exactly analogous equations, which determine the amount of ionization of each salt.

As an example of this, let us consider the dissociation of a weak acid (acetic acid). The dissociation equation is $CH_3COOH = CH_3COO' + H^+$. Applying the law of mass action we obtain the expression [57]

$$\frac{[CH_3COO'][H]}{[CH_3COOH]} = K$$

which is the well-known Ostwald dilution law,[58] as applied to solutions of acetic acid. This law is in agreement with the experimental observations on the so-called weak electrolytes, which comprise substances (mainly organic acids and bases) which are ionized less than 10 or 15 per cent; when applied to the class of strong electrolytes, substances which are ionized 60 per cent or more (all salts, strong acids, and bases), it apparently does not hold, but this discrepancy is without doubt to be attributed to the fact that hitherto it has not been found possible to obtain sufficiently accurate values of the *actual ion concentrations* when the *total* ion concentration is large.

---

[57] Throughout this paper symbols inclosed in brackets (e. g., [A]) denote the concentration of that particular molecular species.

[58] This is usually written slightly differently. Thus, if 1 mole of acetic acid is in solution in v liters of water, and of this γ is ionized, the concentrations of CH_3COO', H^+ and CH_3COOH are, respectively, γ/v, γ/v, and $(1-\gamma)/v$, and the expression becomes

$$\frac{\gamma^2}{(1-\gamma)v} = K$$

10. SOLUBILITY PRODUCT

Let us now examine the nature of the equilibrium between the aqueous solution of a salt and the solid salt itself. To each temperature there corresponds a certain solubility of the salt, i. e., a certain concentration of salt which is in equilibrium with the solid. Now, the salt in solution is present as unionized molecules and as ions; but all the evidence indicates that it is the concentration of the unionized portion which directly determines the equilibrium. The unionized salt here plays the part of intermediary between the solid and the ions; it is in equilibrium with the unionized solid on the one hand and with the ions on the other. Therefore, under constant external conditions, the concentration of the unionized portion will always be constant so long as an excess of solid salt is present.

Consider, now, a system made up of a saturated solution of the salt BA, together with excess of the solid salt, the external conditions remaining constant. On applying the law of mass action, as before, we obtain the relation

$$\frac{[B][A]}{[BA]}=K$$

Now, from what has just been said, [BA] is constant; therefore B] [A] = constant.[59] This is what is known as the constant solubility product.

11. EFFECT OF A COMMON ION IN DIMINISHING SOLUBILITY

If now we add an extra quantity of the ion B^+ (for instance, by addition of the soluble salt BCl), the concentration of A′ must diminish that the solubility product may remain constant. A′ can only fall out of solution along with an equivalent quantity of positive ion; and, since B^+ is the only kind of positive ion in the solution, a certain quantity of the salt BA must be precipitated in order to reestablish equilibrium.[60] Exactly

[59] This, too, is subject to certain limitations, unimportant here, which can not be discussed here. (Cf. footnotes 55, 56.)

[60] A numerical example may make this clearer. The concentration of a solution saturated with respect to silver bromate at 24.5° is 0.0081 *N*. If we assume the salt to be entirely ionized (an assumption which is very nearly true in a salt solution of such a feeble concentration), the constant solubility product is $[Ag^+][BrO'_3]=0.0081\times0.0081=0.0000656$. Now a quantity of silver nitrate is added, which when dissolved in the same water as contains the silver bromate would of itself make the solution 0.0085 *N* with respect to Ag^+ (this would correspond to about 0.01 *N* with respect to the total $AgNO_3$). Suppose that the concentration of silver bromate now remaining in the solution is x, a smaller quantity than before; $[Ag^+]$ is now, therefore, $(0.0085+x)$; $[BrO'_3]$ is x and $(0.0085+x)x=0.0000656$, whence $x=0.0049$. That is, the concentration of silver bromate in a 0.01 *N* solution of silver nitrate saturated with respect to silver bromate is 0.0049 *N*, as compared with 0.0081 *N*, the concentration of its saturated solution in pure water.

analogous reasoning holds for the addition of A′ (e. g., as the soluble salt KA). In other words, the solubility of a substance is lowered by the addition of a second substance yielding an ion common to both.

As common instances of the application of this principle, which is constantly made use of in practical work, the following may be cited: In purifying sodium chloride by recrystallization it is usual to precipitate the salt from a strong brine by the addition of concentrated hydrochloric acid. Sodium sulphide is used to precipitate the more soluble metallic sulphides, while hydrogen sulphide (in solutions of which the concentration of S″ is very small indeed) suffices to precipitate the less soluble sulphides.

The best known application of this principle, and the one which has given a name to the process, is the salting out of soap. When a fat has been saponified with moderately dilute caustic soda, the resulting solution contains glycerin and excess of alkali in addition to the soap, which consists of the comparatively slightly soluble sodium salts of some of the higher fatty acids. Thus the addition of a soluble salt like sodium chloride throws these salts almost completely out of solution as a curdy mass. If the fat has been saponified by a strong solution of caustic soda, the concentration of sodium ion may be great enough to throw the soap out as it is produced.

This is the process known as salting out, which now is used as a convenient term to designate the effect of addition of a common ion in diminishing the solubility of a substance. Incidentally it may be noted that this process of decreasing the solubility by driving back the extent of ionization is merely the limiting case of the commonly used process of driving back the dissociation of a (weak) base or acid (and hence reducing the "strength" of the base or acid) by adding a salt of the base or acid; thus in ordinary analytical work, ammonium chloride is added with ammonia, sodium acetate is added with acetic acid, in order to accomplish this object. One limitation to the general applicability of the process of salting out deserves mention, namely, that if complex ions are formed, the solubility of a substance may be increased, instead of decreased, by the addition of a common ion. Thus, silver cyanide is more soluble in solutions of potassium cyanide

than it is in water; this behavior is due to the formation of the complex ion $Ag(CN)_2'$ by the reaction $(CN)' + AgCN = Ag(CN)'_2$. This reaction, however, is also subject to the law of mass action; application of which yields the equation

$$\frac{[CN'][AgCN]}{[Ag(CN)_2']} = K$$

where K, the so-called complex constant, is exactly analogous to the solubility product of a simple salt.

Application to a specific equilibrium.—As a specific example of the application of these principles to the determination of equilibrium conditions, we shall consider the reversible reaction

$$BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$$

Here both the barium salts are insoluble. For the sake of simplicity we shall assume that the constant conditions are such that the concentration of neither of the sodium salts reaches the saturation point. The reaction may then be written

$$BaSO_4 + CO_3'' = BaCO_3 + SO_4''$$

There are present in the system the following molecular species: Un-ionized $BaSO_4$ and $BaCO_3$, Ba^{++}, SO_4'', CO_3'' [and Na^+ which, however, may be left out of account, since it plays no direct part in the reaction].

We have then the equilibrium equations between these quantities

$$[Ba^{++}][SO_4''] = k_1 \text{ and } [Ba^{++}][CO_3''] = k_2$$

where k_1 and k_2 are the solubility products of $BaSO_4$ and $BaCO_3$, respectively; and therefore, since Ba^{++} is common to both

$$\frac{[SO_4'']}{[CO_3'']} = \frac{k_1}{k_2} = K$$

In words, the ratio of the concentrations of sulphate ion and carbonate ion is constant. Therefore, if, after equilibrium has been attained, we add SO_4'' (as Na_2SO_4), $BaCO_3$ is transformed into $BaSO_4$, until this ratio reattains its constant value; conversely, the addition of CO_3'' causes the formation of $BaCO_3$ at the expense of the $BaSO_4$. In each case the amount transformed is perfectly definite; and the state of equilibrium can always be calculated if

k_1, k_2 and the concentration of either SO_4'' or CO_3'' is known. If the conditions were such that the system should become saturated with respect to sodium sulphate or carbonate (or both), the equation determining the equilibrium would be somewhat more complicated; but the general result would be the same, namely, that the position of equilibrium is determined by the relative solubilities (in the particular medium) of such of the possible products of reaction (which include the original substances) as separate out as solid phases.

C. NEUTRALITY OF AQUEOUS SOLUTIONS

According to the theory of electrolytic dissociation, acidity is attributed to the presence of hydrogen ion (H^+) and alkalinity to the presence of hydroxyl ion (OH') in the solution. Now, it has been found experimentally that the dissociation of pure water, according to the scheme $H_2O \rightleftarrows H^+ + OH'$, is such that $[H^+][OH'] = 1.2 \times 10^{-14}$ at 25°. Now, according to the above scheme, the concentrations of H^+ and OH' in pure water must be equal; each must therefore be

$$= 1.1 \times 10^{-7}$$

The condition of neutrality, therefore, is that $[H^+] = [OH']$, which is equivalent to the statement that either should be equal to 1.1×10^{-7} (at 25°); solutions in which the concentration of H^+ is greater than this are acid, those in which it is less (or the concentration of OH' greater) than this are alkaline. Thus, in a 0.125 *N* solution of hydrochloric acid the concentration of H^+ would be about 0.1 *N* (since such a solution is ionized to about 80 per cent); the concentration of OH' in such a solution would, therefore, be about 1×10^{-13}; for it is understood that the product $[H^+] \times [OH']$ must attain the constant value 1.2×10^{-14} in any aqueous solution, provided that the temperature is 25°.

Now, a good indicator changes color at a definite concentration of H^+; and the concentration of H^+ can be measured directly; a series of indicator solutions may, therefore, be prepared, such that each shows its characteristic color change at a hydrogen ion concentration ten times that characteristic of the solution preceding it in the series.[61] Such a series of indicators may then be used to

[61] Directions for the preparation of such a series have been given by Salm (Zs. Physik. Chem., 63, p. 83 (1908)); the subject has been further discussed in a number of more recent papers.

establish the hydrogen ion concentration of unknown solutions, though when it is used for this purpose care must be taken to exclude possible reactions between the indicator and the components of the unknown solutions; otherwise the results may be of doubtful accuracy.

12. SALT HYDROLYSIS

It is a matter of common knowledge that the aqueous solutions of many salts are not neutral. Thus, for instance, sodium carbonate, sulphide, and silicate are alkaline; the chlorides, nitrates, and sulphates of most polyvalent bases are acid. This behavior is attributed to a process termed "salt-hydrolysis," which may be represented by the reaction $BA + H_2O \rightleftarrows BOH + HA$ and occurs (to an appreciable extent) only when the acid or the base (or both[62]), are weak.[63]

It is impossible to enter here into the theory of hydrolysis or to derive from the law of mass action the relations which determine its extent. Suffice it to say that under constant external conditions the extent of hydrolysis is perfectly definite and depends upon the magnitude of the dissociation constant of the weak acid [64] or the weak base;[65] or rather it is determined by the relation between this dissociation constant and that of water, so that the process of hydrolysis may be regarded as a competition for the strong base (or acid) between the weak acid (or base) and water (which may exercise either basic or acidic functions). Thus, in decinormal solution at ordinary temperatures, sodium chloride is practically not hydrolyzed, sodium acetate is hydrolyzed to an extent which is just appreciable (0.01 per cent), while sodium sulphide is hydrolyzed to somewhere about 90 per cent. With rise of temperature the dissociation constant of water increases faster than that of the acids and bases. Consequently the extent of hydrolysis increases markedly with rise in temperature. At all temperatures the extent of hydrolysis increases with diminishing concentration of the salt (except when both acid and base are weak).

---

[62] This case is of less practical importance, hence its consideration is omitted here.

[63] The strength of an acid (or base), in the sense in which it is used here, is measured by its extent of ionization. Thus, in decinormal solution at 25° hydrochloric acid is ionized to about 85 per cent; acetic acid to about 1 per cent; hydrogen sulphide to about 0.1 per cent; corresponding to this the respective dissociation constants of these acids are 1 (approximately), 1.8×10^{-5} and 9×10^{-8}. The dissociation constant of water is, as given above, 1.2×10^{-14}.

[64] In salts which yield an alkaline solution.

[65] In salts which yield an acid solution.

It is important to observe that in determining the degree of hydrolysis we must employ a method which will not disturb the hydrolytic equilibrium. Thus, an attempt to measure the hydrolysis of a salt yielding an acid solution by titrating the free acid would fail for the reason that as fast as the free acid is neutralized more is formed by the process of hydrolysis, and the solution will not become neutral until all the acid which was originally combined with the weak base has passed into combination with the strong base with which the solution was titrated.

Conversely, the extent of hydrolysis can be diminished by the addition of hydroxyl ions (to alkaline solutions) or of hydrogen ions (to acid solutions). An understanding of this process is important, as it accounts quantitatively for the increased solubility in acid (or base) of certain salts, as follows: If a salt is made up of a strong acid and a weak base only slightly soluble in water, its solubility will be limited by the solubility of the free base formed by hydrolysis, although the unhydrolyzed salt is itself soluble. Consequently increasing the concentration of free acid by driving back the hydrolysis increases the amount of the salt which will stay in solution; this increase continues until the hydrolysis has practically disappeared, after which further increased concentration of acid is without effect on the solubility of the salt. The same explanation holds for the increased solubility, with increase of alkali concentration, of a salt containing a weak, slightly soluble acid. As examples of this we have the increased solubility of salts of iron or aluminum in solutions containing excess of free acid and of sodium silicate or aluminosilicate in solutions containing free base in excess.

II. THE CHEMICAL REACTIONS OF THE COLLOID MATTER OF CLAYS

In this section the principles outlined in the preceding section will be applied in an endeavor to correlate and elucidate the behavior of clays under varying conditions. The experimental observations adduced are in part taken from the voluminous literature pertaining to clays; in part they are the result of original work by the author (H. E. Ashley).

1. DEFINITION OF CLAYS

Clays may be defined as mixtures of minerals of which the representative members are hydrous silicates of aluminum, iron, the alkalies, and the alkaline earths, of which the most characteristic is the hydrated aluminum silicate ($Al_2O_3,2SiO_2,2H_2O$).[66] Some quartz, mica,[67] and feldspar are usually present; the grains of these minerals may show crystal faces (especially in the case of china clays), but commonly they are of irregular shapes.

Upon most of the grains of the constituent minerals there is an enveloping coating of colloidal material, which consists of silicates, silicic acid with hydroxides of aluminum,[68] iron, and manganese, and usually contains some organic matter.[69]

Almost any mineral, as well as various soluble salts, may be present in clays and modify the properties somewhat. The combination of granular and colloidal material is, or should be, in such proportion that when reduced to proper size (by crushing, sifting, washing, or other means) and moistened with an appropriate amount of water plasticity is developed. If too much colloidal material is present, the clay is considered very sticky, strong, or fat; if too little, the clay is called sandy, weak, lean, or nonplastic.[70] The term "nonplastics" for granular materials requires qualification, since most plastic bodies would lose plasticity and become sticky if the granular constituent were removed. The highly colloidal clays are as nonplastic as the clays containing little colloidal material. In one case the clay is too sticky to work; in the other case it is too weak and sandy. Plasticity depends on

---

[66] Mellor and Holdcroft (Pottery Gazette, **36**, pp. 680–686; 1911) present evidence in favor of the view that this is to be considered as a member of a series of complex aluminosilicic acids, which are no more closely related to the silicic acids than, for instance, the ferrocyanides are to the cyanides.

[67] Vogt (Contributions a l'Etude des Argiles et de la Ceramique, published by the Société d'Encouragement pour l'Industrie Nationale, 1906, pp. 193–218, 275–357) has most conclusively proved that muscovite mica ($3Al_2O_3,K_2O,6SiO_2,2H_2O$) is a frequent and considerable constituent of the "clay substance" of many of the clays of France, and often is the predominating constituent in Chinese and Japanese porcelain. It is as plastic as kaolin in a state of exceedingly fine division. (Cf., p. 39, and see also Bourry: Treatise on Ceramic Industries, translated by Rix, pp. 53, 702; 1901.)

[68] It is not at all unlikely that these may be present largely as aluminosilicic or ferrosilicic acids. (Cf., Mellor and Holdcroft, loc. cit.)

[69] For instance, Böttcher (Sprechsaal, **42**, pp. 233, 252; 1908) extracted from fire clay by ether about 0.1 per cent of a yellow waxy material, which had the odor of clay, was soluble in ligroin, benzene, and alcohol, but in water only slightly and with decomposition. It began to flow about 80°, burnt readily without residue, smelling like paraffin. Clay extracted alternately with water and ether settled much more quickly than before, had lost its fatty feel, and had a crystalline sheen.

[70] Cf., p. 38.

a proper ratio between colloidal and granular matter, but within limits it varies with the amount of colloidal material present. According to Schloesing [71] the proportion of colloidal material in a clay is usually small and rarely exceeds 1.5 per cent; a clay containing 0.5 per cent is lean.

It may be noted that it has been shown that the hydroxides of both aluminum and iron possess amphoteric properties [72]; that is, they can behave either as acid or as a base, depending upon the conditions. This is in accordance with certain observations of Hundeshagen,[73] who found that kaolin absorbs basic dyes very strongly, but acid dyes only very weakly, and concluded from this that kaolin may act not only as a weak acid, but also under other conditions as a very weak base. This possible amphoteric character of clays increases their capacity for reacting, but at the same time renders it more difficult to account for or to predict their behavior under all circumstances.

2. ORIGIN OF CLAYS

Clays have been formed by the decomposition of feldspars, though the exact mode of formation is not yet established beyond question. Thus Clarke writes: [74] "That kaolinite (the crystalline mineral of the composition Al_2O_3, $2SiO_2$, $2H_2O$) is the chief residual product of feldspathic decay is the commonly accepted view, but some writers hold that it is not formed by ordinary weathering. According to H. Rösler [75] kaolinite is only produced by pneumatolytic action—that is, by the operation of thermal waters and gaseous emanations. * * * Probably different crystalline silicates yield different residues of this ill-defined class (of hydrous silicates of aluminum and iron), and any or all of them may exist in residuary clays."

Whatever be the exact process by which feldspars are transformed into clays, this much is certain, that the main agency in the removal of the alkalies and silica is water (or dilute aqueous solutions). This removal may be effected by simple solution, for

[71] Chimie agricole, in Frémy's Encyclopédie Chimique, p. 67, 1888.
[72] J. K. Wood, J. Chem. Soc., **93**, p. 411.
[73] Zs. angew. Chem., **21**, p. 2455, 1908.
[74] Data of Geochemistry: U. S. Geol. Survey, Bull. **330**, p. 416; 1908.
[75] Neues Jahrbuch f. Mineralogie, etc., Beil. Bd., **15**, p. 231; 1902.

we know that in the lapse of time water dissolves the constituents of alkaline silicate out of feldspar; the process is probably furthered by mechanical factors.

The complete disintegration of a rock is commonly followed by a removal of the fragmentary material from its original site. This transportation may be effected in various ways—by flowing streams, by glacial ice, or by winds—and it is accompanied to a certain extent by a separation of the rock residues into substances of different kinds. A stream deposits its load first as coarse gravel, then as sand, and finally, often with extreme slowness, as silt or clay. The gravel consists merely of fragments, more or less rounded, of the original rock or of its larger inclusions. The sand contains finer particles of undecomposed minerals, with quartz usually predominating. The silt is composed largely of decomposition products, such as kaolinite, hydroxides of iron or aluminum, and the like. These substances shade into one another, and their exact nature in any specific case will depend upon the thoroughness with which the primary decomposition was effected and upon mechanical factors such as the velocity of the stream.[76]

3. CHARACTER OF THE CLAY SUBSTANCE

As stated above, the characteristic constituent of clays is a hydrous aluminum silicate, the composition of which, as determined by analysis, is given by the formula Al_2O_3, $2SiO_2$, $2H_2O$; as yet, however, the constitution of these substances has not been definitely ascertained.

Löwenstein[77] concluded from weak evidence that the combined water of kaolin is given off in two stages, and therefore that it is not all of the same nature. This view has been shared by several investigators, including Le Chatelier. On the other hand, it was shown by Barnes[78] and confirmed conclusively by Kennedy,[79] and later by Mellor and Holdcroft[80] that the dehydration all takes place in one stage. The main conclusions reached by the last-named authors follow:

There is no definite temperatures above which it can be said that kaolinite[81] decomposes and below which kaolinite does not decompose. The speed of decomposition is accelerated by raising the temperature or by working under reduced pressure. The heating curve of kaolinite shows that an endothermal reaction occurs in the

[76] Clarke, loc. cit., p. 426.

[77] Zs. anorg. Chem., 63, pp. 69–139; 1909.

[78] Clayworker, 23, p. 705; 1895.

[79] Trans. Am. Cer. Soc., 4, pp. 149, 152; 1902.

[80] The Chemical Constitution of the Kaolinite Molecule, Pottery Gazette, 36, pp. 680–686; 1911.

[81] The authors here use the term "kaolinite" for a sample of china clay containing both kaolinite and "clayite"; the latter term has been adopted previously by Mellor (Pottery Gazette, 34, p. 927; 1909) to denote "the noncrystalline variety of the hydrated aluminum silicate (Al_2O_3, $2SiO_2$, $2H_2O$) which occurs in china clay and in most clays yet examined. Kaolinite is crystalline clayite."

vicinity of 500°, and an exothermal reaction just over 800°; the former corresponds with a decomposition of kaolinite into free silica, free alumina, and water. The restoration of from 3 to 4 per cent of water, by heating calcined kaolinite [82] under pressure in steam, corresponds with a rehydration of alumina or silica. The formation of sillimanite (Al_2O_3, SiO_2) in kaolinite when heated over 1200° is due to the recombination of the free alumina with some of the silica formed at about 500°. The exothermal change shown in the heating curve of kaolinite corresponds with a physical change of the free alumina whereby the alumina becomes less soluble in acids, less hygroscopic, and more dense. Kaolinite may be represented as one member of a series of aluminodisilicic acids, and these in turn form one group of a large number of aluminosilicates.

Now, it is quite possible that the aluminosilicic acids are much stronger than the silicic acids, just as hydroferrocyanic acid is stronger than hydrocyanic acid; hence kaolinite, if it is an aluminosilicate, might not be hydrolyzed by water. If it were hydrolyzed, colloidal silica and alumina would be formed. The nature of this process is indicated by the following considerations:

It is well known that the solubility in water of any substance is never absolutely zero, although it may be exceedingly small. Consequently kaolinite in contact with water dissolves to some slight extent and is immediately hydrolyzed.[83] The solution thereby becomes unsaturated with respect to kaolinite; consequently more dissolves, which in turn is hydrolyzed, when still more can be dissolved, and so on. These two simultaneous processes may thus transform an appreciable amount of kaolinite, provided that sufficient time be allowed—a condition which would usually obtain. Whether a definite state of equilibrium is reached can not be stated at present with absolute certainty; it is probable, however, that equilibrium would finally be reached, though the position of equilibrium would likely vary—e. g., with the size of the colloidal (disperse) particles produced, consequently with the rate of the process, which in turn depends largely on the temperature. The products of such hydrolysis are of course alumina and silica, in general in the colloidal state, the degree of dispersion depending upon various factors; in some cases the water might contain salts in quantity sufficient to coagulate them wholly or in part.

---

[82] It may be noted that kaolinite heated to higher temperatures is less sensitive chemically than when dehydrated at lower temperatures, and that the rehydrated material is not plastic. (Cf., p. 38.)

[83] This statement is, of course, subject to the condition that the acid is weak, a condition which holds presumably for silicic acid itself, although, as stated above, it may not hold for the complex aluminosilicic acids.

This point of view is in harmony with conclusions reached by H. Gedroiz,[84] who asserted that aluminum hydroxide, ferric hydroxide, silicic acid, and kaolin are at the moment of their formation by weathering hydrosols, which stay as such or are coagulated, depending on the composition of the soil solution.

It is not pretended that the mode of action outlined above has been effective in all cases; it is given merely as a simple view of the matter, by means of which differences in the gross composition of clays and in the character and amount of their colloid content may be accounted for.

In the lapse of time a renewed crystallization of the colloidal material may be set in. Thus, K. Endell [85] has analyzed and determined the colloid content of clays formed under fuel deposits of different ages, as follows: (1) Weathered basalt from beneath 0.30 m peat contained 60 per cent (by volume) colloidal material; (2) decomposed basalt from beneath 1.50 m peat, 87 per cent; (3) decomposed basalt from under brown coal, 67 per cent; (4) decomposed melaphyre from under bituminous coal, 50 per cent. He concludes that:

> Basic eruptive rocks are in general decomposed to kaolin [86] by overlying peat and its fossil relations, brown coal and bituminous coal. In the course of this decomposition there is an increase in the content of silica, titanium, aluminum, and water and a decrease in the phosphate, iron, alkaline earths, and alkalies, all of which are dissolved out more or less. * * * A comparative consideration of the proportion of colloidal material * * * shows first a gradual increase in colloids, which reaches its maximum with basalt decomposed under peat, then a gradual decrease, which may be attributed to renewed recrystallization of the newly formed colloids in the course of geological periods.

A. GENERAL PROPERTIES OF CLAYS

4. GAUGING THE COLLOID MATTER OF CLAYS

Clays exhibit their characteristic properties only in presence of water; indeed, that water is present is implicit in the definition of clay, for the behavior of the dried-out clay substance differs largely from that which we ordinarily associate with clays. Formerly a variety of ad hoc hypotheses were proposed to account for the properties of clay; but now, since the development of our knowledge of the colloidal state, all of these properties may be correlated with the presence in the clay of colloidal matter.

---

[84] J. Exp. Landw., 9, pp. 272–293, 1908; C. A., 3, p. 2600, 1909.

[85] Sprechsaal, 43, pp. 278, 291, 1910.

[86] By "kaolin" Endell apparently means "clay substance" of formula approximating to that of kaolinite.

The principal properties of clay, besides its absorptive power, which we shall consider later, are *plasticity*, *binding power*, and *shrinkage* on drying or burning.

It is now generally believed that the plasticity of a clay is due to the colloidal substance which it happens to contain. This supposition was clearly stated by T. Schlösing [87] as long ago as 1888, and advocated later by P. Rohland.[88] It has recently been developed more fully by A. S. Cushman,[89] whose experiments upon the binding power of road-making materials are apparently conclusive.[90]

It is unnecessary to marshal here all the evidence in favor of this view; the following example may serve to illustrate how on this view one well-known phase of the behavior of clays may be simply accounted for. When clays have been completely dried, plasticity disappears (and with it the other characteristic properties); when the material is again wetted the plasticity is initially not so great as it was before drying out, but in the lapse of time increases slowly again. This behavior is exactly analogous to that which has been often observed with colloidal systems [91]; that is, the drying-out process in some way changes the state of the solid phase so that the degree of dispersion is less on wetting again than it was originally, and only regains its former value by means of the slow taking up of water, accompanied possibly by some degree of hydrolysis.

On this supposition, too, the other properties can be simply accounted for. Thus, to quote Rohland: [92]

On this hypothesis we may easily account for the phenomena of shrinkage on drying in the air and on burning, especially the fact that the shrinkage ceases before the mass is fully dry. Such a mass is to be regarded as a complex solid meshwork, in the pores of which a liquid phase is present. In this way the shrinkage of the solid network may cease, while liquid is still present in the pores.

The ability of a clay to take up and to hold relatively large amounts of foreign material (such as sand, powdered minerals, etc.) without destroying its other properties is also to be attributed

---

[87] Chimie agricole, in Frémy's Encyclopédie Chimique, p. 67.

[88] Z. anorg. chem., **31**, p. 158, 1902; **41**, p. 325, 1904; **56**, p. 46, 1907; **60**, p. 366, 1908; **65**, p. 108, 1909; Z. Chem. Ind. Kolloide, **4**, p. 5, 1909; J. Soc. Chem. Ind., **29**, p. 12, 1906; **30**, p. 23, 1907; **33**, p. 5, 1910.

[89] U. S. Dept. of Agriculture, Bureau of Chemistry, Bulls. No. 85, 1904 and 92, 1905; Trans. Am. Ceramic Soc., **6**, 1904. Cushman cites several other authorities than those mentioned above.

[90] Clarke, Data of Geochemistry, pp. 425–426.

[91] For instance, see Lottermoser and Rothe, Z. physik. Chem., **62**, p. 375, 1908, who studied the deflocculation of gels of silver iodide and found that they could not be deflocculated once they had been completely dried or precipitated.

[92] van Bemmelen Gedenkboek, p. 28. (Published at Helder, 1910.)

to the presence of colloidal material, which surrounds the foreign particles, and thus binds them together.

Plasticity is exhibited not only by hydrated silicate of aluminum, the usual main constituent of clays, but also apparently by any silicate of a slightly soluble base (e. g., oxide of iron or zinc, magnesia) under conditions comparable to those where ordinary clay develops plastic properties. For example, Rohland states that a clay carrying zinc showed great plasticity,[93] and Le Chatelier [94] reports that a plastic paste may be obtained by grinding mica or glauconite with water for a sufficiently long time.

The shrinkage on burning is closely related to the plasticity, being greater as the plasticity is greater. This is in accord with the ideas stated above, for on drying there is a contraction around each individual grain due to the destruction of the colloidal material as such and the consequent formation of a multitude of cracks. It is practically impossible to dry a mass of pure clay so that it shall be free from cracks. But by suitable admixture of sand or other nonplastic material with the clay these cracks may be rendered small and separated one from another so that they do not endanger the strength of the ware. In order to accomplish this it is essential that the drying process be uniform throughout the mass. To insure uniformity the drying must be conducted very slowly, and more slowly in proportion as the material used was more plastic.

The shrinkage must not be too much reduced by the addition of foreign material; otherwise the hardness of the ware will suffer. Pure clay becomes very hard on drying, while sandy pastes always remain more or less friable. This correlation does not obtain if the burning is performed at a temperature such that a partial fusion of the material may occur; but it does hold for bricks, tiles, and other refractory materials, which are burned at temperatures between 1000° and 1200°.

From the foregoing we see the great practical importance of a knowledge of the amount of plasticity of clay bodies and of the

---

[93] van Bemmelen Gedenkboek, p. 29. Its analysis was: Loss on ignition 7.85 per cent; ZnO, 54.06 per cent; Al_2O_3, 1.64 per cent; SiO_2, 35.39 per cent; Na_2O, 1.80 per cent.

[94] van Bemmelen Gedenkboek, p. 167. Le Chatelier, however, attributes plasticity to the presence of exceedingly small crystalline lamellæ, and is of the opinion that all substances made up of such lamellæ will show plastic properties.

effect of added substances upon the plasticity. This is equivalent to a knowledge of the amount and character of the colloidal material and its behavior to reagents. This behavior we shall now consider in detail, describing first an easily applied test, previously described by the writer,[95] by which the comparative plasticities of clays may be gauged.[95a]

(a) MALACHITE GREEN TEST FOR GAUGING THE COLLOID MATTER OF CLAY

Procedure.—In brief and with slight modifications suggested by later experience the procedure is as follows:

Into a 100 cc cylinder provided with glass or rubber stopper put 50 cc of water. Add 1 gram (or other more suitable proportion) of clay, ground or sieved to the degree of fineness technically used, or to pass 60 mesh. Shake at once by hand to prevent clotting. Add 50 cc malachite green solution (6 g malachite green oxalate per liter). Shake gently for two hours on a mechanical shaker and allow to settle overnight. (It might be preferable to use a centrifugal machine.)

On the following day take out a convenient amount of the supernatant liquid by a pipette, the tip of which is inserted to the 60 cc mark on the cylinder, and run it into one of a pair of 50 cc comparison tubes, such as is used for carbon determinations in steel analysis. Into the other tube put 0.5 cc of the standard dye solution (6 g per liter, as above) and dilute to about 35 cc, the maximum concentration at which a good comparison can be made. Compare the tints in a camera with white glass plate (Eimer and Amend Catalogue No. 3821). Now dilute whichever tube is the darker until the tubes match. If either tube is not large enough for full dilution, make it up to 50 cc, take out 5 cc in a pipette, clean the tube with water, and return the 5 cc contents of the pipette to the tube. To insure uniform mixture

---

[95] H. E. Ashley: The Colloid Matter of Clay and its Measurement, U. S. Geol. Survey, Bull. 388, 1909; Trans. Am. Cer. Soc., **11**, pp. 530–595, 1909.

[95a] EDITORIAL NOTE.—While the malachite green test may yield a fairly good comparative measure of the plasticity of clays, it can hardly be accepted as a measure of the colloid content; for the absorption of a dye by colloidal material depends upon the character (degree of dispersion) as well as upon the amount and composition of the latter. Notwithstanding this, the test may prove of decided service with similar clays or with series of samples of the same clay. See, however, a paper by H. Stremme and B. Aarnio (Zs. prakt. Geol., **19**, pp. 329–349, 467), who have shown that malachite green is affected by the presence of lime or alkalies; they conclude that the Rodenwald-Mitscherlich hygroscopicity determination is the most satisfactory method of gauging the colloid content of clays.

on diluting, empty the tube twice into a 100 cc beaker after each addition. If the dye stains the glassware, it may be removed easily by a little acetic acid.

Keep results in the following form:

Kind of clay	Weight taken	cc of dye solution added	Color comparison				Grams dye remaining in solution		Grams dye absorbed	
			Standard		Test					
			cc taken	Diluted to—	cc taken	Diluted to—	Per cc	Total	Total	Per 1 g clay
Boone....	1	50	0.5	420	10 1	10.4 1.04	0.000 007 43	0.000 743	0.299 257	0.299 257

The number of grams dye in 1 cc of the test solution is then $\frac{1.04 \times 0.003}{420} = 0.000\,007\,43$; the total dye remaining in solution is therefore $0.000\,007\,43 \times$ cc liquid taken (100) $= 0.000\,743$, and the total amount of dye absorbed $= 0.3 - 0.000\,743 = 0.299\,257$.

This does not give the colloidal matter directly, but by comparison with the absorption found under similar conditions with a very plastic clay as standard (for which purpose the writer has used Tennessee No. 3 Ball of the Tennessee Ball & Sagger Clay Co.) the relative plasticity may be gauged. For example, if the clay tested shows a total dye absorption 1.25 times as great as that of the standard (taken as 100) its relative plasticity is 125.

The absorption of malachite green is in all probability an exchange of bases such as is discussed later in this paper. The dye is a salt of a complex ammonia base which forms insoluble compounds with the colloidal acid radicals, while its oxalate radical forms insoluble oxalates with the bases which tend to keep clay coagulated. Therefore its reaction with the colloidal matter is very complete. It fails, indeed (is decolorized), with alkaline and limy clays, which, however, are not included among the clays used for the better classes of clay wares. As both the sulphate and chloride of this dye are soluble in water, no serious interference can be ascribed to such soluble salts as occur in clays. No other dye is so free from objections and so well suited for colloid measurements. (Cf. Table X, pp. 72–74.)

(b) SODIUM CARBONATE TEST

According to Bleininger:[96]

Plasticity is sometimes measured by letting 1 g of clay stand in a solution of normal sodium carbonate, then determining the amount absorbed by the decrease in the strength of solution. The amount of sodium carbonate absorbed is supposed to be proportional to the colloids, which colloids are supposed to be the seat and source of plasticity.

According to the views advanced in this paper, the sodium carbonate precipitates those bases which are combined with gels but is unaffected by those with the sol. The method seems sound, except that an excess of alkali appears to act on the crystal matter if sufficient time is allowed. (Cf. time effect, p. 44; casting, p. 98.)

(c) WATER STORAGE

The more abundant colloidal matter is in a clay the more water it can store in an "air-dry" condition. This is illustrated by the following determinations of the loss of weight of air-dried clay: (1) When heated at 60° in a slow current of air that had been dried by bubbling through strong sulphuric acid; (2) when heated further to 130°.

The table of relative colloid content shows that the amount of water absorbed by clays from the air at ordinary temperature and humidity and given up again to dry air at 60° or 130° is very nearly proportional to the colloid content. As humus matter is the most absorbent colloid in soils, it follows that humus is of value in dry weather as a water reservoir.

	Loss from "air-dry" condition to—		Relative colloid content by malachite green oxalate test
	60° C	130° C (total)	
	Percent	Per cent	
Texas, Edwards County, white fire clay	3.08	3.78	154
Potters' Supply Co., Tennessee ball No. 3	1.60	2.11	100
J. Poole, No. 20 English ball	1.35	1.77	98
Jas. P. Prall, New Jersey No. 1 sagger	1.28	1.61	100
P. L. Ryan, New Jersey No. 1 sagger	1.24	1.54	78
Moore & Munger, English ball	1.22	1.46	91
Edgar Bros.' Co., Florida kaolin	0.91	1.13	33
Johnson-Porter Clay Co., Tennessee X wad	0.45	0.53	22
J. Poole, No. 1 china clay	0.30	0.44	24
Potter's "flint" (quartz)	0.05	0.03	0

[96] Private notes on lectures at Ohio State University, 1905.

B. REACTIONS OF THE COLLOIDAL MATTER OF CLAYS

Our investigations have shown that the reactions of the colloidal matter of clay are very similar to those of soaps;[97] that the conditions of solubility and insolubility are parallel, but that the colloidal matter of clay is probably more readily reacted upon. In either case we have a weak acid, only slightly soluble in the free state, the salts of which are all hydrolyzed and, excepting those of the alkalies and ammonium, only slightly soluble. Hence wherever, on addition of a reagent, exchange of bases is possible, the behavior exhibited by the clay will be akin to that of the corresponding soap. The fatty and soapy feel of highly colloidal clays so often mentioned by practical men as well as by writers on ceramics may be due to a real similarity rather than to a chance resemblance. This analogy with soaps is not inconsistent with the known facts about clays; it has proved a most helpful and suggestive guide in planning these investigations and it has never misled.

On the basis of this analogy some of the reactions exhibited by clays may be exemplified as follows:

(*a*) Excess of KOH or KCl added to the K-sol[98] reduces the solubility of the latter, giving rise to a gel. In this case, therefore, a salting-out effect produces coagulation.

(*b*) Addition of HCl or $CaSO_4$ to the alkali sol produces by exchange of bases the H or Ca compound, either of which, being less soluble than the original sol, appears as a gel. Here we have coagulation produced by exchange of bases.

(*c*) On the contrary, if NaOH or $Na_2C_2O_4$ is added to the H or Ca gels, the Na sol is regenerated; in other words, addition of such substance produces deflocculation.

In the actual case of a clay the reactions will be more complicated, owing to the multiplicity of possible reactions consequent upon the number of radicals present. Moreover, in accordance with the principle of mass action, the reactions will in general be incomplete. Their nature and extent is predicable from the solubility relations of the various possible solid phases. Unfor-

---

[97] Keppeler (Z. angew. Chem., 22, pp. 526–527; 1909) has noted a parallelism between the emulsification of fats by soaps and the effects produced upon clays by salts of acids of high molecular weight, but does not seem to have pursued the idea further. (See also Zsigmondy-Alexander, pp. 214–219.)

[98] This form of abbreviation is used for the sake of convenience to denote the sol which is formed by the action of water on a clay containing combined potash.

tunately, however, our knowledge of these relations is, if not lacking altogether, barely qualitative, far less quantitative, in character, so that in part we are forced to reason from analogy.

5. VARIETY OF CLAYS AND MINERALS TESTED

In this investigation use was made of as wide a range of clays as possible. English and American kaolins and ball clays, brick surface clays, sagger clays, peat, and surface clays containing much organic matter, shales, slate, No. 1 and No. 2 fire clays, and fuller's earth. The slate was least affected, shale next, and No. 1 fire clay next in order; the others were readily acted upon.

6. TIME REQUIRED FOR THE REACTIONS OF CLAYS

The reactions of clays are in general by no means instantaneous; usually a period of at least several hours is necessary for the attainment of the (comparatively) stable state assumed under any given set of conditions. This effect has been noted by various writers.

Thus Böttcher [99] found that, when alkali in excess of the proportion giving minimum viscosity was added to clays, the viscosity decreased with lapse of time, attaining a constant value in from 24 to 48 hours. This reliquefaction was accelerated by frequent shaking, and was accompanied by a decrease in the electrical conductivity of the liquid and in the concentration of alkali in the liquid. Moreover, it was not due to any action of carbon dioxide. Böttcher considered this effect to be a mechanical absorption of the alkali by the clay which by decreasing the alkali concentration would cause it to approach more nearly to the proportion giving minimum viscosity. According to the views expressed in this paper, it is to be attributed to a metathetical reaction between the clay and the alkali, a reaction which requires an appreciable time for its completion.

Morse and Curry [100] made numerous tests on this time effect and found that, while most of the change took place within an hour or two, some was still observable after 72 hours.

Similar results were obtained with many reagents in the course of the present work. For example, it was found that the amount

[99] Sprechsaal, 42, 1909; passim.

[100] 19th and 20th reports N. H. Agr. Expt. Sta., p. 275; 1908. See also Wo. Ostwald, Kolloidchemie, 412; 1910.

of calcium hydroxide required to keep some clay in suspension increased rapidly with the duration of contact with the clay.

Weber [101] found that casting slip, though perfectly fluid during the stirring operation, would occasionally on standing thicken to a gelatinous mass. He attributed the effect to the action of salts, especially sulphates and carbonates. This is doubtless true; the time effect being in part the slow solution of such slightly soluble substances as gypsum, which then gradually react with the clay. But it may also be due in part to a slow reaction between free silica of the clay and the alkali present.

Böttcher [102] has used measured amounts and concentrations of ammonia and of the hydroxides and carbonates of the alkalies to deflocculate equal weights of a stoneware clay. He made casting slips and determined their viscosity with an efflux viscosimeter with an orifice of 2 mm; he then diluted a portion of his slip in test tubes, obtaining series similar to those described in the present paper, but he did not measure the bulk of the sediments. He found a minimum of viscosity of the thick slip to coincide with a maximum of suspension of the diluted slip in the test tubes. This observation serves to show that the effect of the reagent depends less upon its concentration in the liquid medium than on the relative amounts of reagent and clay; moreover, it is good evidence that viscosity is not the main factor in suspension.

7. EFFECT OF CONCENTRATION OF THE REAGENT

That the concentration of reagent in the solution may be of less importance in determining the final state of the system than the ratio of reagent to clay is a point deserving further attention.

This is illustrated by the following table, which contains the results of tests made on Albert Lea Brick & Tile Co. yellow clay (Minnesota) with 0.1 molar sodium oxalate, the total volume being always 100 cc.

Weight of clay	Amount of reagent giving maximum suspension	Amount of reagent per gram clay
grams	cc	cc
20	60	3.0
5	13	2.6
1	11	11.0
0.1	11	110.0

[101] British Patent No. 6560; Mar. 18, 1909.

[102] Sprechsaal, 42, 1909; passim.

From this table it appears that with the larger amounts of clay the predominating factor is the ratio of reagent to clay; but with the smaller amounts of clay it is the concentration of reagent in the solution.

This behavior is entirely in accord with the views expressed in this paper and is directly attributable to the various solubility relations. If these were known approximately, the behavior of the system clay-reagent-water could, we believe, be roughly predicted for all ratios of the components.

8. OBSERVATIONS ON THE ACIDITY OF CLAY EXTRACTS

With reference to the acidity of soil extracts, Cameron and Bell [103] write:

> Soil extracts are usually either neutral or faintly acid to litmus. On boiling in platinum vessels, however, to eliminate carbon dioxide or possibly other volatile acids, in the vast majority of cases the solution will show an alkaline reaction with iodeosin, phenolphthalein, or litmus.

According to Morse and Curry:[104]

> The water extracts of soils seldom react acid * * * the water-bath residues of the water extract of soils are nearly always alkaline to phenolphthalein * * *. Most clay, clay soils, and muck, and some other soils, yield acid solutions when extracted with salt solutions.

And again:

> A clay, practically free from organic matter, came to our notice. The water extract of this clay was neutral to methyl orange, litmus, and phenolphthalein, and the clay itself decidedly acid toward litmus. Also when this clay was treated with sodium chloride for a quantitative estimation of its acid content, a strongly acid solution was obtained * * *. The large amount of acid in solution was decidedly at variance with the amount of organic matter in the clay.

The inference from these statements is that carbon dioxide is largely responsible for the apparent acidity of clays and soils. But carbon dioxide will hardly account for the increased acidity on addition of a salt, e. g., sodium chloride; this can be due only to the liberation of hydrochloric acid as the result of a metathetical reaction between the salt and the clay. This serves to confirm the view, repeatedly expressed in this paper, that the behavior of clays is conditioned largely by the possibility and occurrence of such metathetical reactions.

---

[103] U. S. Dept. of Agr., Bureau of Soils, Bull. 30, p. 14; 1905.

[104] 19th and 20th reports N. H. Agr. Expt. Sta., pp. 271–272; 1908.

It was conjectured that there might be some relation between the plasticity of a clay and its acidity. Consequently the acidity of the cold-water extracts of a large number of clays was determined by the indicator method, using the series of indicators as given by Salm.[105] The acidity of the water extracts as determined in this way varied all the way from a concentration of hydrogen ion of about 10^{-3}, through neutral solutions, down to values of about 10^{-11}; but no relation between acidity of the extract and the plasticity or other qualities of the clay could be detected.

The results (in many cases of several determinations with that particular clay) are brought together in the following table:

Acidity of Water Extracts from Various Clays and Minerals

Hydrogen ion concentration [106]	Variety of clay	Hydrogen ion concentration	Variety of clay
10^{-3}	Jas. P. Prall, New Jersey, sagger clay, crude or dialyzed	10^{-5}–10^{-6}	Johnson Porter Clay Co., Tennessee ball No. 9
	Edgar Bros., New Jersey, No. 10 sagger	10^{-6}–10^{-7}	Brunt Mesaba iron ore
	Pike's No. 20, English ball		Groveport, Ohio, surface clay
10^{-3}–10^{-4}	Mandle-Sant Clay Co., Tennessee ball No. 3		Canton, Ohio, shale
10^{-4}	Geo. Knowles & Sons, No. 15 English china		Potter's "flint," (ground sand rock)
	Hammill & Gillespie A I English china		Fine white mica
	Champaign, Ill., joint clay		Fuller's earth (Eimer and Amend and R. J. Waddell)
10^{-4}–10^{-5}	Hall Clay Co., Georgia kaolin		Johnson Porter Clay Co., Tennessee ball No. 10
	Harris Clay Co., Penland, N. C., kaolin		Albert Lead, Michigan, yellow clay
	Edgar Bros. Co., Florida kaolin		Fort Pierre, South Dakota, sticky clay
	J. Poole, No. 1 English china	10^{-7}–10^{-8}	Edwards County, Tex., white fire clay
10^{-5}	Geo. Knowles & Son, No. 12 English ball	10^{-8}	Highland Fireclay Co., Missouri, No. 1 fire clay
	W. H. Wynn, Pennsylvania No. 1 and No. 2 fire clay		Owl Clay Co., Florida, fuller's earth
10^{-5}–10^{-6}	Diamond Clay Co., Ohio, No. 2 fire clay	10^{-8}–10^{-9}	Athens, Ohio, red fire clay
	Aluminum Co. of America bauxite		Peoria, Ill., joint clay
	Atlanta Mining & Clay Co., Georgia kaolin	10^{-9}	Brandywine Summit, Pa., soda feldspar
			Herron Lake, Minn., surface clay
			Albany, N. Y., slip clay
		10^{-9}–10^{-10}	Maine Feldspar Co., potash feldspar
		10^{-11}	Wyoming bentonite
			Calcined aluminum hydroxide

[105] Zs. physik. Chem., 63, pp. 83–108; 1908. It may be observed that a special investigation would be necessary in order to determine just in how far the application of this method is justifiable in determining the acidity of clay extracts. For instance, exchange of bases might well take place between the indicator (which is usually a salt) and particles of clay substance contained in the extract; if such a reaction took place, the indicator test would probably be quite misleading.

[106] See footnote 105.

Three of the most plastic clays of the table (Prall sagger, Tennessee No. 3, and Pike's No. 20 ball) give strongly acid extracts; on the other hand, the moderately plastic kaolins have about the same acidity as some of the highly plastic clays.

The clays investigated with respect to the acidity of their water extracts may be grouped roughly as follows:

Cracking clays: Neutral, but showing a considerable range on either side of the neutral point.

Fuller's earths, quartz, mica: Neutral.

Fire clays: Showing considerable range, but tending to be slightly acidic.

Shales: Weakly acidic.

Kaolins: Somewhat more strongly acidic.

Ball and sagger clays: Still more acidic, in general, though some of them range down to neutral.

C. EXAMINATION OF AN INSOLUBLE KAOLIN

A series of tests were made on the Georgia sagger clay (kaolin) of the Hall Clay Co. Its relative colloid content is 26, as compared with Tennessee ball clay No. 3 taken as 100.[107] The acidity of the clear aqueous extract was about 10^{-5} N, as determined by the indicator method.

Five gram portions of the clay were rotated for one hour with (*a*) 98 cc water, (*b*) 97 cc water and 1 cc HCl (specific gravity 1.20), and allowed to settle overnight. Qualitative tests on the clear liquids showed that the water soluble salts were mainly calcium sulphate and a trace of alkali chloride. Decidedly more calcium salt was present in the acid extract, indicating that a certain amount of replacement had taken place.

9. EFFECT OF REPEATED EXTRACTION WITH WATER

Into each of four glass-stoppered 100 cc graduated tubes was put 5 g of the clay with 98 cc distilled water, making a total volume of 100 cc. The tubes were rotated on the shaking machine for 1 hour; after standing for some time each contained 81–83 cc of clear liquid and 19–17 cc of sediment. Seventy-five cc of the clear liquid was siphoned off, replaced by water, the tube shaken, and allowed to stand overnight. This process was repeated until

[107] See U. S. Geol. Survey, Bull. 388, p. 49; 1909; cf. p. 41.

an equivalent dilution of 8000 times the original had been reached. It was found that the bulk of sediment increased somewhat with dilution. This is in agreement with the observations that the sediment becomes bulkier on prolonged contact with water and indicates that the amount of colloidal material increases under these conditions.

10. EFFECT OF ADDITION OF SODIUM HYDROXIDE TO THE CLAY AFTER REPEATED EXTRACTION WITH WATER

After a dilution of 8000 times had been reached the tubes were treated as follows:

Tube	A	B	C	D
Removed liquid (cc)	1	5	10	30
Added 0.1 *N* NaOH (cc)	0.1	1	5	10
Total volume (cc)	99	96	95	80

The tubes were then shaken for one hour and allowed to stand overnight, when readings were made. Successive additions of reagent were made,[108] as specified in the following table, in which the results are brought together.

TABLE I

Hall Clay Co. Georgia Sagger Clay (Kaolin). Effect of Addition of NaOH to the Clay, Previously Extracted Repeatedly with Water

Tube	A					B				C				D			
Total additions (in cc) of 0.1 *N* NaOH	0	0.1	0.3	0.5	0.7	1	2	3	4	5	7	8	10	10	15	20	30
Clear	81	80.5	...	...	...	...	...	...	...	...	...	...	...	...	...	...	78
Turbid [109]	...	...	79.5	5	2	1	1	([109a])	1	1	3	2	12	60	64	68	...
Deeply turbid	...	...	...	...	...	...	...	...	...	...	...	74	64.5	...	...	...	...
Dense	...	...	...	84	92	88.5	91	93.5	93	85.5	71.5	...	...	...	...	...	...
Sediment	19	19.5	20.5	11	6	5.5	5	4.5	5	8.5	19.5	22	23.5	20	21	22	22

[108] In each case the reading was taken after the tubes had again been shaken for an hour and allowed to stand overnight.

[109] In this and the other tables turbid signifies that objects can still be detected through the liquid; deeply turbid, that objects can no longer be detected, but light is very evidently transmitted; dense, that little, if any, light is transmitted.

[109a] Trace.

The above results are considered to be due to a replacement by sodium of (1) any acid hydrogen (2) of the calcium in the original gel; this results in the formation of the sodium sol, which, however, is salted out again at the higher concentrations of alkali, thus accounting for the later increase in bulk of the sediment and for the final clarification of the liquid.

When the clay had not been previously extracted with water, its behavior in presence of soda was almost the same as the above, as might be expected from the nearly complete absence of soluble salts.

A similar series of experiments was performed with samples of this clay which had been repeatedly extracted with hydrochloric acid. Into each of four tubes was put 5 g clay along with 1 cc concentrated hydrochloric acid and 97 cc water. These were shaken one hour, allowed to settle, decanted, and refilled, this series of processes being repeated until a dilution of 8000 times the original volume of liquid was reached. The liquid over the clay was brilliantly clear at all stages of the dilution. Then successive additions of 0.1 *N* NaOH solution were made exactly as in the series presented in Table I, with results which are brought together in Table II.

TABLE II

Hall Clay Co. Georgia Sagger Clay (Kaolin). Effect of Addition of NaOH to the Clay Previously Extracted Repeatedly with HCl

Tube	G				H		
Total additions (in cc) of 0.1 *N* NaOH	0	0.1	0.3	0.5	1	2	3
Clear	72.5	71	77	74	71	.....	.....
Turbid	.....	.....	.....	.....	.....	1	1
Deeply turbid	.....	.....	.....	.....	.....	.....	.....
Dense	.....	.....	.....	.....	.....	90.5	92
Sediment	27.5	28	22	26	25	5.5	5

Tube	I			J						
Total additions (in cc) of 0.1 *N* NaOH	5	7	8.5	10	15	20	[109b]30	[109b]50	[109b]75	[109b]100
Clear	.....	.....	.....	.....	.....	.....	.....	.....	.....	85.5
Turbid	1	1	1	1	1	2	20	51	81	.....
Deeply turbid	.....	.....	.....	.....	.....	.....	64	27	.....	.....
Dense	89	91	92.5	73	78.5	88	.....	.....	.....	.....
Sediment	5	5	5	6	5.5	?	16	23	21	17.5

[109b] These additions were made with 2.5 *N* NaOH, so that the total volume should not be unduly increased.

As was to be expected, this behavior is practically identical with that of the clay extracted with water. For, according to our interpretation, the action of the hydrochloric acid can only be a replacement by hydrogen of the bases originally present; this process leaves the gels as such, because the solubility relations of the H-compound are similar to those of the compounds with the

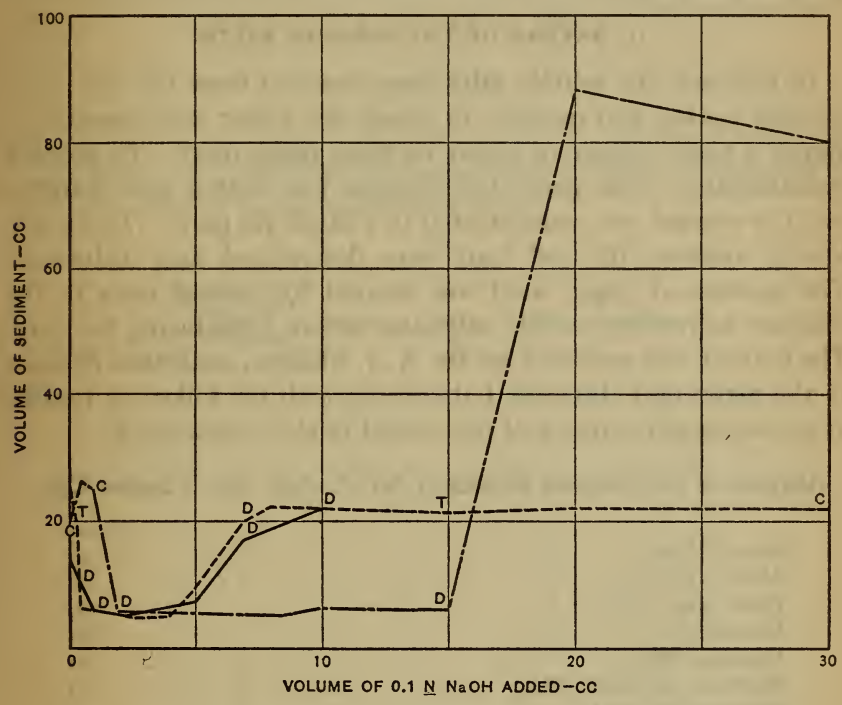


Fig. 1.—*Effect of additions of NaOH to kaolin* (*Georgia sagger clay, Hall Clay Co.*)

Cf. Tables I and II. —— Untreated; - - - - extracted with water; — - — - repeatedly extracted with dilute HCl, followed by water. The letters refer to the appearance of the supernatant liquid; C=clear, T=turbid, D=dense.

alkaline earths. For this same reason, the action of soda upon the H-gel is similar to its action upon the gels originally present. In other words, extraction of this particular clay with hydrochloric acid is without apparent effect upon its subsequent behavior in presence of solutions of sodium hydroxide. The behavior of this clay is more plainly shown in Fig. 1.

D. EXAMINATION OF A SOLUBLE CLAY

A similar investigation was made of the No. 1 light sagger clay of James P. Prall, Woodbridge, N. J. This clay closely resembles J. R. Cutter's No. 1 sagger clay and P. L. Ryan's No. 1 sagger clay, and behaves in many respects like Geo. Knowles & Sons' No. 12 English ball clay.

11. NATURE OF THE SOLUBLE SALTS

In this case the soluble salts were removed from the clay by a dialysis lasting two months, in which the water was changed 33 times, a total volume of about 16 liters being used. To prevent contamination with glass, the dialyzer was coated with paraffin and the extract was concentrated in a block tin pan. (In the following analysis tin and lead were determined and deducted.) The parchment paper used was treated for several days in the dialyzer to remove soluble sulphates before introducing the clay. The extract was analyzed by Mr. A. J. Phillips, analytical chemist in the Structural Materials Laboratory, with the following results, expressed as percentages of the weight of clay taken (50 g).

Analysis of the Dialyzed Extract of Jas. P. Prall, No. 1 Sagger Clay

	Per cent
Silica [110] (SiO_2)	0.091
Alumina (Al_2O_3)	.205
Ferric oxide (Fe_2O_3)	.149
Lime (CaO)	.085
Magnesia (MgO)	.001
Sulphuric anhydride (SO_3)	.174
Sodium oxide (Na_2O)	.033
Potassium oxide (K_2O)	.039
Organic matter	.064
Not determined (includes water, chlorine, etc.)	1.033
Total, dried at 110°	1.876

Qualitative analysis of the hydrochloric acid extract of this clay showed that its composition was similar to that of the water extract above.

[110] The occurrence of silica in the dialyzed extract is, at first sight, puzzling; but such an occurrence is quite usual, for Dr. Oswald Schreiner, of the Bureau of Soils, has assured the writer that in his dialyses a portion of the silica is invariably present in the extract. Indeed, this is to be expected.

EFFECT OF ADDITIONS OF SODIUM HYDROXIDE.

The effect of successive additions of NaOH on the behavior of this clay, both in the crude state and after dialysis, was tested in a way precisely similar to that just described for the Georgia sagger clay, except that a column of only 50 cc with 5 g of clay was used. The results are presented in Table III, and in part in Fig. 2, which shows the appearance of the tubes after they had been allowed to settle.

TABLE III

Sagger Clay (James P. Prall, Woodbridge, N. J.). Effect of Addition of NaOH to the Clay (A) in the Crude State; (B) After Removal of the Soluble Salts by Long Dialysis with Water

(A)

Total addition (in cc) 0.1 *N* NaOH	Clear	Turbid	Dense	Sediment
0.1	43.6	.....	.....	6.4
0.4	43.8	.....	.....	6.2
0.7	43.3	.....	.....	6.7
1	42.6	.....	.....	7.4
2	.....	41.5	.....	8.5
3	.....	26.5	20	3.5
5	.....	2	44.8	3.2
6	.....	.....	46.6	3.4
8	.....	.....	47	3
10	.....	.....	47	3
16	.....	2.5	44.1	3.4
24	.....	4.4	44.1	1.5
32	.....	21.5	.....	28.5
50	.....	37.3	.....	12.7

TABLE III—Continued

(B)

Total addition (in cc) 0.1 *N* NaOH	Clear	Nearly clear	Turbid	Dense	Sediment
0	35.5	.....	.....	.....	14.5
0.1	.....	36	.....	.....	14
0.4	.....	.....	35	.....	15
0.7	.....	.....	31	.....	19
1	.....	.....	.....	44.5	5.5
2	.....	.....	.....	45.5	4.5
3	.....	.....	.....	47	3
5	.....	.....	.....	47	3
8	.....	.....	.....	47	3
10	.....	.....	.....	47	3
16	.....	.....	.....	47.5	2.5
20	.....	.....	.....	47.5	2.5
25	.....	.....	.....	47.5	2.5

Total addition (in cc) 2.5 *N* NaOH	Clear	Turbid	Dense	Sediment
1.5	.....	.....	47	3
2	.....	5	43	2
2.5	.....	7	41	2
3	.....	13	36	1
3.5	.....	19	30	1
4	28.5	.....	.....	21.5
8	23	.....	.....	27

The table shows that there is a decided difference in behavior toward NaOH of the crude clay and of the clay from which the soluble salts have been removed.

In presence of the greater concentration of NaOH the liquid seemed to change to a thin jelly, which thickened as the concentration increased; concurrently the bulk of granular sediment seemed to shrink and finally almost to disappear. This is attributed to the fact that the thickening gel is able to hold in suspension progressively coarser grains, until finally gel and grains become intimately and uniformly mixed. On the diagram (Fig. 3) the total volume occupied by this mixture of gel and sediment is given by the line marked "recoagulated."

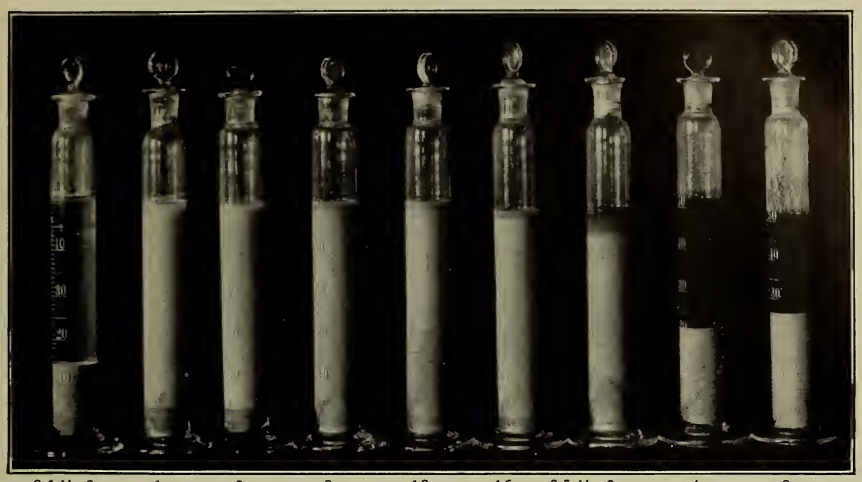


Fig. 2.—*Effect of additions of NaOH to a dialyzed sagger clay (No. 1, Jas. P. Prall, Woodbridge, N. J.)*

Cf. Table III and Fig. 3. In each tube 5 grams clay; amount of NaOH as given above. Photograph taken after the tubes had been allowed to settle

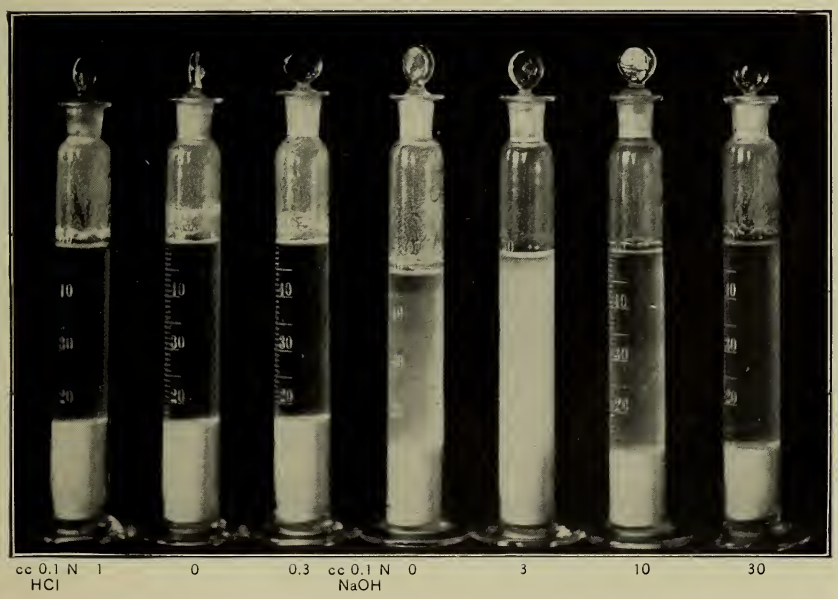


Fig. 5.—*Effect of additions of HCl and of NaOH to an English china clay (Hammill and Gillespie's A 1)*

Five grams clay in each tube; amount of reagent as stated above

13. SOLVENT ACTION OF SUCCESSIVE PORTIONS OF WATER

Unlike the Hall kaolin, the Prall sagger clay can not be freed of soluble salts by repeatedly shaking with water, settling, and decanting; for, after a few portions of water are removed, a portion of the clay goes into very permanent suspension.

An attempt was made to determine how much of this clay is removable by extraction with water. A 5-gram portion made up to 100 cc with water was shaken for an hour; after standing overnight, about 90 cc of the liquid was siphoned off and replaced by

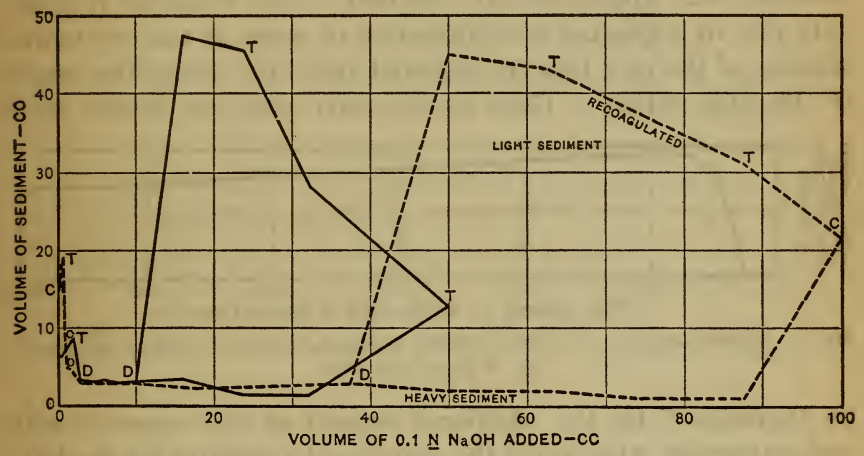


Fig. 3.—*Effect of additions of NaOH to a sagger clay* (*No. 1, Jas. P. Prall, Woodbridge, N. J.*)

Cf. Table III and Fig. 2. —— Untreated; - - - - Dialyzed. The letters refer to the appearance of the supernatant liquid; C=clear, T=turbid, D=dense.

fresh water. This process was repeated 62 times without any indication of approaching a clear extract.

The relative turbidity of each of these extractions was determined by pouring the liquid into a graduated Nessler tube provided with a stopcock near the bottom, shaking up the contents [111] to insure that the turbidity would be uniform from top to bottom, drawing off the liquid until the print of a newspaper placed beneath the tube could be read through the remaining liquid, and

[111] The necessity of shaking was established by a special experiment, which showed that the turbidity of a liquid which has remained undisturbed for some time may be three or four times as great at the bottom as at the top. Cf. Bodländer (Investigation of Suspensions I., Neues Jahrb. Min. 1893, II., p. 150), who writes: "For making comparable tests with suspensions which have stood quietly for a long time under definite conditions it is necessary that the test portions should always be taken from equal depths, because on long standing the amount of kaolin increases with the depth."

reading the depth of liquid at this point. The results are presented graphically in Fig. 4.

When the clay was shaken with the water for more than one hour a higher turbidity was recorded; when it was allowed to stand for a longer period than overnight (as when a Sunday intervened) a lower result was obtained. When the test was stopped, 3.5 grams clay still remained in the tube.

Fig. 4 shows that the highest turbidities were obtained in the earlier extractions, and that after a number of extractions the turbidity was approximately constant. This behavior is probably due to a gradual transformation of some of the crystalline silicates of the clay into the colloidal state, this being the source of the daily supply. These results agree with the figures given

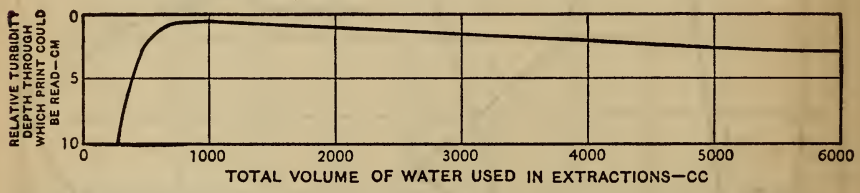


Fig. 4.—*Relative turbidity of the extracts obtained by repeated extraction of sagger clay (No. 1, Jas. P. Prall) with water*

by Parmelee [112] for the additional amount of clay removed with each extraction when using the centrifugal apparatus for mechanical analysis.

The action of varying amounts of water upon two clays was also investigated. One-gram portions of clay were mixed with portions of distilled water; after occasional shakings and settling for several weeks, measurements were obtained as recorded in Tables IV and V.

TABLE IV

Effect of Varying Amounts of Water on Crude Sagger Clay (Prall)

Volume of water and clay (cc)	50	300	400	1,000
Clear	47	.....	.....	.....
Turbid	.....	294	280	300
Deeply turbid	.....	.....	116	698
Sediment	3	6	4	2

[112] Trans. Am. Ceramic Soc., 11, pp. 479–480; 1909.

TABLE V

Effect of Varying Amounts of Water on a Surface Clay From Groveport, Ohio

Volume of water and clay	12.5	25	50	100	200	1,000
Clear	4.5	.....	.....	.....	.....	.....
Nearly clear	.....	17	.....	.....	.....	.....
Turbid	.....	.....	42.5	.....	194	994
Dense	.....	.....	.....	94	.....	.....
Sediment	8	8	7.5	6	6	6

The relative turbidity of the 1000 cc liquid (Table V) was the same as that of the 50 cc liquid, indicating that in the former case there was about 20 times as much matter in suspension as in the latter. These results all show the increased formation of colloidal material attending the use of a greater bulk of water.

The idea that the suspensions produced by the action of water on clay are due not to the fineness of the original material directly but to the fine state of division of the matter produced by reactions between the water and clay, is in harmony with a number of observations. For instance, Hall and Monson [113] found that pure silica would remain turbid but a short time in water; on the other hand, we found that impure silica (ground sandrock) gave a fairly permanent suspension in water, attributable to the alterations, produced by the water, of the alkaline and other impurities of the sandrock.[114] These impurities would with comparative readiness be acted upon and transformed into the colloidal state; whereas the silica itself is very inert, and in contact with water under ordinary conditions is transformed only to an inappreciable extent. Moreover, Atterberg,[115] from experiments on the influence of various substances (saturated $Ca(OH)_2$ soln., 5 per cent solns. of HCl and NaCl) on the rate of sedimentation of sand grains of various sizes, concluded:

> A distinctly visible formation of floccules, as with the coagulation of clay water, is not shown, even with the finest sand grains (0.002–0.001 mm) isolated by me. Flocculation visible to the eye appears to occur only with still finer particles of matter, with the colloids.

[113] J. Agr. Sci., 2, p. 246; 1907. [114] See Fig. 24. [115] Landw. Vers. Sta., 69, p. 134; 1908.

This is confirmed by Schloesing,[116] who found that addition of an alkaline-earth salt or of an acid produced no effect on the sedimentation in distilled water of suspensions of fine sands free from colloid matter.

All of these observations indicate that the coagulation or sedimentation is not a mechanical effect, but is due to the occurrence of a reaction the product of which settles out.

EFFECT OF VARYING THE TEMPERATURE OF THE WATER

On the basis of the views advanced in this paper we should expect that rise of temperature would cause differences of behavior. For instance, the action of water should be more pronounced at higher temperatures. This effect is illustrated by the following experiments:

(*a*) A 50-gram portion of X Wad Clay (Johnson-Porter Clay Co., Tennessee) was deflocculated with 70 cc 0.1 *N* NaOH and elutriated in the Schulze apparatus with water at various (constant) temperatures. The percentage residue on the 120-mesh sieve in each case and in the overflow is given below.

(*b*) A similar elutriation was made with feldspar (Maine Feldspar Co.) without previous treatment with alkali.

TABLE VI

Influence of Varying the Temperature of the Water in Elutriations with the Schulze Apparatus

(*a*) DEFLOCCULATED X WAD CLAY

Temperature of water	On 120-mesh sieve	Can 1	Can 2	Can 3	Overflow
Degrees					
10	3.06	21.14	21.78	7.46	46.11
15	2.32	21.84	21.18	5.18	49.03
25	2.26	24.44	14.98	3.74	54.13
35	2.08	29.96	6.16	3.60	60.75
40	2.24	26.86	1.68	5.44	63.33

(*b*) FELDSPAR

Degrees					
17	.....	13.14	29.04	7.98	49.24
40	.....	18.22	4.06	3.62	74.10

[116] Chimie Agricole, in Frémy's Encyclopédie Chimique, p. 68; 1888.

Now we should expect that at higher temperatures the carrying capacity of the water would be smaller if anything, on account of the diminution of density and of viscosity; yet we find a decreased aggregate residue in cans 2 and 3 and a great increase in the amount carried off by the overflow. This shows that the average size of the particles was smaller the higher the temperature, which indicates an increase in the action of water with the temperature; presumably, therefore, an increased rate of solution and a greater amount dissolved.

F. GENERAL BEHAVIOR OF CLAYS TOWARD REAGENTS

The standpoint adopted in the present paper is that the behavior of a clay toward a reagent is determined by the possibility of a more or less complete metathetical reaction between them; the actual result in each case depending on the form or state in which the product (or products) of a particular reaction appears. In other words, the behavior toward reagents is determined by the solubility relations of the possible solid phases; the clay "solution" is then the suspension of the products of reaction, not of the unaltered clay.

Before proceeding to a detailed account of the action of various substances we shall present additional evidence in favor of the above point of view and of its superiority to some of the other hypotheses which have been put forward to correlate some of the effects observed.

This point of view was advocated by Hall and Monson,[117] who state that "soluble salts such as cause flocculation merely interchange bases with the complex hydrated double silicates which make up kaolin."

They give the following table showing the comparative power of flocculating kaolin suspensions possessed by equivalent (about 0.001 *N*) solutions of salts, acids, and bases (the alkalies and most alkaline substances act as deflocculants).

[117] J. Agr. Sci., 2, pp. 244–256; 1907.

SALTS		ACIDS		BASES	
$Al_2(SO_4)_3$	20	HCl	20	$CaH_2(CO_3)_2$	10
$CaCl_2$	>10	HNO_3	19	$Ca(OH)_2$	3
$Ca(NO_3)_2$	10	H_2SO_4	13	$Ba(OH)_2$	3
$Ba(NO_3)_2$	10	Acetic acid	9		
$CaSO_4$	> 5	Oxalic acid	2.5		
$MgSO_4$	< 5	Tartaric acid	2.5		
KCl	> 2	Carbonic acid	0.5		
KNO_3	> 2	Citric acid	0		
NaCl	> 1	Phenol	0		
K_2SO_4	< 1				
$NaNO_3$	< 1				
Na_2SO_4	0.5				

The general character of these results is such as we might anticipate if coagulation were the sequel of a chemical reaction; on any other theory it would be hard to account for the similarity of effect shown by substances which would be expected to show similar chemical reactions with the constituents of clays. Considerable evidence in favor of these views has already been presented (p. 22 et seq.); the following may also be given. Gorgeu [118] found that kaolin would displace (though not, of course, completely) carbonic acid and chlorine from alkali carbonates and chlorides, respectively. J. Dumont [119] measured the amount of carbon dioxide gas set free when 1 cc N K_2CO_3 solution remained in contact with several colloids for periods varying from 2 to 66 hours. His results, expressed in mg CO_2 set free by the colloid, follow.

Hours	Noncolloidal fine sand 20 g	Plastic clay 4 g		Kaolin 4 g		Gelatinous silica 4 g	Ferric hydroxide 4 g	Aluminum hydroxide 4 g
		Normal	Calcined	Normal	Washed			
2	0.00	4.75	8.41	0.00	0.18	1.08	0.91	2.18
16	0.00	3.61	6.54	0.36	0.00	0.74	1.68	4.07
24	0.00	3.30	1.69	0.00	0.18	0.55	1.84	5.90
40	0.00	1.70	3.02	0.18	0.00	0.54	2.60	4.02
66	0.00	2.62	1.32	0.00	0.00	0.36	2.77	3.64
Total	0.00	15.98	20.98	0.54	0.36	3.27	9.80	19.81

[118] Ann. chim. phys. [6], **10**, p. 145; 1887.

[119] Compt. rend., **142**, p. 345; 1906.

According to the views here advocated, any reaction which is accompanied by a net decrease in solubility of the various components produces an increase in the degree of flocculation; conversely, any reaction which results in products somewhat more soluble than the original constituents produces more or less deflocculation.

Now, it has been asserted by Foerster [120] and by Rohland [121], apparently independently, that the concentration of hydroxyl ion is the essential factor in effecting the deflocculation of clays. It is without doubt one of the factors, in the same way that every condition affects the degree of flocculation to some extent; but the following evidence, we believe, demonstrates that the concentration of hydroxyl ion is relatively a very unimportant factor in promoting this deflocculation.

14. CONCENTRATION OF HYDROXYL ION A MINOR FACTOR IN PROMOTING THE DEFLOCCULATION OF CLAYS

The following tests were made on 5-gram portions of No. 2 fire clay (W. H. Wynn & Co., West Decatur, Pa.) in the way described previously (p. 48); varying amounts of (*a*) oxalic acid, (*b*) potassium oxalate, (*c*) ammonium oxalate, were added, and determinations were made of the amount of clay in suspension and of the concentration of hydroxyl ion.

---

[120] Die chemische Industrie, 28, [24], pp. 733–740; Dec. 15, 1905. [121] Z. anorg. Chem., 41, p. 325; 1904.

TABLE VII

Deflocculation of a No. 2 fireclay

(*a*) ADDITION OF 0.1 MOLAR OXALIC ACID

cc added	0	0.05	0.1	0.2	0.3	0.5	1	1.5	2	3
Turbid	42	7	5	4	3	6	15	43	42.5	42.5
Deeply turbid							28			
Dense		36	40	40	41	37				
Sediment	8	7	5	6	6	7	7	7	7.5	7.5
−log OH′ [122]	9	9	10	10	10	10	10.5	11	11	11

(*b*) ADDITION OF 0.1 MOLAR POTASSIUM OXALATE

cc added	0	0.5	1	3	7	10	15	20	30	48
Clear								42.5	42.5	42.5
Nearly clear	42.7						43			
Turbid		3	3	4	43.5	43				
Dense		41.5	42	40						
Sediment	7.3	5.5	5	6	6.5	7	7	7.5	7.5	7.5
−log OH′	9	9	9	7	7	6.5	6.5	6.5	6.5	6.5

(*c*) ADDITION OF 0.1 MOLAR AMMONIUM OXALATE

cc added	0	0.5	1	3	6 5	10	20	30	98	
Clear									93.7	
Nearly clear								93.3		
Turbid	93	7	6	6	94	93.5	93·5			
Dense	7	88.8	89.5	89.5						
Sediment	7	4.2	4.5	4.5	6	6.5	6.5	6.7	6.3	
−log OH′	9	9	8	7	7	6	6	6	6	

[122] The hydroxyl ion concentrations are given in this way for the sake of clearness. This is, of course, merely another way of stating that the concentration of OH′ is 10^{-9}, etc. The values given may be considered as logarithms of the *dilution* of OH′.

From the above table it is evident that the maximum of suspension occurs at different concentrations of hydroxyl ion; In (*a*) at 10^{-10}, in (*b*) at 10^{-9}; and in (*c*) about 10^{-8}.

Analogous results were obtained on treating kaolin with various reagents. The following table, which gives the maximum of suspension with 5-gram portions of Harris Clay Co., Penland Kaolin (North Carolina), renders it evident that the concentration of OH′ is certainly not the essential factor.

TABLE VIII

The Hydroxyl Ion Concentration and the Maximum Deflocculation of Kaolin

Volume of reagent giving maximum cc	Reagents (each 0.1 molar)	−log OH′	Volume of sediment cc
48 or 98	Pure water	9	12
0.2	Oxalic acid	9	11
0.4	Sodium-dihydrogen phosphate, NaH_2PO_4	9	8.5
0.5 to 20	Sodium silicate	3–9	6
0.4 to 2	di-sodium-hydrogen phosphate, Na_2HPO_4	6–8	7.5
3	Sodium oxalate, $Na_2C_2O_4$	7	5
3	Potassium oxalate, $K_2C_2O_4$	7	6
3	Ammonium oxalate $(NH_4)_2C_2O_4$	7	6.3
10	Aniline	7	9
0.4 to 10	Tri-sodium phosphate, Na_3PO_4	2–7	7
1	Lime, $Ca(OH)_2$	6	10
1	Barium hydroxide, $Ba(OH)_2$	5–6	7
1	Potassium cyanide, KCN	6	7
3	Sodium sulphide, Na_2S	6	6.5
3 to 30	Sodium carbonate, Na_2CO_3	3–5	6
4	Sodium hydroxide, NaOH	3	5.5
4	Potassium hydroxide, KOH	2–3	7

The foregoing evidence is, we believe, conclusive against the idea that the concentration of hydroxl ions is the essential factor in promoting deflocculation; but it in no way conflicts with the idea that the degree of flocculation is conditioned by the relative solubilities of the various possible solid phases, and that the concentration of OH′ is merely one of the minor factors affecting the solubility, and possibly also the degree of dispersion, of the various substances.

We shall now consider in greater detail the behavior of clay toward a number of reagents.

15. DEFLOCCULANTS

The principal deflocculants are solutions of the alkalies and of salts which by hydrolysis are alkaline; but, as we shall see, other substances may also exert a deflocculating effect. The behavior of clay in contact with sodium hydroxide (Fig. 5, plate facing p. 54) is similar to that observed with the other alkalies, but the effect

of potassium hydroxide and ammonium hydroxide are progressively weaker (Figs. 6, 7, 8, 9). The latter can exert a coagulating effect only at the highest concentrations.

The mechanism of the action of alkalies upon clay we conceive to be somewhat as follows: The alkali reacts with the constituents of the clay and forms an alkali silicate or aluminosilicate, which in solution is hydrolyzed to some extent, so that part of it is present as a sol. Further addition of alkali increases the amount of sodium

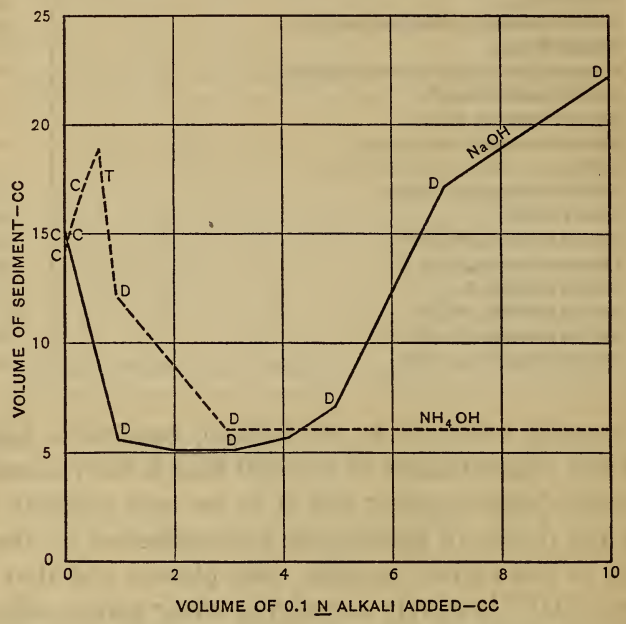


Fig. 8.—*Comparison of the effects of additions of NaOH and of NH_4OH to Georgia kaolin (Hall Clay Co.)*

Five grams clay; total volume 100 cc. Letters refer to the appearance of the supernatant liquid; C=clear, T=turbid, D=dense.

salt in solution and in the sol state up to a certain point at which an increase of the alkali concentration begins to set back the hydrolysis and to cause a diminution in the amount of sol. This process goes on progressively until at a certain concentration most of the clay is again coagulated. On this view we should expect the effect of potassium compounds to be less than that of the corresponding compounds of sodium, for the salts of the former are usually the more soluble, while the still weaker effect of

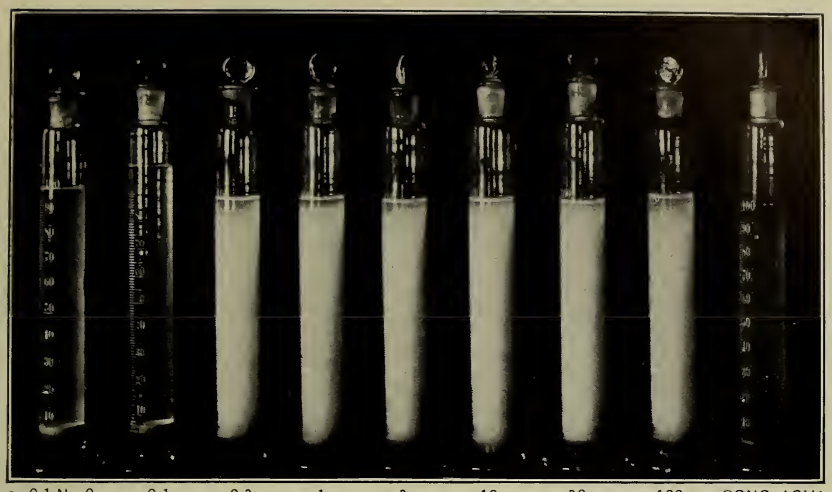


Fig. 6.—*Effect of additions of NH_4OH to a fire clay (No. 2 Diamond Clay Co., Nelsonville, Ohio)*

In each tube 5 grams clay; amount of NH_4OH as given above

Fig. 7.—*Effect of additions of NH_4OH to a Tennessee ball clay (No. 9, Johnson-Porter Clay Co.)*

In each tube 5 grams clay; amount of NH_4OH as given above

ammonia is due to its weakness as a base, wherefore it can not set back the hydrolysis and so cause recoagulation except at the greatest concentrations.

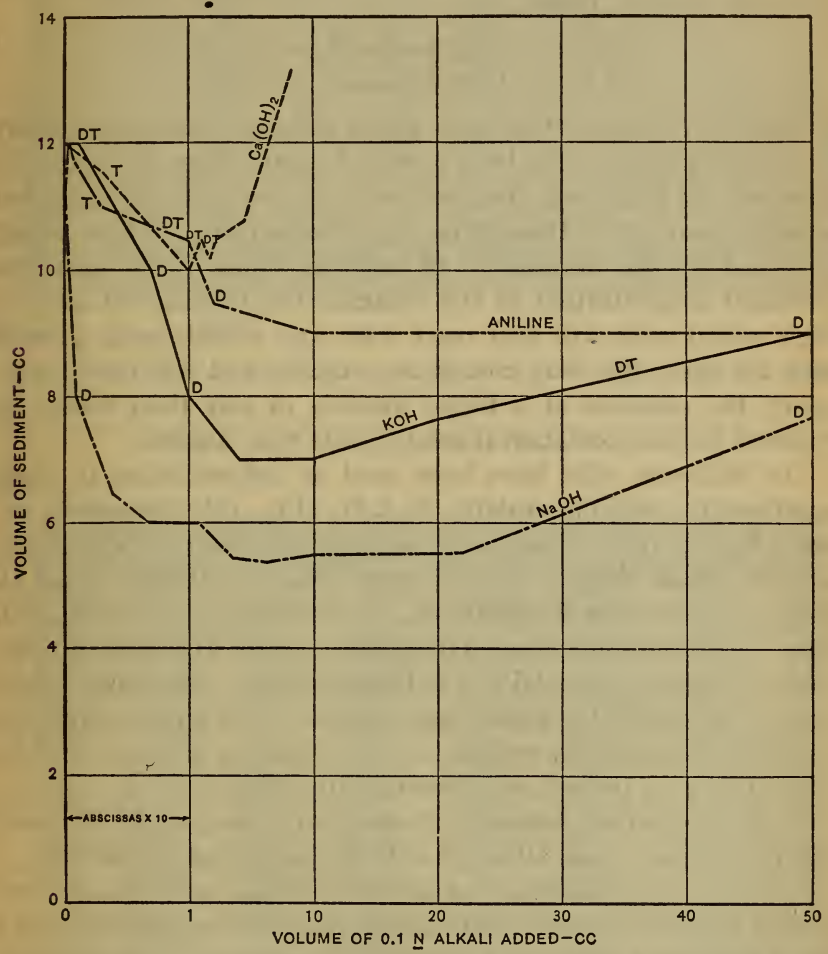


Fig. 9.—*Comparison of the effects of additions of various alkalies (NaOH, KOH, aniline, $Ca(OH)_2$) to kaolin (Harris Clay Co., Penland, N. C.)*

Five grams clay; total volume 50 cc. Letters refer to the appearance of the supernatant liquid; T=turbid, DT=Deeply turbid, D=dense.

The mode of action of hydrolyzable salts is in part the same as that of the caustic alkalies; but another mode of action comes into play here, which occurs with all soluble salts, which (1) do not

give an acid reaction in aqueous solution, (2) contain an acid ion which gives an insoluble compound with bivalent and trivalent bases. This mode of action may be exemplified by sodium carbonate or oxalate, thus:

$$Na_2CO_3 + Ca\ gel \rightarrow CaCO_3 + Na\ sol$$
$$Na_2C_2O_4 + Ca\ gel \rightarrow CaC_2O_4 + Na\ sol$$

That is, we remove the bases which conserve coagulation (that is, form less soluble gels) by a double decomposition and form the more soluble alkali salt, thus promoting deflocculation. Addition of larger amounts of the salt may produce a recoagulation, which is caused by the diminution of solubility consequent upon the increased concentration of the common ion (salting-out action). Such added salts will also react with any soluble salts present with the clay; this may complicate matters and will render necessary the addition of a larger amount of salt than would be required for deflocculation if soluble salts were absent.

The following salts have been used as deflocculators in these experiments: Sodium oxalate, $Na_2C_2O_4$ (Fig. 10); potassium oxalate, $K_2C_2O_4$ (Figs. 11 and 13); ammonium oxalate $(NH_4)_2C_2O_4$; sodium silicate (Fig. 22); soft soap (Fig. 21); borax, $Na_2B_4O_7$ (Fig. 12); potassium phosphate, K_3PO_4; sodium phosphate, Na_3PO_4 (Fig. 13); disodium hydrogen phosphate, Na_2HPO_4; sodium dihydrogen phosphate, NaH_2PO_4; sodium-hydrogen-ammonium phosphate $NaHNH_4PO_4$; potassium cyanide, KCN; potassium ferrocyanide, $K_4Fe(CN)_6$; sodium arsenite, $NaAsO_2$; sodium sulphide, Na_2S (Fig. 13); potassium permanganate, $KMnO_4$.

With a given clay sodium carbonate is not necessarily the most effective of the group, although it is the most used industrially.

Fig. 13 shows the effect of several alkaline precipitants—trisodium phosphate, potassium oxalate, and sodium sulphide—on a No. 2 fire clay containing a considerable amount of soluble salts. It shows that the range within which complete deflocculation takes place is very narrow and that the salting-out action commences at once with further additions of reagent.

The manner in which calcium sulphate suppresses the deflocculating effect of an alkali is shown in Fig. 14. The clay used was a 5-gram portion of the Tennessee ball clay No. 3 of the Mandle-Sant

Fig. 10.—*Effect of additions of HCl and of sodium oxalate to flint fire clay* (*W. H. Wynn & Co., West Decatur, Pa.*)

In each tube 5 grams clay; amount of reagent as given above. Maximum deflocculation occurred with 7 cc 0.1 molar $Na_2C_2O_4$ solution

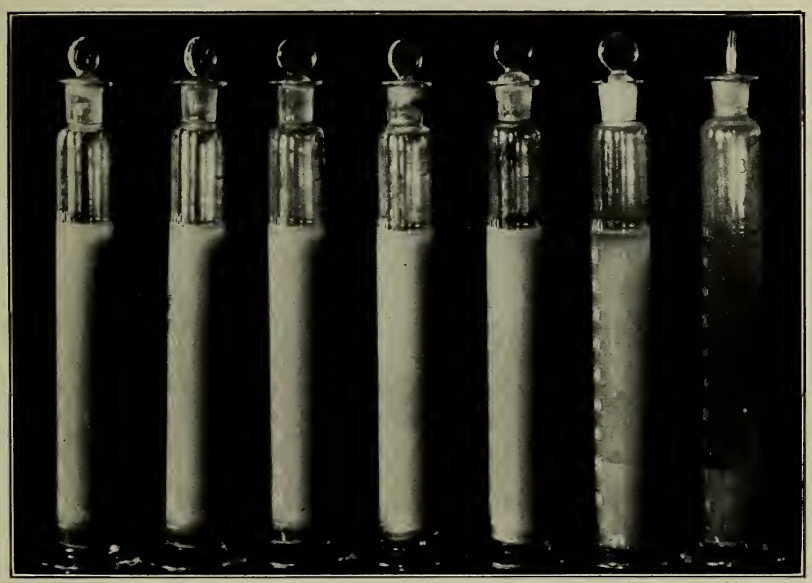


Fig. 11.—*Effect of additions of potassium oxalate to Tennessee ball clay* (*No. 3, Potters' Supply Co.*)

In each tube 5 grams clay; amount of reagent as given above. Maximum deflocculation occurred with 20 cc 0.1 molar $K_2C_2O_4$ solution

Clay Co.; the abscissas represent the amount of 0.1 *N* NaOH solution added; the ordinates are the additions of 0.1 molar $CaSO_4$.

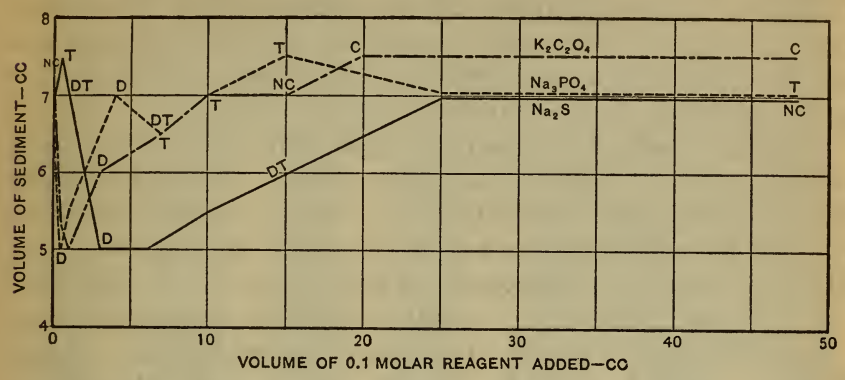


Fig. 13.—*Effect of additions of reagents (potassium oxalate, trisodium phosphate, sodium sulphide) to fire clay (No. 2, W. H. Wynn.)*

Five grams clay; total volume 50 cc. Letters refer to the appearance of the supernatant liquid; C=clear, NC=nearly clear, T=turbid, DT=deeply turbid, D=dense.

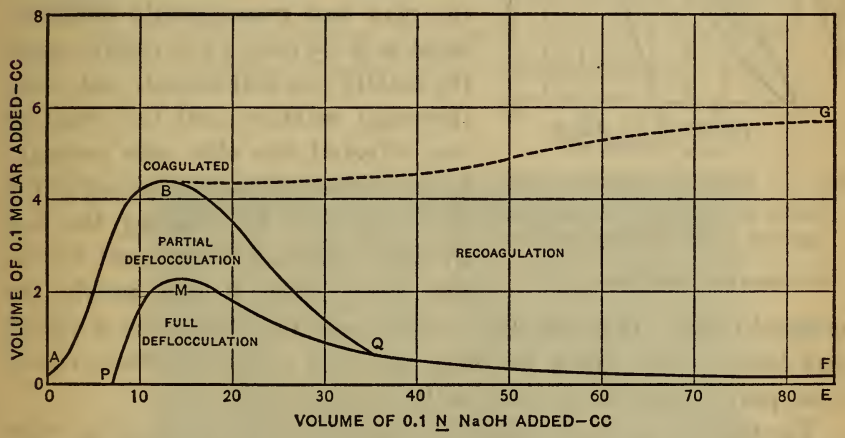


Fig. 14.—*Effect of simultaneous additions of NaOH and $CaSO_4$ to a ball clay (No. 3, Mandle-Sant Clay Co.)*

Five grams clay; total volume 50 cc.

The clay was partially deflocculated in water and was fully deflocculated when 7 cc NaOH had been added (point *P*); and further additions up to a total of 85 cc NaOH (point *E*) continued to keep all the colloid clay in suspension. About 0.2 cc $CaSO_4$ (*A*)

sufficed completely to coagulate the clay, with complete clarification of the liquid; and further additions up to a total of 8 cc $CaSO_4$ continued to keep the clay wholly coagulated. When both $CaSO_4$ and NaOH were added to the clay, the colloid matter was wholly deflocculated only with those quantities represented by points within the area *PMQFEP*.

In other words, with this clay slight additions of $CaSO_4$ very rapidly narrowed the range of concentrations of NaOH effecting deflocculation until 2.3 cc of the $CaSO_4$ solution limited full deflocculation to but one proportion of the NaOH solution, viz, 15 cc at the point M. Concentrations of $CaSO_4$ given by the line *ABG* wholly coagulated the clay and kept it at nearly the original bulk; larger amounts also kept the clay coagulated, but the bulk became gradually larger as the distance above the line *ABG* increased. In the area *QBGF* the clay was momentarily deflocculated as if by only 15 cc NaOH when the NaOH was first added; but when thorough mixture and full reaction was effected the clay was recoagulated. The bulk of the recoagulated clay was very large along the line *QF* and gradually decreased to the line *BG*, where it had nearly the original bulk. The area *ABQMP* represents proportions of $CaSO_4$ and NaOH with which the clay assumed an intermediate condition, partly coagulated and partly deflocculated.

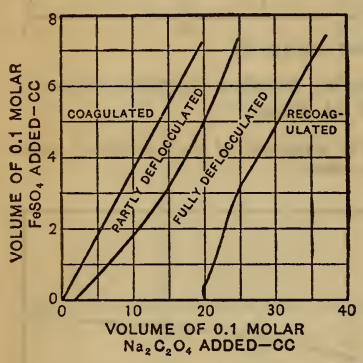
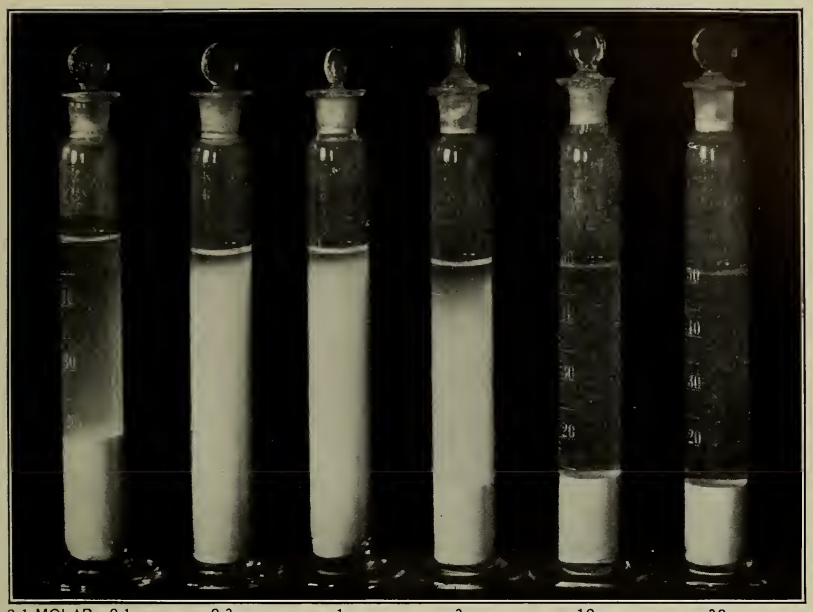


Fig. 15.—*Effect of simultaneous additions of $Na_2C_2O_4$ and $FeSO_4$ to a ball clay (No. 3, Mandle-Sant Clay Co.)*

Five grams clay; total volume 50 cc.

The effect of sodium oxalate in combating the coagulating effect of additions of ferrous sulphate to the same clay is shown in Fig. 15. The amount of sodium oxalate required for deflocculation is evidently almost strictly proportional to the amount of ferrous sulphate added; a certain additional amount, whatever the original concentration, effects recoagulation.

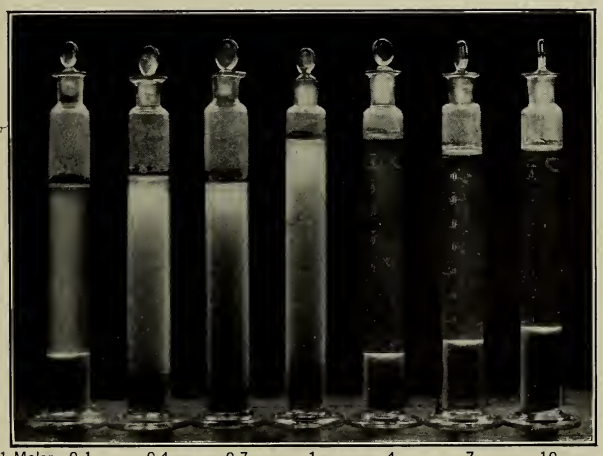
A few experiments were made with organic substances. Aniline acts as a very weak deflocculating agent. (See Fig. 9.) Glycerin appears to be without action on clays.



cc 0.1 MOLAR $Na_2B_4O_7$ 0.1 0.3 1 3 10 30

Fig. 12.—*Effect of additions of borax to English china clay* (*No. 1, J. Poole*)

In each tube 5 grams clay; amount of reagent as given above



cc 0.1 Molar CaO 0.1 0.4 0.7 1 4 7 10

Fig. 16.—*Effect of additions of lime to English china clay* (*No. 1, J. Poole*)

In each tube 5 grams clay; amount of $Ca(OH)_2$ as given above

BIVALENT DEFLOCCULANTS.

Compounds of bivalent elements are in general coagulants; a few exceptions may be noted.

Hydroxides of Calcium and Barium.—The deflocculating action occasionally shown by calcium hydroxide or barium hydroxide (Figs. 16, 17, 18) is believed to be due to an action upon such soluble salts as Na_2SO_4 or $(NH_4)_2SO_4$, resulting in the formation of a deflocculating alkali, or possibly in some cases to an action by which the amount of coagulant with the clay is decreased. In this connection there is opportunity for further research.

In 1907 A. Lottermoser [123] said that barium hydroxide and calcium hydroxide show a decreasing effect (as compared with alka-

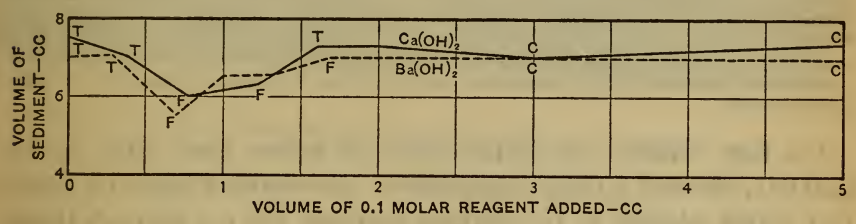


Fig. 18.—*Effect of additions of lime and of baruim hydroxide to a fire clay* (*No. 2, W. H. Wynn.*)

Cf. Table IX; C=clear, T=turbid. F denotes that the clay is deflocculated.

lies?) as hydrosol formers on clay. Notwithstanding this prior publication, in 1909 E. Weber [124] patented the addition to casting slips of calcium oxide (CaO), barium oxide (BaO) or peroxide (BaO_2), "which on contact with water will be converted into hydroxides; or of other compounds of the alkaline earths and lead which give insoluble sulphates and carbonates," in order to remove those compounds that interfere with the use of alkalies in preparing casting slips.

The following tables give the data obtained with barium hydroxide and with calcium hydroxide upon No. 2 fire clay. (See also Fig. 18.)

[123] Z. physik. Chem., 60, p. 456; 1907.

[124] British Patent No. 6560 (Mar. 18, 1909).

TABLE IX

No. 2 Fire Clay from W. H. Wynn, Decatur, Pa. (5 grams)

(*a*) ACTION OF 0.1 MOLAR $Ba(OH)_2$

cc added	0	0.3	0.7	1	1.3	1.7	3	7	15	30
Clear	.....	.....	.....	.....	.....	.....	43	43	43	43
Turbid	43	43	7	7	10	13	.....	.....	.....	.....
Dense	.....	.....	37.5	36.5	33.5	30	.....	.....	.....	.....
Sediment	7	7	5.5	6.5	6.5	7	7	7	7	7

(*b*) ACTION OF 0.1 MOLAR $Ca(OH)_2$[124a]

cc added	0	0.4	0.8	1.2	1.6	2	3	5	8	10
Clear	.....	.....	.....	.....	.....	.....	93	92.6	92.5	92.7
Turbid	92.5	93	14	16	92.7	92.7	.....	.....	.....	.....
Dense	.....	.....	80	77.7	.....	.....	.....	.....	.....	.....
Sediment	7.5	7	6	6.3	7.3	7.3	7	7.4	7.5	7.3

[124a] Owing to the impossibility of preparing 0.1 molar $Ca(OH)_2$, the equivalent amount of 0.02 molar solution was used.

On first mixing the latter series of tubes, that with 0.4 cc $Ca(OH)_2$ showed a dense suspension. On shaking again by hand just before placing in the shaking machine the 0.4 and 0.8 tubes showed dense suspension. After one hour on the machine the dense suspension had shifted to the 0.8 and 1.2 tubes. In other words, only a portion of the clay colloid was acted upon when first mixed, and 0.4 cc $Ca(OH)_2$ was sufficient to put it in suspension. When with further shaking more of the clay colloid was exposed to the action of the lime, a proportionately larger amount of lime was required to effect suspension. This behavior was frequently observed with other reagents and clays.

Barium Carbonate.—Barium carbonate within narrow limits is an energetic deflocculating agent. Its effect is apparently to stop the effect of calcium sulphate by completely precipitating it from solution: $BaCO_3 + CaSO_4 = BaSO_4 + CaCO_3$; or it may react with Na_2CO_3, which then exerts a deflocculating action. Lead acetate might be expected to give a similar reaction, but failed when tried with Prall Sagger clay.

ACIDIC DEFLOCCULANTS

Oxalic Acid.—Even oxalic acid may act as a deflocculant (Fig. 19), probably by reacting with some calcium salt.

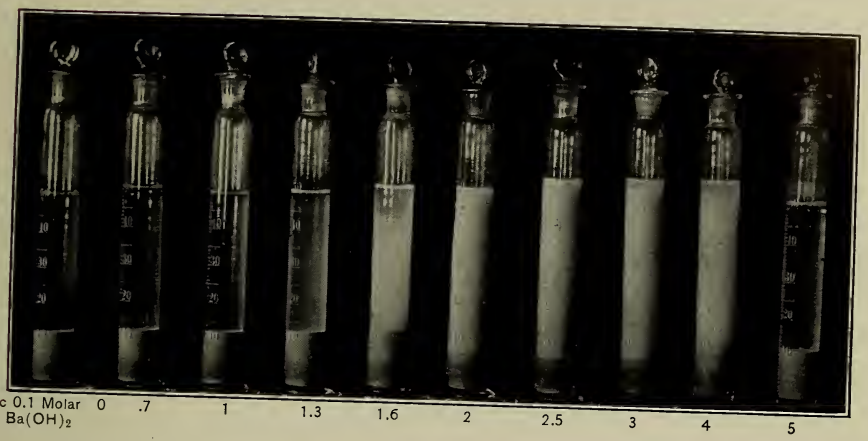


Fig. 17.—*Effect of additions of barium hydroxide to New Jersey sagger clay (No. 1, Jas. P. Prall, Woodbridge, N. J.)*

In each tube 5 grams clay; amount of $Ba(OH)_2$ as given above

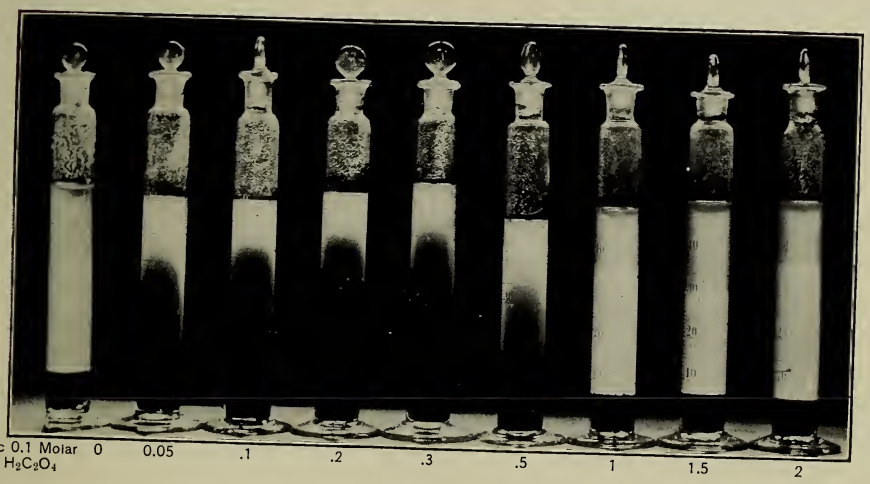


Fig. 19.—*Effect of additions of oxalic acid to a fire clay (No. 2, W. H. Wynn)*

In each tube 5 grams clay; amount of $H_2C_2O_4$ as given above

Tannic Acid.—Tannic acid appears to exert its deflocculant effect by taking into solution iron (or possibly aluminum) from colloid gels. It appears to be without action on clays not containing iron or aluminum, and deflocculates and is strongly colored by clays containing iron (Fig. 20). In the case of W. H. Wynn No. 1 fire clay the iron of the clay was wholly insoluble in water, but soluble in the tannic acid.

While the most probable cause of the deflocculating action of oxalic acid and of tannic acid is the removal of coagulating bases, yet that would leave equivalent amounts of hydrogen with the colloid matter. It seems possible, then, that certain free colloid

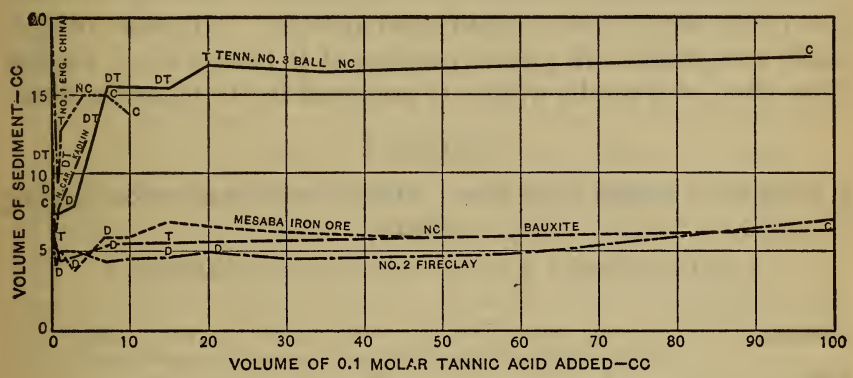


Fig. 20.—*Effect of additions of tannic acid to various clays, etc.*

Five grams substance; total volume 50 cc. Letters refer to the appearance of the supernatant liquid; C=clear, NC=nearly clear, T=turbid, DT=deeply turbid, D=dense.

acids within very narrow ranges are more soluble than the corresponding salts of the bivalent and trivalent metals.

DEFLOCCULATION BY HUMUS AND BY COLLOIDAL SUBSTANCES

Puchner [125] states that humus matter prevents the coagulation and sedimentation of a soil by salts, such as calcium chloride, even when the particles are large enough to be removable by filtration.

On the other hand, Dr. Chase Palmer, of the chemical laboratory of the United States Geological Survey at Washington, has informed the writer that he has found that the dissolution of silica in water in the presence of humus acids is merely accidental;

[125] Landw. Vers. Sta., 70, pp. 249–267; C. A., 3, p. 1566; 1909.

that the dissolution of each is caused by a slight alkalinity of the water. Moreover, he has coagulated silicic acid by organic acids of the same order of strength as the humus acids.

Colloidal substances may also deflocculate clays, the effect being probably similar in character to the effect of one colloid upon another. This question has been studied by Buxton and Rahe,[126] who found that two colloids will mutually dissolve or coagulate in a manner depending upon their specific nature and upon the proportions of each present.

DEFLOCCULATION BY DYESTUFFS

The deflocculation produced by dyestuffs is probably another case of the effect of one colloid upon another. A number of dyestuffs were tried, with 5-gram portions of J. Poole's No. 1 English china clay, with results which are presented in the following table:

TABLE X

J. Poole No. 1 English China Clay. Effect of addition of various coloring matters

(*a*) JANUS GREEN B (II MONAZO COLORING MATTER)[127]

Grams dye	0	0.01	0.02	0.03	0.04	0.14	0.24	0.34
Clear	29	34	34	34	.....	.....	.....	.....
Turbid	.....	.....	.....	.....	35	39	.....	.....
Dense	.....	.....	.....	.....	.....	.....	41	41
Sediment	21	16	16	16	15	11	9	9

(*b*) CONGO-RUBIN (III DISAZO COLORING MATTER).

Grams dye	0	.....	0.01	0.02	0.03	0.08
Clear	29	.....	[127a] 9	.....	.....	.....
Dense	.....	.....	[127b] 34	44	45	43
Sediment	21	.....	[127c] 7	6	5	7

[126] J. Med. Res., 20, pp. 113–136; 1909.
[127] Classification of Schultz and Julius's Organic Coloring Matters, 2d ed.
[127a] Pink.
[127b] Purple.
[127c] Blue.

TABLE X—Continued

(*c*) MALACHITE GREEN OXALATE[128] (X TRIPHENYLMETHANE COLORING MATTER)

Grams dye	0	0.01	0.02	0.04	0.06	0.11	0.16
Clear	29	[128a] 34	[128b] 28	20	21	27	28
Sediment	21	16	22	30	29	23	22

(*d*) METHYL ALKALI BLUE (X TRIPHENYLMETHANE COLORING MATTER)

Grams dye	0	0.01	0.02	0.03	0.04	0.09
Clear	29	.....	.....	.....	10	.....
Turbid	.....	.....	3	.....	.....	.....
Dense	.....	44	42	45	34	44
Sediment	21	6	5	5	6	6

(*e*) FAST ACID VIOLET R (XI XANTHENE COLORING MATTER)

Grams dye	0	0.01	0.02	0.03	0.04	0.05	0.06	0.08	0.13
Clear	29	.....	4	.....	.....	12	3	3	.....
Turbid	.....	40	37	.....	.....	32	.....	.....	.....
Dense	.....	.....	.....	43	44	.....	42	42	45
Sediment	21	10	9	7	6	6	5	5	5

(*f*) ACID ALIZARINE BLACK EXT. (XIII ANTHRACENE COLORING MATTER)

Grams dye	0	0.01	0.02	0.03	0.08	0.13	0.18
Clear	29	18	.....	.....	.....	35?	34?
Turbid	.....	22	([128c])	([128c])	([128c])	([128c])	([128c])
Dense	.....	.....	43	42	39	.....	.....
Sediment	21	10	7	8	11	15	16

[128] Malachite green, although coagulating this and most other clays, deflocculates—e. g., a clay from Fort Pierre, S. Dak.—when the clay is in sufficient excess. A sufficient excess of dye to coagulate the clay is present in the test for estimating colloid content (p. 40). The unsuitability of many dyes for the colloid test is due to their deflocculating clays with the concentrations best suited for color comparisons.

[128a] Colorless.

[128b] Blue.

[128c] Opaque.

TABLE X—Continued

(*g*) METHYLENE BLUE DBB EXTRA CONC. (XVII THIAZINE COLORING MATTER)

Grams dye	0	0.01	0.02	0.045	0.095
Clear	29	[128a] 33	[128a] 32	31	[128b] 37
Sediment	21	17	18	19	13

(*h*) INDIGO CARMINE DRY (XXI INDIGO DERIVATIVE).

Grams dye	0	0.01	0.02	0.045	0.095
Clear	29	[128c] 39	38	[128b] 39	[128b] 39
Sediment	21	11	12	11	11

[128a] Colorless. [128b] Opaque. [128c] Dark blue.

16. COAGULANTS

The following reagents in these experiments acted invariably to coagulate the clays tested: Carbonic acid, H_2CO_3; potassium dichromate, K_2CrO_4; sodium acetate, $NaC_2H_3O_2$; hydrochloric acid, HCl; ammonium chloride, NH_4Cl; sodium chloride, NaCl; zinc chloride, $ZnCl_2$; magnesium chloride, $MgCl_2$; barium chloride, $BaCl_2$; calcium chloride, $CaCl_2$; ammonium nitrate, NH_4NO_3; sodium sulphate, Na_2SO_4; ammonium sulphate, $(NH_4)_2SO_4$; magnesium sulphate, $MgSO_4$; calcium sulphate, $CaSO_4$; ferrous sulphate, $FeSO_4$; ferric sulphate, $Fe_2(SO_4)_3$; lead acetate, $Pb(C_2H_3O_2)_2$.

Effect of Valence.—It is commonly understood that the precipitating power of metallic salts for negative colloids increases greatly in passing from a small valence to a larger,[129] e. g., NaCl to $CaCl_2$ to $AlCl_3$ to $SnCl_4$. However, on trying these four reagents with the sol obtained by water extraction of the Prall sagger clay, only $CaCl_2$ gave prompt precipitation, NaCl followed shortly after, $SnCl_4$ was hydrolyzed on standing over night and carried down the clay sol enmeshed, while $AlCl_3$ had no apparent effect. Here the clarification evidently depended on the specific solubilities of the reaction products of these salts and the clay used.

[129] U. S. Geol. Survey Bull. 388, p. 27; 1909. J. prakt. Chem., 25, pp. 431–452; 1882.

Jordis [130] also came to the conclusion that the precipitating power of valence depends on the insolubility of the products, those with high valence usually being most insoluble.

Coagulation by Freezing.—Coagulation is often brought about by freezing.[131] This is probably a salting out effect, due to concentration of salts in the mother liquor as the ice crystals separate out.

ADDITION OF SOAP TO CLAYS

The effect of soap upon ball and china clays is worthy of examination; the results are presented in Table XI and in part in Fig. 21.

TABLE XI

ADDITIONS OF ENGLISH "CROWN" SOFT SOAP TO 5 GRAMS J. POOLE'S NO. 1 ENGLISH CHINA CLAY

cc 1 per cent soap solution	0.1	0.3	1	3	10	30	98
Clear	81	.....	.....	.....	.....	.....	.....
Turbid	.....	78	81	84	83	2	93
Dense	.....	.....	.....	.....	.....	93	.....
Sediment	19	22	19	16	17	5	7

ADDITIONS OF ENGLISH "CROWN" SOFT SOAP TO 5 GRAMS MANDLESANT CLAY CO. TENNESSEE BALL CLAY NO. 3

cc 1 per cent soap solution	0	0.5	1	3	5	7	10	15	25	48
Turbid	1	1	1	1	1	1	1	1	1	1
Dense	41	41	39	35	35	35	35	35	35	35
Sediment	8	8	10	14	14	14	14	14	14	14

The effects are of the same nature as those already discussed—with the china clays exchange of bases and sol formation; with the ball clay, salting out only. (See p. 111 for applications of this knowledge to cleansing processes.)

[130] Zs. Chem. Ind. Kolloide, **3**, p. 25; 1908.

[131] Zs. Chem. Ind. Kolloide, **3**, pp. 195, 196, 203. Müller: "Studien über die natürlichen Humusformen, p. 187; 1887. Landw. Versuchssta., **33**, p. 1; 1887; **58**, p. 187; 1903. Wohlny: Zersetzung der organischen Stoffe, p. 219; 1897. Landw. Jahrbücher, **12**, p. 222; 1883; **20**, p. 786; 1891; **21**, IV, p. 344; 1898. Mitt. der Landw. Inst. Univ. Breslau, **4**, p. 113; 1908. Forschungen a. d. Gebiet d. Agrikulturphysik **2**, p. 450; 1879.

18. EFFECT OF ADDITIONS OF SODIUM CARBONATE AND SODIUM SILICATE TO CLAYS

A few experiments on the effect of additions of sodium carbonate together with sodium silicate on the behavior of clays and clay mixtures were performed. The results are presented in the diagrams of Fig. 22, in which the contour lines show the volume of the sediment for additions up to 5 cc of 0.1 molar solutions of each of these reagents (cf. pp. 100-101).

As regards the behavior of clay in media other than water, very little work has been done, and little is known about it. Kerosene is commonly used in the Seger volumenometer by reason of its accepted freedom from action on the clay. It is stated by Hilgard [132] that the presence of alcohol or ether materially reduces the tendency to flocculation.

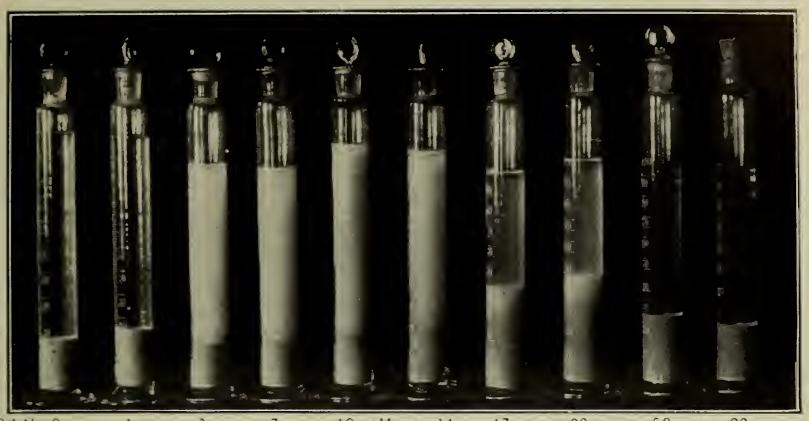
For purpose of comparison, the effect of additions of caustic soda and, in some cases, of hydrochloric acid to some other mineral substances was investigated, namely, to fuller's earth (Fig. 23); potter's "flint" (ground sand rock) (Fig. 24); feldspar (Fig. 25); mica (Fig. 26); iron ore (Fig. 27). The results obtained are apparent from the photographs reproduced in Figs. 23–27. Pure water seems to give the maximum effect with the ground sand rock and with the feldspar; this is doubtless due to their natural alkali content, which on addition of water forms an alkaline solution sufficiently concentrated to effect deflocculation.

Additions of sodium hydroxide were also made to bauxite and to air-dried peat, but produced only incomplete deflocculation.

III. APPLICATIONS

In the foregoing pages we have endeavored to show that the general behavior of clays is conditioned very largely by the possibility of a metathetical reaction between clay and reagent. The possibility of reaction is determined by the solubility relations of the possible solid phases (original substances and possible products) in the particular media. These relations are not known to us quantitatively, but we may, by reasoning from analogy and by inference from the phenomena observed, obtain some qualitative

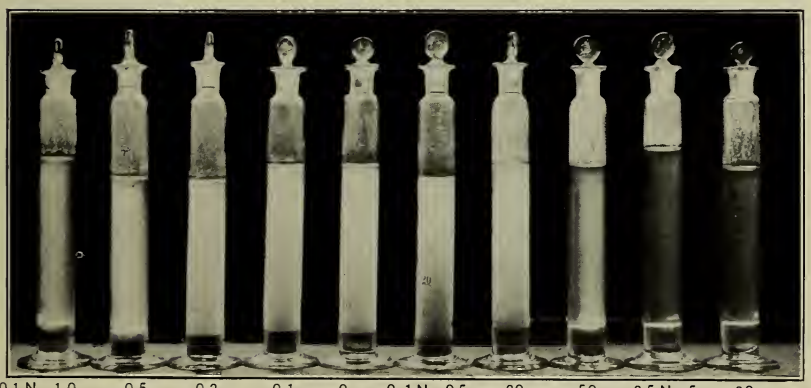
[132] Am. J. Sci., 3, 17, p. 207; 1879.



cc 0.1 N NaOH 0 1 3 7 10 (Max) 14 17 20 50 98

Fig. 23.—*Effect of additions of NaOH to Fuller's earth (Owl Commercial Co., Quincy, Fla.)*

In each tube 5 grams; amount of NaOH as given above. Maximum effect was observed with 10 cc 0.1 N MaOH



cc 0.1 N HCl 1.0 0.5 0.2 0.1 0 cc 0.1 N NaOH 0.5 20 50 cc 2.5 N NaOH 5 20

Fig. 24.—*Effect of additions of HCl and NaOH to quartz (dry-ground Pennsylvania "Sand Rock," Potter's Mining and Milling Co.)*

In each tube 5 grams; amount of reagent as given above

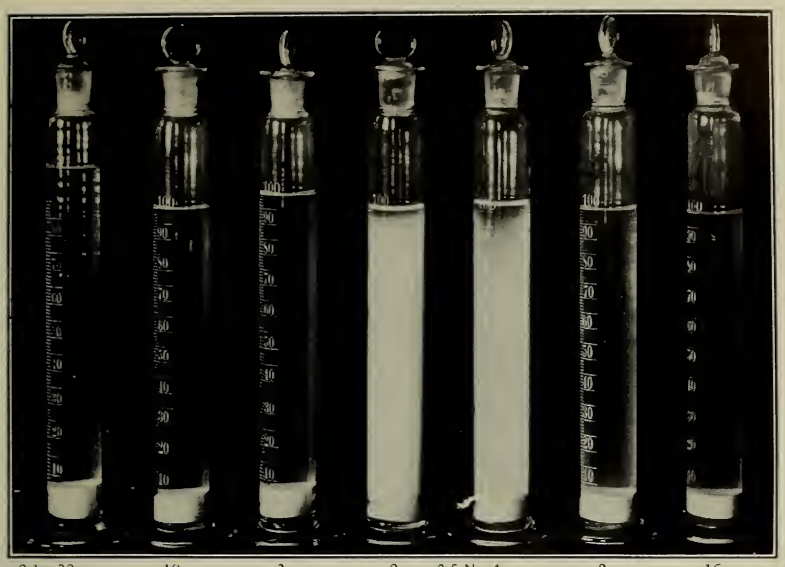


Fig. 25.—*Effect of additions of HCl and of NaOH to dry-ground orthoclase (Maine Feldspar Co., Auburn, Me.)*

In each tube 5 grams; amount of reagent as given above

Fig. 26.—*Effect of additions of HCl and of NaOH to flake mica*

In each tube 5 grams; amount of reagent as given above

cc 1 per cent Soap solution 0.1 0.3 1 3 10 30 98

Fig. 21.—*Effect of additions of soft soap to an English china clay (No. 1, J. Poole)*

Cf. Table XI. In each tube 5 grams clay; amount of reagent as given above

cc 0.1 N NaOH 50 30 20 15 10 7 4 Max. (betw. 4 and 1) 1 0.7 0.4 0.1 0 cc 0.1 N HCl 0.1 0.4 10

Fig. 27.—*Effect of additions of HCl and of NaOH to Mesaba iron ore*

In each tube 5 grams; amount of reagent as given above. Maximum effect occurred with ¼ cc 0.1 N NaOH

information with regard to these relative solubilities. This information can then be applied to the discussion and elucidation of

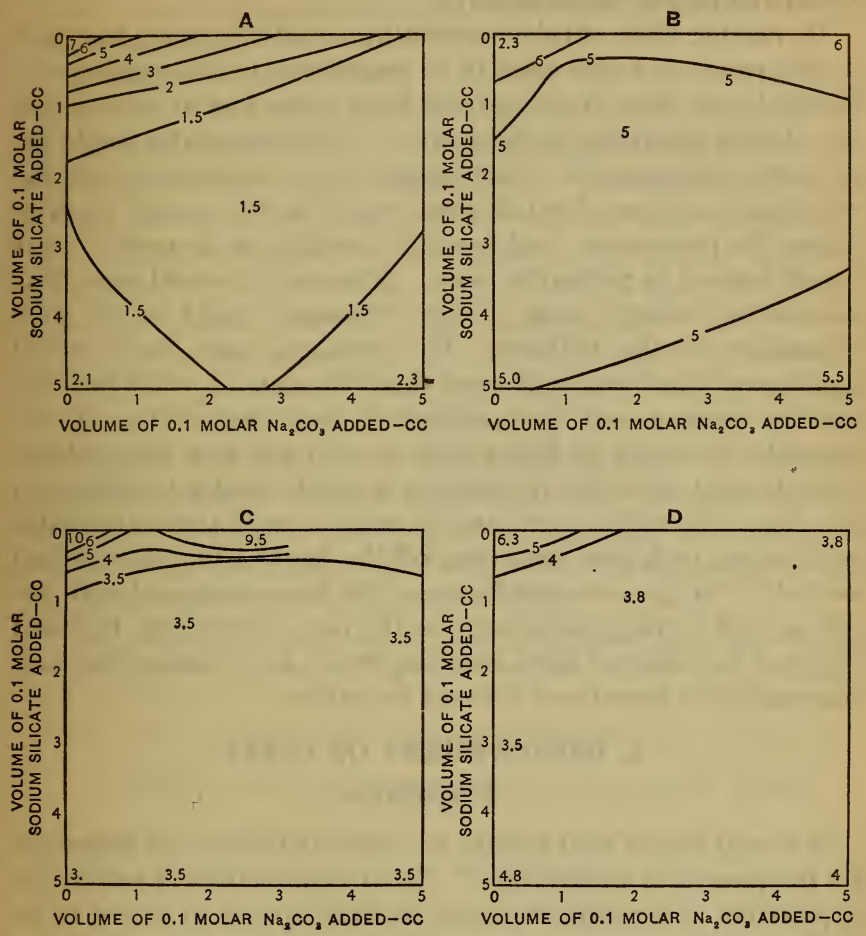


Fig. 22.—*Effect of simultaneous additions of sodium carbonate and sodium silicate to clays and to a body mix*

Amount of reagents as given above; total volume 100 cc. A, 5 grams Tennessee ball clay No. 3; B, 5 grams English china clay (No. 1 J. Poole); C, 2.5 grams Tennessee ball clay No. 3, 2.5 grams English china clay No. 1; D, 1.25 grams Tennessee ball clay No. 3, 1.25 grams English china clay No. 1, 0.5 grams potash felspar, 2.0 grams quartz. The numbers inside the diagrams represent the volume (in cc) of the sediment; the "contour" lines are drawn through the points at which equal volumes of sediment were observed.

specific problems. The purpose of this section is to make a few such applications.

Before proceeding to the specific applications we desire to mention a few points with regard to the general question of the regulation and improvement of clays.

By making series of tube experiments, similar to those described in this paper, it would seem to be practicable to determine quantitatively the effect of any reagent upon a clay and to make direct use of such knowledge in the pottery. Such knowledge would be, of course, independent of any theory; but, we believe, that the principles made use of in this paper would be of great aid in correlating the phenomena, and hence in enabling us to predict what would happen in particular cases. Moreover, it would seem that systematic research work of this character would be of great advantage to the industry. For instance, such work should enable one to ascertain the most desirable state of a clay for each specific purpose and to transform it into that state. If, for example, it should be found that an acid gel, free from soluble salts, is most desirable, it would be a simple matter to blunge up the clay with a little acid and to wash several times thereafter with water, each time decanting off the liquid after the clay had settled. This process would remove the bases combined with the gel, as well as the soluble salts in the clay. Moreover, it would improve the color of clays carrying iron. In a similar way any base might be introduced if found desirable.

A. IMPROVEMENT OF CLAYS

1. WEATHERING

It is well known that certain fire clays and shales are improved by the process of weathering.[133] The colloid matter of such clays is probably in a condition similar to a dry sponge in regard to its ability to take up water; so that the weathering increases plasticity by promoting a thorough penetration of water. The process is promoted by drying out in summer, which, by coagulating any sol and by partially setting some of the gels, increases the porosity of the mass and the ease of penetration for subsequent additions of water. Weathering is also promoted by freezing in winter. First, by heaving the grains farther apart and, second, by con-

[133] U. S. Geol. Survey Bull., 388, p. 13, 14; 1909; Bull. 330, pp. 467, 1908.

centrating the soluble salts in the mother liquor from which the ice crystals separate, and so causing any clay sol to be coagulated. Both of these actions facilitate the subsequent movements of water through the clay.

Weathering may, however, proceed too far. The writer knows of a case where fresh-mined shale made a paving brick giving a rattler test better by 2 or 3 per cent than brick made from the same shale after it had weathered two or three months. The swelled sponge of the weathered clay did not burn to as dense a product as the fresh-mined unexpanded clay. In an opposite [134] case the absorption of moisture from the damp air of a drier caused the block of unweathered fire clay to expand and crack.

Another action taking place at the same time is the removal of soluble salts by the rain or hose water applied to the pile of weathering clay. We know absolutely nothing as to whether the working properties of the clay and the strength of the product are injured or improved by this removal of salts. We do know that salts liable to cause scum are removed, but whether these salts are otherwise desirable and which, if any, is most beneficial is an uninvestigated question. Langenbeck [135] says:

> Those who form their ware freehand on the potter's wheel insist that a clay loses much of its plasticity in washing, becoming "punky"—that is, elastic rather than plastic.

Too much pugging or wedging is also said to cause punkiness.

2. EFFECT OF SALTS CONTAINED IN SLIP-HOUSE WATER

The soluble salts in slip-house water may have very important effects. The blunging of clay is slower in hard water than in pure water; addition of suitable alkali would undoubtedly hasten the blunging, but would at the same time lessen the plasticity of the clay.

The specific nature of the salts may make special difficulties. It is well known that sulphates, whether derived from the clay or from the slip-house water, tend to collect at the edges of pottery ware, causing "dry edges," on which the decoration is dulled or wholly spoiled. It would seem that the potter, as well as the brickmaker, could with advantage use barium carbonate in his mix to

[134] Trans. Am. Cer. Soc., 11, pp. 385, 390, 1909.

[135] Chemistry of Pottery, p. 79, 1895.

overcome the difficulties caused by sulphates. Seger [136] therefore proposed that barium carbonate be added to pottery mixes to precipitate the sulphates that cause dry edges, etc.; this is stated by Joshua Poole to be a frequent practice in the Staffordshire district.

If the slip-house water takes up salts from the clays rather than adds them, they by throwing away all the filter-press water, the quantity of soluble salts in the clays can be reduced.

When one of our largest potteries commenced operations it used exactly the same materials (usually from divided shipments) and the same body formula as another plant which was then successfully operating. But there was complaint in the clay shop of loss of ware. The help claimed that the body was not as plastic as at the old plant. This condition lasted for some months, and gradually was lost sight of. Now, the clay bins were made of concrete, and there was some seepage of ground water inward. The blungers were lined with brick, laid in cement. The troughs from blunger to agitator and from sifter to agitator were of cement. The agitators were lined with cement. After some months' running the bottoms of the agitators were so worn that it was necessary to reline them. In all of these places, then, the clays could take up free lime from the cement. This investigation has shown that under certain conditions lime may be an effective deflocculating agent (p. 69, Fig. 18); apparently it was responsible for the trouble. If such is the case, then in another such instance it would be easy to add acetic acid or vinegar in sufficient amount to overcome the trouble wholly and with no disadvantageous effects.

Seger,[137] however, added 0.1 per cent of calcium oxide to a porcelain body to prevent efflorescence of iron salts and said it was without ill effect on the clay; the reason being that it was probably completely neutralized in precipitating the iron salt.

Before leaving this question it may be said that we are as yet ignorant of the effect of varying the base in combination with the gel; as to whether, for instance, the H gel is superior to an alka-

[136] Collected Writings: Am. Cer. Soc. Translation, pp. 649, 1148, 1902. Langenbeck: Chemistry of Pottery, pp. 55, 153, 1895.

[137] Collected Writings: Am. Cer. Soc. Translation, p. 1149, 1902.

line-earth gel or vice versa. It is, however, generally accepted that a clay becomes most plastic when it sours or becomes acid on ageing;[138] this evidence, nevertheless, would not of itself justify the statement that H gels are to be preferred.

Simcoe and Smith [139] made experiments in which they varied the relative amounts of "plastics" and "nonplastics" in dust-pressed wares. They found no great difficulty with a body composed entirely of ball clay, but had to add gum tragacanth to tender bodies.

3. TREATING EXCESSIVELY COLLOIDAL CLAYS

On the other hand, a clay may be too plastic to work satisfactorily; so that, if it is to be worked at all, some method of reducing its colloid content must be employed.

To accomplish this purpose, Bleininger [140] has investigated a method of heating excessively colloidal clays before use in the brick machine, so as partly to destroy their ability to take up so much water. It consists in heating the clays to a temperature of 250° to 300° C., a process which is accompanied by decided increases in the specific gravity of the clay and by a "setting" of the colloidal material. The "setting" is perfectly analogous to the changes produced in other colloids by heating and referred to earlier (p. 38); it consists of a shrinking together of the colloidal particles as they lose water, with the formation of harder and larger particles, which are then attacked by water with comparative slowness. Hence, the plasticity of a clay is reduced by the process of preheating, except it be allowed to remain again in contact with water for a comparatively long time.

The temperature used is chosen so that sufficient unaltered colloidal material is left for plasticity.

Terry [141] said that in drying china clay on fire-brick flues previous to shipment "The temperature should never be allowed to rise so high that the workmen can not walk on the tiles, otherwise the clay may become baked and damaged."

---

[138] Seger: Collected Writings, p. 722, 1902.

[139] Trans. Am. Cer. Soc., 12, pp. 196–204, 1910.

[140] Trans. Am. Cer. Soc., 11, pp. 392–406; 1909; 12, pp. 504–516; 1910; and especially Bull. Bureau of Standards, 7, pp. 143–196; 1911, where the subject of preheating of clays is fully discussed.

[141] Pigments, p. 176; 1893.

It seems probable that in some cases the addition of a suitable reagent would dissolve the excess of the colloidal constituent, making a sort of thick solution to replace the ordinary tempering water, and also giving a denser product of higher crushing strength. Such a product might require unusual care in drying.

It would be desirable to ascertain if addition of acid would improve the working qualities of the alkaline clays often found in arid regions.[142]

4. USE OF COLLOID ADDITIONS

It has been the custom for many years to make colloidal additions to clay bodies, especially in pottery work; such as gelatine, glue, starch, gum arabic, dextrin, milk, and silicate of soda.[143] They are generally added to assist the cementing properties of a slip (such as the slip used in sticking handles on cups), or in some cases to diminish the amount of water required (silicate of soda, tannin).

In India [144] many additions are made to the local clays used for pottery. Among these are cow dung, leaves, horse dung, mule dung, rotten paper, gum, and starch. Some of the additions probably are valued more for their mechanical properties than for their colloid properties, as in the following cases: 29 g cotton wool to 1 kg clay; also 0.5 kg babul tree gum, 1 kg belgiri, 0.5 kg brown paper, 0.5 kg old cotton wool to 1 kg common black clay (this product is used for making unburned toys).

Simcoe and Smith [145] say:

> Many potters have for years used some sort of gum in their body, mixing in the blunger about a quart of a starchy mass to 3,000 pounds of body. * * * Bourry [146] also speaks of the use of gums under the head of "Agglomerative and agglutinative material," specifying the use of glue, gum, lichen, dextrin, soap, sugar, and molasses, and for ordinary ware, tar. He further states that they use black soap and parchment glue in the soft French porcelain. * * * We do not put our scraps back into the blunger. * * * It is a common experience with every plastic clay, or clay having gum in it, that you get into trouble with the filter press.

They also found the addition of kerosene and lard oil, mixed 3:1, to assist the clay to free itself from the molds, and with no injurious effect on plasticity.

---

[142] Seger: Collected Writings, Am. Cer. Soc. Translation: p. 722.
[143] U. S. Geol Survey Bull. 388, p. 12; 1909. Kerl-Cramer-Hecht, pp. 1513, 1514, 1515; 1907.
[144] Pottery Gazette, 35, pp. 1158–1160; October, 1910.
[145] Trans. Am. Cer. Soc., 12, p. 199; 1910.
[146] Treatise on Ceramic Industries, p. 70; 1901.

Bourry further mentions grease, milk, and an emulsion of casein in boric acid.[147]

Gum tragacanth and starch are used in making porcelain teeth.[148]

Zimmer [149] has given a good example of the proper method of adding colloidal material to a clay. He mixed the clay slip with silicate of soda, which, because of the soluble nature of the addition, gives a most uniform and intimate penetration. Then he added sufficient hydrochloric acid to react with all the alkali of the silicate of soda and coagulate the silica from it as gel. The excess of acid and sodium chloride was then washed out. This gave a plastic clay of unusually high shrinkage, and improved the color. A similar amount of silicic acid prepared separately, air dried (but containing 43 per cent H_2O), when added to the same clay, made it very short and hardly workable.

A failure to secure sufficiently intimate mixture may account in part for the unsatisfactory results obtained by Grout[150] after adding colloidal alumina or silica to clays.

Acheson[151] reports both deflocculation and improved plasticity from the use of tannin with clays, the effect depending, of course, on the quantity of tannin used and on the nature of the clay. Some of those who have tried to verify his results have encountered twisting and warping of ware, and so have condemned them. This lack of success may, however, be due to an imperfect incorporation of the reagent with the clay.

It would seem as if faults due to imperfect mixing led Keppeler[152] to his patented process of improving clays. This consists, first, in deflocculating by alkali; second, making an addition of colloidal material from humus; third, reprecipitating all together by adding acid.

Auclair.[153] has patented the preparation of a pure crystalline ceramic paste by dissolving out the colloids with alkali and

---

[147] Treatise on Ceramic Industries, p. 738.

[148] John Q. Byram: Principles and Practice of Filling Teeth. New York: Consolidated Dental Mfg. Co., p. 13; 1908. George Evans: A Practical Treatise on Artificial Crown-Bridge and Porcelain Work. Philadelphia: S. S. White Dental Mfg. Co., 7th ed., p. 343; 1905.

[149] Trans. Am. Cer. Soc., 3, pp. 30–32; 1901.

[150] West Va. Geol. Survey, 3, pp. 47, 49, 1906.

[151] Trans. Am. Cer. Soc., 6, p. 31, 1904. British Patent No. 7776, Apr. 3, 1907.

[152] Z. angew. Chem., 22, p. 526, 1909. German Patent No. 201987, Aug. 4, 1906. Chem. Abstracts, 3, p, 494, 1909.

[153] French Patent No. 372858, Dec. 22, 1906: Chem. Abstracts, 2, p. 2436, 1908.

removing the sol by filter pressing. Recently the writer[154] gave reasons for thinking that the colloidal material of kaolin has greater shrinkage than that of ball clays. It seems likely that a safer body mixture could be made if all the colloid matter were derived from the ball clay. Hence there seems good reason for the patent for removing colloids from kaolin. The principal objection to the use of ball clays is that they carry much dirt, mainly granules of iron minerals. It would seem to be feasible to dissolve out by suitable reagents the colloidal material of ball clays, leaving a residue containing most, if not all, of the discolorants. The colloid could be coagulated by acid when required, and could be very uniformly incorporated with other materials; for instance, with the crystalline kaolin mentioned above. Of course, these would be expensive processes; but the demands upon the ceramic industry for high-grade products are daily becoming more exacting, and for some purposes nothing is too good.

Use of Slip Kiln Increases Colloid Content.—It is well known that boiling a clay with water for even a very short time decreases the content of crystalline quartz and kaolinite and increases the proportion of colloids. Thus Hilgard[155] said that boiling serves "to reduce the kaolinite ingredient of soils and clays to the amorphous plastic, diffusible modification. As to boiling, I have succeeded in rendering diffusible and very plastic the 75 per cent of clayey ingredient in a white, chalky pipe clay, resembling kaolin, and which naturally is but very slightly plastic, by boiling for about 85 hours."

In agreement with this, L. Solon[156] stated that "the materials employed for making soft porcelain in France in the early days were more plastic than when boiling was abandoned as a useless complication." C. F. Binns[157] has said practically the same thing in regard to the replacement of the slip kiln in England by the filter press for bone china.

If, however, the clays being dried by fire should become overheated beyond the boiling point of water the setting (or coking) of the gels would lead to a loss of plasticity. Such appears to have been a common experience in Germany.[158]

---

[154] Trans. Am. Cer. Soc., **11**, p. 550, 1909. U. S. Geol. Survey Bull., **388**, p. 53, 1909.
[155] Am. J. Sci., (3) **17**, p. 211, 1879.
[156] Pottery Gazette, p. 1293 (Nov. 1, 1907). Trans. Eng. Ceram. Soc., **5**, p. 72, 1905.
[157] Trans. Am. Cer. Soc., **12**, p. 177, 1910.
[158] Kerl-Cramer-Hecht, p. 269, 1907.

5. INCREASE OR DECREASE OF REFRACTORINESS

Clays may presumably be rendered less fusible by treating them with soluble salts of such character that—by means of the exchange of bases—the bases entering form compounds melting at a higher temperature than those originally present.[159] Conversely, pottery clays may be made to mature at a lower temperature by removing the more refractory bases by treatment with solutions of alkali salts, e. g., common salt, potassium nitrate, etc.[160]

6. SOLUBLE COBALT STAINS

The simple addition of cobalt as chloride, sulphate, or nitrate to stain a clay ware is not practicable, for the writer has found that only about half of it is taken up by the clay, the rest remaining with the filter press water. As cobalt salts are rather expensive, this loss could not be viewed with complacency. Moreover cast ware could not be made with a body so colored, for in drying the cobalt would effloresce at the edges and so color them more deeply than the rest. It is necessary, therefore, to precipitate the cobalt compound with an alkali ($NaOH$, KOH, Na_2CO_3, but not NH_4OH) just before using, or to use it as a ground frit. Such soluble cobalt additions are in practice made to earthenware bodies containing calcium carbonate, but the precipitation as carbonate is incomplete and unsatisfactory.[161]

7. PURIFYING KAOLIN

In the preparation of china clay for the market the crude clay is made up into a slip with water, and the coarse rock débris, mica, etc., removed by settlement in troughs or by sifting. The clay is then concentrated by filter pressing or by sedimentation, followed in either case by drying. It is a more or less common practice to accelerate the sedimentation by adding alum[162] to the slip. As from 30 to 50 per cent water is to be removed by the "dry," it is evident that a certain amount of undesirable sulphates is included in such cases.

---

[159] See also Kerl-Cramer-Hecht., p. 175, 1907.

[160] Ibid., p. 195.

[161] Kerl-Cramer-Hecht., pp. 1140, 1141, 1907.

[162] Alum or ammonium carbonate: Sprechsaal, p. 244; 1904. Alum, Ries: Clays of the U. S. East of the Mississippi River, p. 35; 1903.

For paper clays, one of the commercial requirements is a white color in the raw condition; hence it is desirable that certain organic matters of red or yellow tint be removed or bleached. For whiteware clays it is essential that dark burning iron compounds should be removed from the raw clay. A. G. Salamon and several associates have covered both these cases in a series of patents, in each of which the clay is treated with some reagent, filter pressed, and then the excess of the reagent washed out on the filter press. The patents are as follows:

British patent, 13179 (June 20, 1908). "A weak solution of alum, or of sulphate of alumina, or, sometimes, sulphuric acid."

British patent, 21260 (Oct. 8, 1908). Chlorine water and a little sulphuric acid.

British patent, 2294 (Jan. 30, 1909). Oxalic acid at 55°.

British patent, 2295 (Jan. 30, 1909). Sulphurous acid or a suitable sulphite, bisulphite, or other compound of sulphurous acid which is capable of combining with the coloring matter and forming soluble salts or compounds.

Karl Langenbeck[163] decolorizes kaolin, etc., containing iron, by subjecting it to hydrogen sulphide to form ferrous sulphide, which is then removed by oxidation and lixiviation.

B. MECHANICAL ANALYSIS OF CLAYS

Mechanical analysis is a name given to the operation by which the clay is separated into groups of grains of different sizes, the amount of each size being weighed. The coarser sizes are separated by taking advantage of the different rates at which they fall in water, the finest being the slowest to settle. The mechanical analysis of paving brick shales is very important; for, in a general way, the finest grained paving brick shales make the weakest brick. The finest grained pottery clays have the biggest loss in the kilns.

The data obtained make possible a criticism of present methods of conducting the mechanical analysis of clays.

---

[163] U. S. Pat., 893590.

8. PREPARATION OF CLAYS FOR MECHANICAL ANALYSIS

Shaking with cold distilled water in sufficient quantity will deflocculate a clay perfectly if all its colloid matter is in the form of soluble alkaline compounds, but otherwise not. If more water is used than the quantity that just suffices, the crystal matter will be attacked and tend also to go over to the colloid form. If hot water is used, or if grinding is resorted to, the above actions will be greatly accelerated.

The use of hard water will tend to keep the colloid matter coagulated on the crystal grains.[164] In elutriations with incompletely deflocculated clay there is a tendency to ball up and to adhere to the walls of the apparatus,[165] which is wholly absent with perfect deflocculation. Also the fractions of incompletely deflocculated clay on drying shrink, crack, and roll up, none of which is the case with wholly granular residues; such shrinkage is, of course, a direct consequence of the presence of collodial material in the fractions.

Kashinskii[166] compared the efficacy of shaking and boiling as means of deflocculation; and found that by long-continued shaking one obtains, in general, fewer particles less than 0.01 mm, and a greater number of particles of 0.25–0.05 mm, than by boiling; this difference is equalized to some extent if the shaking is carried on with large quantities of water.

9. EXTRACTION WITH ACID, WATER, AND AMMONIA

The method of Schloesing[167] is the most generally applicable of the methods in use. He extracts the clay with a portion of nitric or hydrochloric acid and then washes till the filtrate is no longer acid; this removes the soluble salts and most of the basic ions of the gels. He then treats with ammonia, in proper proportion, which forms the ammonia sol of the colloids and leaves the crystals bare.

---

[164] Sachse and Becker: Landw. Vers., **43**, p. 15; 1894. Z. Chem. Ind. Kolloide, **3**, p. 198; 1908.

[165] Kerl-Cramer-Hecht: p. 79; 1907. Hilgard: Am. J. Sci., (3) **17**, pp. 205–214; 1879. Wiley: Agricultural Analysis, I, p. 209; 1894. Seger: Collected Writings, Am. Cer. Soc. Translation, p. 1110; 1902.

[166] J. Exp. Landw., **9**, pp. 188–194; Chem. Abstracts, **3**, p. 2601; 1909.

[167] Compt. rend., **136**, p. 1629; 1903; **137**, p. 369.

J. Dumont[168] has a suggestive, but less general, scheme. The sample of soil, after treatment with a 60 per cent calcium nitrate solution to float off vegetable water, is boiled for at least one hour in 4 per cent oxalic acid, filtered, washed with nitric acid to remove calcium oxalate, and subsequently with distilled water, after which it is digested for 1 or 2 days with 20 per cent ammonia. It is then centrifuged at 1000 r. p. m. to remove sand, settled 24 hours to give loam, treated with ammonium carbonate to precipitate the clay, and then with hydrochloric acid (or is evaporated) to obtain the humus. The sands are centrifuged 10 minutes with Thoulet liquid (potassium mercuric iodide, sp. gr. 2.8) to remove ferromagnesian minerals, then with liquids of smaller specific gravity to separate quartz, orthoclase, and mica. His methods appear to be rather drastic for the best results.

10. EXTRACTION WITH AMMONIA

The Bureau of Soils[169] of the United States Department of Agriculture take 5 grams clay, 75 cc water, add 10 drops strong ammonia, and shake violently for 6 hours. The shaking is much in excess of what would be required with a proper choice and manipulation of solvents. The ammonia is found by them to be useless on soils containing carbonates, and is omitted with such soils. Its action in such cases is to assist in salting out the colloids rather than to assist in dissolving them. Ammonia will be found most effective with acid soils low in soluble salt content. It forms the ammonia sol from these and thus uncovers the grains, except it be prevented by the salting out effect of the soluble salts present or of excess of the reagent.

11. EXTRACTION WITH SODIUM HYDROXIDE

The Tonindustrie Kalender recommends 1 cc sodium hydroxide solution (strength?) to 40 grams of clay. This is a more vigorous reagent than ammonia, and so can overcome more soluble salts. On the other hand, if the clay is alkaline, it will assist the more vigorously in salting out the colloids, and so hinder deflocculation.

---

[168] The Mineralogical Analysis of Arable Soils: Compt. rend., **140**, 1111; 1905. Enveloping Films of Soil Grains: Compt. rend., **149**, 1087; 1910.

[169] Bureau of Soils, Bull. **24**, 9, 20; 1904.

Best Proportion of Alkali.—In general, alkalies are efficient for removing the colloid coating from the grains when, first, the clay is not already alkaline, second, soluble salts are low, third, the colloid is not combined with polyvalent bases, such as calcium, magnesium, iron, or aluminum; fourth, just the right amount of alkali, as determined by tube experiments, is used.

It is exceedingly important that a slight excess of alkali shall not be added. In Fig. 2, which shows the effect of sodium hydroxide on the New Jersey sagger clay of Jas. P. Prall, it will be noticed that about 3 cc 0.1 *N* NaOH reduces the bulk of sediment to 3 cc. This sediment presents a clean, granular appearance. With this quantity the sol in the tube above the sediment has reached its maximum density; up to 37.5 cc may be added without producing any further change in appearance. With further additions, a gradual stiffening of the gel seems to set in, accompanied by a diminution of its volume and an increased carrying power. As it takes up first the finest part of the sediment, then the coarser portions, the sediment appears to diminish, to become less distinct, and finally to become identical with the coagulated gel. Obviously while the colloid matter is able to buoy up the granular matter of the clay it is in a very unsuitable condition for the mechanical analysis.

12. USE OF ALKALINE PRECIPITANTS

We do not know if anyone else has used alkaline precipitants to deflocculate clays for mechanical analysis, but we find them very efficient where the gel is combined with polyvalent bases or the soluble salts contain polyvalent bases. We have used sodium oxalate mostly, but potassium and ammonium oxalate seem to be nearly as efficient. In special cases, other reagents might be especially adapted to remove the compounds present; but any reagent giving perfect deflocculation should be satisfactory.

C. METHODS OF MECHANICAL ANALYSIS

Sedimentation and Elutriation.—The two general methods of mechanical analysis are sedimentation and elutriation; the former requires the more skilled operator and frequent standardization of the sizes of grain. The principal difference between the two

is that the former is intermittent, while the latter is continuous and usually employs a much larger volume of water. It is well established that water exerts a solvent effect upon minerals, and that this effect is greater the higher the temperature. Hence, it is desirable that, in mechanical analysis, the volume of water used and its temperature be kept as low as possible. This consideration is a strong argument for discarding elutriation methods and adopting sedimentation. It seems probable that instead of running elutriations until the overflow is clear, they should be run only for a definite length of time. Further, when ordinary tap water is used in elutriation, a great volume is required; consequently there is liability that the bases in it will undo the work of the deflocculating agent. This has happened when sodium oxalate had been used with the clay.

This difficulty may be obviated by combining sedimentation and elutriation, as follows: The greater part of the sol may be removed by sedimentation and decantation four times repeated, using distilled water and removing 90 per cent of the liquid each time; then the granular residue may be elutriated with tap water. In such a case, where 30 minutes were allowed for each sedimentation, it was found that 0.3 per cent crystalline matter was lost which ought to have remained in the third can.

An alternative method is to decant into the third can,[170] to wash the sediment into the first can, and to fill the second can with distilled water; and then elutriate with tap water. Most of the sol will then have overflowed from the third can before the tap water reaches it.

Another difficulty noticed in elutriations with metal cans is a tendency for fine clay that should overflow to lodge on the conical bottom and the vertical sides. This is due to a partial corrosion of the metal of the can and can not be obviated by using a sharper cone. It was evidently observed by Parmelee and Moore [171] in their comparative study of methods of mechanical analysis, for in one of their experiments they had the inside of the cans varnished.

---

[170] Trans. Am. Cer. Soc., **6**, p. 185; 1904; **8**, p. 245; 1906; **11**, pp. 469, 489; 1909. Proc. Engrs. Soc. West Pa., **25**, p. 570; 1910.

[171] Trans. Am. Cer. Soc., **11**, p. 477; 1909.

Sedimentation methods include those where gravitation is the force causing the grains to collect at the bottom of the vessel, and those where centrifugal force causes a much more rapid collection. Owing to the packing action of the centrifugal machine, the liquid overlying the grains is easily decanted, while a disturbance of the loose-lying grains in a sedimentation experiment is best avoided by siphoning off the water. The centrifugal soil elutriator of Yoder [172] is apparently impracticable as the sediment packs in so as to stop the flow; it is really a sedimentation apparatus.

It is desirable to study whether slightly alkaline water will give better results than pure water in making the successive changes; also whether there is a limit to the number of changes of water that should be employed (to minimize the solvent effect upon crystal grains). Accordingly, a number of experiments were undertaken, the results of which are brought together in the following table. In each case the amount of reagent used was the minimum amount required for complete deflocculation, except where several proportions of one reagent were tried.

It is thought that in some of the runs with the Tennessee No. 3 ball clay too much alkali was used.

It should be said that the experiments were made before the ideas announced in this paper were fully developed.

---

[172] Utah Expt. Sta., Bull. 89, p. 16; 1904. Out of print.

TABLE XII

Effect of Method of Preparation on Comparative Elutriations with the Schultze Apparatus

Clay	Reagent added to 50 g clay	Can 1, 0.05773*	Can 2, 0.03543*	Can 3, 0.01671*	Overflow, 0.0050*	Remarks
Maine Feldspar Co., orthoclase	Tap water, boiled..	4.7	22.3	22.3	50.7	
	Distilled water, cold	13.14	29.64	7.98	49.24	
Harris Clay Co., North Carolina:						
Kaolin.....	Tap water, boiled..	0.10	7.08	31.64	61.18	Overflow turbid for 48 hours
Same sample, dyed with malachite green	Tap water, boiled..	1.12	6.04	77.58	15.26	
	30 cc 0.1 N $Na_2C_2O_4$.	2.38	29.04	10.28	58.30	Do.
	10 cc 2.5 N NaOH..	2.14	27.62	10.30	59.94	Do.
		2.68	27.94	10.56	58.78	Do.
Hall Clay Co., Georgia, kaolin	Tap water, boiled..	1.80	1.08	11.84	85.28	
	10 cc 0.1 N NaOH..	1.96	9.76	6.02	82.26	
J. Poole, No. 1 English china clay	Tap water, boiled..	0.2	nil	16.9	82.8	
	30 cc 0.1 N NaOH.	0.4	10.86	9.48	79.62	
Knowles, No. 15 English china clay	Tap water, boiled..	0.1	0.9	24.6	74.4	
	30 cc 0.1 N NaOH.	0.22	14.64	9.82	74.98	
Hamill & Gillespie, A1 English china clay	Tap water, boiled..	.....	.....	17.4	82.6	
	2 cc 2.5 N NaOH..	0.08	10.82	9.08	80.02	
Atlanta M. & C. Co., Georgia, washed kaolin	Tap water, boiled..	3.60	9.26	17.98	69.16	
	50 cc 0.2 N $Na_2C_2O_4$.	2.06	6.92	4.36	86.66	
Edgar Plastic Kaolin Co., Florida, kaolin (dyed)	Tap water, boiled..	1.7	48.5	20.4	29.4	
	20 cc 0.1 N NaOH..	0.46	4.36	4.67	90.51	
	6 cc 2.5 N NaOH...	0.16	3.34	6.44	90.06	
Knowles, No. 12 English, ball	Tap water, boiled..	8.64	4.88	3.9	82.6	
	8 cc 2.5 N NaOH...	2.82	2.22	0.66	94.30	
	100 cc 0.2 N $Na_2C_2O_4$	11.52	4.32	0.80	83.36	First can largely coarse stuff that screens would catch
Johnson-Porter C. Co., Tennessee, ball No. 9	Tap water, boiled..	3.08	3.74	12.76	80.42	
	8 cc 2.5 N NaOH...	1.82	3.50	0.98	93.70	Apparently cleaner than $Na_2C_2O_4$
	100 cc 0.2 N $Na_2C_2O_4$	2.50	5.46	1.32	90.72	
Mandle-Sant C. Co., Tennessee, ball No. 3	Tap water, boiled..	9.24	3.64	8.84	78.28	Residue caked
	140 cc 0.1 N NH_4OH	0.74	0.90	1.88	96.48	
	90 cc 0.1 N NH_4OH.	0.16	0.48	1.59	97.77	
	50 cc 0.1 N NaOH..	0.21	0.16	0.83	98.81	Best value
	150 cc 0.1 N NaOH	0.01	0.31	0.92	98.76	
	80 cc 0.1 N NaOH;	0.02	0.24	0.43	99.31	

*These numbers represent the average diameter (in mm) of the particles.

TABLE XII—Continued

Clay	Reagent added to 50 g clay	Can 1, 0.05773	Can 2, 0.03543	Can 3, 0.01671	Overflow, 0.0050	Remarks
Jas. P. Prall, New Jersey, No. 1 light sagger	Tap water, boiled..	2.56	3.30	15.24	78.90	Third can caked
	Distilled water, boiled	5.62	18.78	6.84	68.76	All 3 cans caked
	Boiled, then dropped in 1 liter 0.1 *N* NaOH while running	3.85	7.96	1.93	86.26	Residues not caked
Diamond Clay Co., Ohio, fire clay	Tap water, boiled..	65.98	5.50	5.90	22.62	61.64 per cent on 120 mesh. 4.34 per cent in first can
	50 cc 0.2 *N* $Na_2C_2O_4$.	42.70	13.96	4.68	38.66	29.46 per cent on 120 mesh. 13.24 per cent in first can. Each grain microscopically homogenous but compound
	Same, boiled 5 minutes in 200 cc liquid	29.58	10.94	3.58	55.90	19.60 per cent on 120 mesh. 9.98 per cent in first can. Appears the same as above
	Same, boiled 10 minutes in 400 cc liquid	32.73	14.30	1.74	51.23	12.23 per cent on 120 mesh. 18.30 per cent in first can
Joint clay, Champaign, Ill. (normal)	80 cc 0.1 *N* NaOH..	6.70	26.56	5.07	61.66	
Same (preheated to 300°)	.....do.....	30.12	37.25	4.39	28.23	Set gel in can residues

The preceding table compares results obtained on the one hand by boiling (1 or 2 minutes) with hard tap water, then shaking mechanically at least an hour, and, on the other hand, by treating cold with a deflocculating agent, then shaking mechanically for an hour. Boiling decreases the size of grain in the first and second cans with feldspar and with the purer kaolins (Harris, Hall, Poole, Knowles, and Hammill and Gillespie). Microscopic examination showed separate, nonadherent grains from the cold runs in which a deflocculating agent was used; hence it follows that boiling [173]

[173] As it was Seger's practice to boil clays for the mechanical analysis, his results are affected by this error. Seger: Collected Writings, Am. Cer. Soc. Translation, pp. 45, 1108; 1902.

was too severe a treatment and reduced the size of grain by dissolving crystal matter.

The same effect is shown with the fire clay. With a cold sodium oxalate addition the results are quite different from those obtained after boiling with sodium oxalate. Under the microscope the crystal grains of the fire clay on 80-mesh and coarser sieves were apparently cemented aggregates, though each grain was a single mineral and not a conglomerate. The boiling dissolved crystal matter from the exposed surfaces, thus giving too small residues on elutriation.

With the more thoroughly disintegrated and plastic kaolins (Atlanta and Edgar) and ball and sagger clays, the colloid matter was present apparently in sufficient amounts to protect the crystal grains from solution in boiling tap water, and indeed the colloid matter was not fully removed by the tap water with any of the clays of this class. So the use of a deflocculating agent is imperative with the highly colloidal kaolins and ball and sagger clays.

It will be noticed where runs were made on the same clay with sodium hydroxide (NaOH) and sodium oxalate ($Na_2C_2O_4$); Harris, Knowles No. 12, and J. P. C. Co., Tennessee No. 9, that in each case less clay passed the third can when the sodium oxalate was used. This is attributed to the soluble salts in the tap water of the elutriator; they are precipitants for clay, and partly undid the work of the sodium oxalate.

A possible method of partial mechanical analysis is the use of immiscible liquids of appropriate specific gravity to separate the various constituents of clays by flotation. A number of experiments along this line were tried, using carbon tetrachloride or carbon disulphide (usually with some admixture of ether, to diminish the surface tension at the boundary with the aqueous phase); but, so far as these experiments went, the method was not very satisfactory.

D. DETERMINATION OF THE SOLUBLE SALTS IN CLAYS

Closely related to the question of the proper methods of mechanical analysis is that of the determination of soluble salts; the same influences affect both processes in comparable ways.

The main difficulty in soluble salts determinations has been to know when to stop. After such common salts as the sulphates of calcium, magnesium, and sodium, and sodium chloride have been removed by successive extractions with cold water, then without a break (or rather with decided overlapping) alkaline silicates are removed. While some of the alkaline silicates so removed are derived from the colloid portion of the clay, there is a tendency for the crystal portion of the clay to go over to the colloid form. This tendency is increased when hot water is used.

When extractions are made with a salt solution, metathesis, as we have seen, is likely to occur; even such insoluble substances as calcium phosphate are subject to decomposition by salt solutions. Hence extraction by salt solutions is inadmissible, as it is liable to give much more than the true water-soluble bases of a soil.

Schreiner and Failyer [174] remark that dried soils give up their soluble salts in somewhat greater concentration than fresh damp soils. Similar observations were collected by Ehrenberg.[175] Bleininger [176] in his investigations on destroying excessive plasticity by preheating clays, noted that heating the clays to 250 to 300° C seems greatly to facilitate movement of the soluble salts through the pores of the clay. These temperatures, which are necessary to drive off the hygroscopic water of the clays, decidedly increase the porosity of the clays. The gels "set" to a structure similar to that of charcoal.

Ries even found larger amounts of soluble salts in Wisconsin clays which had been soft burned than in the crude clays.[177] This may have been in part due to taking up sulphates from the fire gases or to oxidation of pyrites to sulphate.[178] Hard-burned clays yielded less than soft burned.

---

[174] U. S. Dept. Agr., Bur. Soils, Bull. **31**, p. 11.

[175] Z. Chem. Ind. Kolloide, **3**, p. 201; 1908.

[176] Trans. Am. Cer. Soc., **12**, pp. 513, 514; 1910.

[177] Clays of Wisconsin: Wisconsin Survey, Bull. **15**, p. 22; 1906.

[178] Kerl-Cramer-Hecht, pp. 517, 518; 1907. According to Ost, Tech. Chemie, Berlin, p. 129; 1890; through Z. prakt. Geol., **11**, p. 51; 1903. At Ampsin, near Liege, the acid fumes from roasting zinc ores are brought into contact with alum shales, whereby both potassium and aluminum are dissolved and alum is formed.

13, PROPOSED METHOD OF SOLUBLE SALT DETERMINATION

The following method of soluble salt determination is proposed as worthy of study:

Take 100 grams of air-dry clay, heat at 300° C for one hour, and weigh. (Or heat to constant weight at 105° C in air dried by bubbling through strong sulphuric acid.) The loss equals hydroscopic moisture. Crush to pass a 60-mesh sieve; put into a vessel containing one liter of cold water; shake one hour; let settle over night. Siphon or decant off a definite volume, even if turbid. Add from a burette a measured portion of magnesium sulphate just sufficient or a little in excess of the amount required to coagulate the clay sol. In aliquot portions of the resulting settled or centrifuged clear liquid the various determinations, including acidity, are to be made by usual quantitative methods. The silica present may necessitate an evaporation to dryness with hydrochloric or nitric acid. Organic compounds may require special treatment or ignition. From the total sulphuric anhydride found is to be subtracted that added as magnesium sulphate. If we assume that no magnesium was present as a soluble salt, which is nearly the case in the presence of a turbid solution, we may assume that the magnesium added as sulphate minus the magnesium found equals the magnesium used in coagulating the clay; also that from the alkali found is to be deducted an amount equivalent to the magnesium used in coagulating the clay.

E. SCUM ON CLAY WARES AND ITS PREVENTION

Soluble salts are the cause of scum when they are carried to the surface of the clay and are deposited there on evaporation of the water. Now, colloidal matter opposes to some extent the flow of solutions through it; especially it slows down the rate of diffusion of salt solutions through it. Indeed, the studies of Bechhold [179] (and of others since his time) on the process now termed "ultrafiltration" indicate that the pores of a colloidal medium may be of such dimensions as not only to retard but actually to retain the larger molecules.

Hence, even though analysis should indicate a fairly high content of soluble salts, a brick made from such clay may not scum if

[179] Zs. physik. Chem., 66, pp. 257–318; 1907.

the clay has sufficient colloidal material in a suitable condition to prevent the appearance of the soluble matter at the surface. Their appearance at the surface is in part conditioned by the manner of drying. For instance, A. F. Greaves-Walker [180] writes:

> Where a clay contains soluble salts, they are not deposited on the surface at all, or at least to a less degree, where the drying is steady and rapid than where it is slow and discontinuous.[181] It seems that rapid drying causes the water to come through the pore channels of the clay as through a filter and a sort of osmosis is set up, by which the saline matters are retained inside the mass of the clay while the water escapes as vapor from the outside. But where the drying is slow the salts get through this barrier and arrive on the surface plentifully.

On the other hand, drying must not be too rapid, for, according to Orton [182]—

> Rapid drying of clay wares must not proceed much faster than capillary flow. Practically we always have a strain on the drying surface. If the tensile strength is good, the surface will stand under the strain until the float water is removed. * * * Glass pots are blanketed, and uncovered for an hour at a time for evaporation. While blanketed, capillary flow is bringing more moisture to the surface.

14. USE OF BARIUM CARBONATE TO PREVENT SCUM

Of the salts commonly found in clays, only the sulphates require consideration as the cause of efflorescence on fired ware.[183] The difficulty caused by soluble sulphates can be obviated by adding barium carbonate. But another difficulty arises—how to determine the proper quantity to add, for barium carbonate, besides reacting with the soluble sulphates, will also react with some of the colloidal matter present, in each case with the simultaneous formation of a (probably soluble) carbonate of the base displaced. There is every reason to believe that the barium carbonate acts first upon the soluble sulphates, and secondly upon the colloids. Indeed, Dutoit and Duboux [184] have shown this to be so in the case of wines. If the amount of sulphuric anhydride in the clay has been accurately determined, it would seem that the theoretically equivalent amount of barium carbonate might be added. If the clay were worked sufficiently after the addition of barium carbonate, it is conceivable that the reaction between the slightly soluble barium carbonate and the sulphates would be nearly com-

---

[180] J. Ind. Eng. Chem., 2, p. 375; 1910.
[181] Kerl-Cramer-Hecht, p. 517; 1907.
[182] Private Notes on Lectures at Ohio State University.
[183] Kerl-Cramer-Hecht, p. 517; 1907.
[184] Schweiz. Wochschr., 46, pp. 672–678; Chem. Abstracts, 3, p. 469; 1909.

plete. That this is unlikely to be so in practice is probably the reason for the direction given by Seger [185] to use twice the theoretical quantity. The necessity of a double quantity may also be due to a reaction with the colloidal material, or to both causes together.

Another reason hitherto unrecognized is the simultaneous formation of alkaline carbonates mentioned above; these tend to deflocculate the clay and thus to lessen the plasticity. But if an excess of barium carbonate is used, it will inhibit this deflocculation and thus preserve the plasticity.

"*Practical*" *Test.*—The "practical" test for the barium carbonate requirement of a clay, consisting in adding to equal weights of clay a series of increasing weights of barium carbonate, shaking with water, and finding which members of the series completely precipitate all the barium added, is liable to lead to wasteful use of barium carbonate by reason of the combination of the latter with the harmless colloids of the clay.

Hirsch [186] made an excellent study of this test. While he did not understand the cause of the excessive taking up of barium, he found a means of combating it. He directed that 4 grams aluminum chloride be used in the test with 100 grams clay and that the test with barium would then be "faultless." The action of the aluminum chloride is to combine with the colloids and render them so insoluble that they are not affected by the barium carbonate, which consequently under these conditions reacts only with the soluble sulphates.

F. CASTING PROCESS

In the casting process for the manufacture of clay wares the clay body, made into a slip of creamy consistency with water, is poured into a plaster-of-Paris mold. The mold absorbs the water rapidly from the slip in contact with it, and a layer of the clay body forms on the surface of the mold. When the layer reaches the desired thickness the excess of still liquid slip is poured out. On standing longer the formed ware loses some more water to the plaster and shrinks sufficiently to come loose from the mold.

[185] Kerl-Cramer-Hecht, p. 523; 1907.

[186] Tonindustrie-Zeitung, 28, p. 491; 1904. U. S. Geol. Survey Bull., 388, pp. 37–39; 1909.

Obviously the less the amount of water in the slip the quicker the layer will form on the plaster, the less drying of the molds will be required, and the molds may be filled at more frequent intervals. This process is used on the one hand for table and sanitary ware and on the other hand for the manufacture of high-grade refractories, such as glass pots.

15. USE OF ALKALI TO DECREASE WATER REQUIREMENT

A bulky highly colloidal clay exhibits a large shrinkage when the water is given up again by drying and evaporation. When such a bulky clay is treated with soluble hydroxides or other alkaline precipitants so as to form the alkali compounds of the colloid matters, it usually requires only about half as much water to bring it to the creamy consistency of a casting slip as would be required for the clay in its ordinary condition. The clay also loses its plasticity.[187] In other words, when the alkali compounds of the clay colloids are dissolved or suspended in water, plasticity is absent; in the sol (deflocculated) condition they are quite fluid. Kosmann[188] first suspected the solvent effect of the alkaline addition. He thought that a "certain part of the silica in the clay substance is dissolved by the soda and by the removal so effected of these intervening silicic acid particles a mechanical alteration of the mass is effected in the sense of dilution and greater mobility." If we include with silicic acid the other colloidal constituents present, the portion of Kosmann's views above given is correct.

Żebisch[189] attributed the diminished water requirement of casting slip when alkali is used to a depression of the capillary coefficient, and asserted that, on the other hand, acid solutions, with a greater coefficient, will penetrate between the clay particles to a greater extent. The Landolt-Börnstein tables (second edition) fail to show any acid or alkaline solution with a capillary coefficient greater than that of water. Żebisch's explanation of the greater density of casting slips when alkali is used is therefore unconvincing.

---

[187] Kerl-Cramer-Hecht, pp. 279, 305; 1907. Seger: Collected Works, Am. Cer. Soc., translation, p. 722; 1902.

[188] Tonind.-Ztg., p. 382; 1895. Kerl-Cramer-Hecht, p. 307; 1907.

[189] Sprechsaal, p. 1005; 1894; pp. 303 et seq.; 1895. Kerl-Cramer-Hecht, p. 306; 1907.

Hitherto the choice of deflocculants for the casting process has been almost wholly an empirical process. Weber,[190] whose patented casting process for glass pots and other refractories is used in more than 20 factories, after describing the use of alkalies, the sodium salts of carbonic, phosphoric, oxalic, and boric acids, barium hydroxide, and calcium hydroxide, said:

> Which of the above-named alkalies should be used, and the quantity, must be found out for each clay separately according to its position.

Foerster[191] noticed that calcium sulphate hinders the action of alkalies in preparing clays for casting and that its effect can be offset by the use of a precipitant for lime, as sodium carbonate. Weber[192] patented the use of precipitants for calcium sulphate. In his specification he gave the following example, which shows that he is not clear as to the difference in action of alkali hydroxides and of alkaline precipitants:

> 450 kg fat refractory Stourbridge clay and chamotte.
> 0.350 kg barium hydroxide, $Ba(OH)_2+8H_2O$, or
> 0.220 kg barium carbonate, $BaCO_3$.
> 120 kg water.
> 0.600 kg sodium hydroxide (NaOH), or the corresponding amounts of sodium carbonate (Na_2CO_3) or sodium silicate ($Na_2O,xSiO_2$).

16. CHOICE OF DEFLOCCULANT

The methods given in this paper make it possible to determine, first, what amounts of soluble salts are in the clay; second, what bases are combined with the gel; and, third, what reagents are best suited chemically to react with these, and to dissolve the colloid matter of the clay.

17. JOINT USE OF SODIUM CARBONATE AND SODIUM SILICATE

Fig. 22[192a] illustrates the separate and joint action of sodium carbonate and sodium silicate on a ball clay and a china clay and a body made from them. The proportions used in ordinary work while variable, and determined by tradition or experiment, are about 0.1 per cent of each. The lower right-hand figure shows that the deflocculation is not complete at this concentration. While Böttcher says that he successfully cast a stoneware clay

---

[190] Trans. Eng. Cer. Soc., 8, I, p. 16; 1909.
[191] Die chem. Ind., 28, pp. 733–740; 1905.
[192] Brit. pat. 6560 (Mar. 18, 1909).
[192a] See p. 76.

with the proportion of sodium hydroxide giving maximum deflocculation, it should be determined practically whether this point or some point short of it gives best results.

In studying Fig. 22, one naturally tries to find what ratio of sodium carbonate to sodium silicate is most advantageous, or whether one should be used exclusively. The reasons are not evident from the diagram. If sodium carbonate is used alone, the stream when poured into the mold breaks into numerous drops. This causes the entanglement of air bubbles. Wherever one of these air bubbles gets into the ware, a crack will develop, and a piece of ware be ruined. If sodium silicate is used alone, the slip is liable to flow in strings like thick sirup. A proper balance between these two effects is secured by using a suitable mixture of the two reagents. The slip will then pour in a clean-cut solid stream, with but slight tendency to draw in air bubbles.

The writer is informed that some three plants making sanitary ware of fire clay have tried and abandoned Weber's process. Their difficulties were said to be (1) that ware made by the process was "rotten" or lacking in strength; (2) that the fine material of the clay seemed to collect at the surface, leaving only large grains in the center; (3) that the ware stuck to the molds; and (4) that the plaster of the molds was rapidly attacked.

The first and third objections indicate that the plasticity was too thoroughly destroyed; that it would have been better, therefore, to use less reagent, and so to retain some of the plastic strength of the clay. The fourth objection also indicates the use of reagent in excess of the amount that the clay would react with.

The second and third objections the writer has found to occur with a No. 1 fire clay treated with just sufficient reagent to give maximum deflocculation. In the writer's experiment with this fire clay the water requirement was the same with or without the alkaline addition.

It would appear that for the casting process a certain amount of shrinkage is essential in order that the ware may free itself properly from the molds; so that the clay must originally have sufficient of the constituent that shrinks (colloid), and consequently that the shrinkage must not be unduly suppressed by the alkaline addition.

18. ADDITION OF SOAP TO POTTERY BODIES

Soft soap is occasionally added to pottery bodies to make them more suitable for casting.[193] Trouble is occasionally experienced in a pottery when through mischance or malice soap gets into a blunger of clay and causes a decrease in plasticity.

While the best condition for casting appears to be somewhat short of total deflocculation, the converse is not necessarily true for plastic working. It is true that the gel must be present in suitable amount for good working properties; but whether the presence of some sol is advantageous is not known.

In Sprechsaal, page 1049, 1903, several correspondents tried to assist a questioner who found his casting body thicker after adding soda. One thought he used too much soda. A second said that a clay containing organic acids is not suited for casting. A third suggested that perhaps it had been acidified for turning and so neutralized the soda; or that the water contained some salt precipitated by carbonate of soda. The fourth said that clays carrying hydrated silicic acid are unsuited for pouring. "The more soda one uses the more gelatinous the mass becomes."

G. REGULATION OF GLAZES AND ENGOBES

Glazes are mixtures composed largely of alkaline silicates, natural or artificial. If the amount of alkali present is sufficient to keep the colloidal material in suspension, there is danger that the crystal and glassy grains may fall to the bottom of the dipping tub and set so firmly as to cause the dipper much trouble. The condition desirable in a glaze is that all the colloidal material should be in the form of a thin jelly, which then holds up the granular matter. This condition may be obtained either by the addition of coagulants or thickness, for which purpose the following have been used.[194]

Coagulants: Barium(?), strontium and magnesium sulphates nitric,[195], sulphuric, hydrochloric and boric acids; and vinegar.

Thickeners: Blood, milk, sirup, dextrin, gum arabic, plastic clay.[196]

---

[193] Kerl-Cramer-Hecht, p. 306, 1907.

[194] A. E. Mayer: Trans. Am. Cer. Soc., 11, pp. 369–374, 1909.

[195] Nitric acid forms a poisonous compound with lead, if present.

[196] Langenbeck: Chemistry of Pottery, p. 124; 1895.

Calcium nitrate, ammonium nitrate, and ammonium carbonate are also said to be effective coagulants, especially the last;[197] and starch and common flour paste are used as thickeners. According to Jul. Grünwald,[198] the best coagulants are ammonium carbonate, magnesium oxide, and borax.

Even when a glaze has almost set, the grinding may be continued after a small addition of hydrochloric acid, nitric acid, barium chloride, or calcium chloride.[199] In France, sea salt is added to porcelain glazes,[200] also vinegar [201] to the glaze for frit porcelain.

The following materials are used in the manufacture of glazed oven tile:[202] Common salt, sodium nitrate, potassium nitrate, which act as coagulants; borax, sodium carbonate, potassium carbonate, which act either as deflocculants or coagulants, according to the amount used. Addition of common salt has in this case the further effect of improving the color by reacting with the iron to form a volatile chloride.

Carter [203] called white lead "a raw flotative ingredient." In the writer's experience the "Old Dutch process" white lead, by reason of its bulky colloid nature, stays in suspension much better than some of the denser crystalline rapid process white leads. Similarly the natural bulky English cliffstone paris white stays in suspension better than some of the more crystalline precipitated calcium carbonates.

Both the thickeners and the coagulated gels also act as adhesives; the additions are sometimes made principally for this latter purpose.[204] With engobes in particular, but often with glazes, a third function of the addition is often to regulate the shrinkage of the slip or glaze. For instance, Seger [205] introduced colloidal alumina into a glaze in order that its shrinkage might produce the craquelé effect.

---

[197] Kerl-Cramer-Hecht, pp. 342, 350, 353; 1907.
[198] Keramische Rundschau, pp. 358–359; 1910.
[199] Kerl-Cramer-Hecht, p. 1149; 1907.
[200] Ibid, p. 1405; Keramic Studio, p. 172; 1903.
[201] Kerl-Cramer-Hecht, p. 1509; 1907. Keramic Studio, p. 172; 1903.
[202] Kerl-Cramer-Hecht, p. 1085; 1907.
[203] Trans. Am. Cer. Soc., 5, p. 293; 1903.
[204] Kerl-Cramer-Hecht, pp. 1004, 1006, 1007; 1907.
[205] Collected Writings. Am. Cer. Soc., Trans., p 733; 1902.

The shrinkage will be a minimum when that proportion of deflocculant is used which produces maximum sol formation; it will increase with either smaller or larger amounts of reagent, and, in the latter case, may or may not reach, or exceed, that of the untreated material.

The effect of substances which act only as coagulants, upon a mixture containing some sol, is to increase the shrinkage. Substances that act only as thickeners and adhesives will tend to increase the shrinkage.

Ammonia is the only substance which in general acts only as a deflocculant; though in sufficiently great concentrations, even it produces coagulation. The other alkalies and alkaline precipitants act as deflocculants or coagulants according to the amount used. The simple mineral acids and most salts act as coagulants only. Silicate of soda is a deflocculant, thickener, and adhesive. Gum arabic and gum tragacanth appear to be thickeners and adhesives only; sour milk appears to be both a thickener and coagulant.

19. SHRINKAGE REGULATION

According to Geijsbeek[206]—

> An engobe on biscuit body should be so compounded that its shrinkage should be nothing, because the body on which it is applied does not shrink any more. An engobe for stoneware has to shrink at the same rate as the shrinkage of the stoneware body on which it is applied.[207] In making an engobe on green ware, we have to use some plastic clay.

Many have observed that the result of the use of highly colloidal materials (obtained either naturally or by very fine grinding) is to increase the bulk[208] and shrinkage [209] of glazes, thus producing cracking,[210] crawling,[211] peeling,[212] and rolling up,[213] or beading [214]

---

[206] Trans. Am. Cer. Soc., 6, p. 210; 1904.

[207] Seger: Collected Writings, Am. Cer. Soc. Trans., pp. 438, 622, 626, 628; 1908. Stull: Trans. Am. Cer. Soc., 12, p. 713; 1910. Bourry: Treatise on Ceramic Industries, p. 236; 1901.

[208] Ashley, Trans. Am. Cer. Soc., 9, p. 56; 1907.

[209] Hottinger, Trans. Am. Cer. Soc., 2, p. 132; 1900. Ashley, ibid., 12, p. 444; 1910.

[210] Seger, Collected Writings, Am. Cer. Soc. Trans., p. 589; 1902. Carter, Trans. Am. Cer. Soc., 5, p. 293; 1903. Geijsbeek, ibid., 4, p. 51; 1902.

[211] Purdy, ibid., 4, pp. 66, 70, 74; 1902.

[212] Carter, ibid., 5, p. 293; 1903.

[213] Seger, Collected Writings, p. 1147. Ashley, Trans. Am. Cer. Soc., 9, p. 56; 1907.

[214] Carter, ibid., 5, p. 293; 1903.

when too thickly applied[215] or when sweated in drying or in the early stages of burning.[216] The ill effects of sweating are probably due to the condensation of acids from the combustion gases upon the glaze or engobe.[217]

These defects may be overcome by selecting less plastic clays,[218] by calcining some of the clays, by using less clay ,[219] by adding granular materials,[220] by coarser grinding, by dry grinding,[221] by diluting the glaze, soaking the bisque ware, or dipping the green ware at an earlier stage of drying [222] (any of which makes the layer taken up thinner),[223] or by using a deflocculant.[224]

Deflocculants may be used in glazes or engobes to be applied to bisque bodies, as they decrease the amount of colloidal material and so cut down shrinkage. Their use is not common for this purpose. The quantities giving the best effects are so minute that an experimenter would ordinarily use too much, and so entirely miss the effect.

As some substances are either deflocculants or coagulants, according to the amounts used and the nature of the mixture to which they are applied,[225] it is not always easy to decide which is the case with an example taken from ceramic literature; but generally enough reagent is used to cause coagulation.

20. LACK OF ADHESION

On the other hand, some very similar faults occur when there is a deficiency of colloids in the glaze or engobe or when the colloids present are in the sol form. A lack of adhesion [226] to the ware may be due to a lack of gel in the glaze, to dust or oil on the

---

[215] Seger, Collected Writings, p. 589. Purdy, Trans. Am. Cer. Soc., **4**, p. 74; 1902. Carter, ibid., **5**, p. 293; 1903. Binns, ibid., **11**, p. 170; 1909.

[216] Purdy, ibid., **4**, p. 74; 1902. Stull, ibid., **12**, p. 721; 1910.

[217] Seger, Collected Writings, p. 217.

[218] Geijsbeek, Trans. Am. Cer. Soc., **4**, p. 52; 1902. Jackson, ibid., **11**, p. 171; 1909.

[219] Purdy, ibid., **4**, pp. 66, 74; 1902; **11**, p. 169; 1909. Binns, ibid., **11**, p. 170; 1909.

[220] Geijsbeek, ibid., **4**, p. 51; 1902. Purdy, ibid., **11**, p. 169; 1909. Kerl-Cramer-Hecht, p. 1187; 1907. Seger, Collected Writings, p. 1147. Binns, Trans. Am. Cer. Soc., **11**, p. 170; 1909.

[221] Carter, ibid., **5**, p. 293; 1903.

[222] Stull, ibid., **12**, p. 714; 1910.

[223] Seger, Collected Writings, p. 439. Shaw, Trans. Am. Cer. Soc., **11**, p. 121; 1909. Purdy and Brown, ibid., **11**, p. 237; 1909.

[224] Stull, ibid., **12**, pp. 718, 763; 1910.

[225] Stull, Trans. Am. Cer. Soc., **12**, p. 723; 1910.

[226] Seger, Collected Writings, pp. 623, 627.

ware,[227] to crystals of soluble salts at the surface of the ware,[228] to a lack of porosity of the body,[229] or to a lack of fluxes to cause the fired engobe to adhere.[230] Such faults are known as crawling,[231] scaling,[232] flaking,[233] beading,[234] and especially as dusting[235] or rubbing.[235]

They are obviated by adding adhesives such as gum tragacanth,[236] ball clay in place of china clay,[237] plaster of Paris before setting,[238] mucilage,[239] dextrine (3 per cent)[240] glue,[241] sirup or sugar water,[242] glycerin,[243] ox blood,[244] potato starch (2 per cent),[245] by coagulating the sol (which is in a way equivalent to adding adhesives) by such coagulants as borax in excess,[246] sodium carbonate in excess,[247] plaster of Paris,[248] salsoda (2 per cent),[249] magnesium sulphate,[250] or boric acid.[251]

In some cases it is thought by the users that these added salts themselves act as adhesives;[252] that when they crystallize the crystals hold the whole together.[253] This is possible, but in most cases unlikely.

---

[227] Ibid., pp. 588, 627, 1115. Purdy, Trans. Am. Cer. Soc., **4**, p. 74; 1902. Stull, ibid., **12**, p. 713; 1910.

[228] Seger, Collected Writings, p. 1147; 1902. Hottinger, Trans. Am. Cer. Soc., **9**, p. 520; 1907.

[229] Seger, Collected Writings, p. 588.

[230] Ibid., p. 450.

[231] Purdy, Trans. Am. Cer. Soc., **5**, pp. 161, 162; 1903. Barringer, ibid., **5**, p. 265; 1903. Stull, ibid., **10**, p. 241; 1908.

[232] Seger, Collected Writings, p. 589. Hottinger, Trans. Am. Cer. Soc., **9**, p. 520; 1907.

[233] Stover, Trans. Am. Cer. Soc., **11**, p. 172; 1909. Stull, ibid., **10**, p. 220; 1908; **11**, p. 607; 1909.

[234] Purdy, ibid., **5**, p. 162; 1902. Stephani, ibid., **11**, p. 615; 1909. Stull, ibid., **11**, pp. 611, 615; 1909.

[235] Purdy, ibid., **4**, p. 75; 1902.

[236] Purdy and Krehbiel, Trans. Am. Cer. Soc., **9**, p. 337; 1907. Worcester, ibid., **10**, pp. 452, 482; 1908. Orton, ibid., **10**, p. 561; 1908 (3 g per l.). Taxile Doat, Keramic Studio, p. 78; 1904.

[237] Purdy, Trans. Am. Cer. Soc., **4**, p. 75; 1902. Stull, ibid., **11**, p. 607; 1909. Seger, Collected Writings, p. 624.

[238] Purdy, Trans. Am. Cer. Soc., **4**, p. 75; 1902.

[239] Seger, Collected Writings, pp. 471, 472. Binns, Trans. Am. Cer. Soc., **5**, p. 52; 1903.

[240] Stull, ibid., **10**, p. 220; 1908.

[241] Stephani, ibid., **11**, p. 615; 1909.

[242] Seger, Collected Writings, p. 628.

[243] Ibid., pp. 631, 634.

[244] Ibid., p. 1115.

[245] Kerl-Cramer-Hecht, p. 1102; 1907.

[246] Purdy, Trans. Am. Cer. Soc., **4**, p. 75; 1902; **5**, p. 162; 1903. Stull, ibid., **10**, p. 241; 1908; **11**, pp. 611 615; 1909. Kerl-Cramer-Hecht, p. 1102; 1907.

[247] Purdy, Trans. Am. Cer. Soc., **4**, p. 75; 1902. Stull, ibid., **11**, p. 615; 1909.

[248] Purdy, ibid., **4**, p. 75; 1902. Stull, ibid., **11**, p. 615; 1909. Stephani, ibid., **11**, p. 615; 1909.

[249] Purdy, ibid., **5**, p. 161; 1903.

[250] Shaw, ibid., **11**, p. 521; 1909.

[251] Stephani, ibid., **11**, p. 615; 1909.

[252] Barringer, Trans. Am. Cer. Soc., **5**, p. 265; 1903; 5 per cent sodium carbonate, borax, calcium sulphate, cobalt chloride. Orton, ibid., **10**, p. 561; 1908; sodium carbonate, borax, plaster of Paris.

[253] Purdy, ibid., **4**, p. 75; 1902.

Bleininger [254] suggested that, in some of these cases, the added salt may undergo a Sorel cement reaction with part of the glaze.

That the action of adhesives upon clays is essentially different from that of deflocculants and coagulants was demonstrated by treating a ball clay, a china clay, a feldspar, and a quartz with gum tragacanth. In one series the gum used was dissolved in cold water; in the other series hot water was used. The solution in cold water was very imperfect; the gum would settle with the clay, etc., and by its own bulk increased the bulk of the sediment. The solution in hot water seemed homogeneous, and the gum was not a constituent of the sediment. It did not prevent the sedimentation of the clay, though the process was less rapid because of the increased viscosity of the medium. But in none of these series with gum tragacanth was any deflocculant or coagulant effect noticed. Fickendey [255] found starch to be without influence.

Feldspar, because of its alkalinity, tends to assume the sol state. It has been found to cause cracking,[256] crawling,[256-257] and beading.[257] The remedies proposed are decrease of feldspar,[257] replacement by Cornwall stone [256] (which, having been subjected naturally to leaching, has less readily soluble matter), and addition of whiting [257] (the varities of which used in potting usually have a notable gel content).

In some cases, owing to the refractoriness of a Bristol glaze or engobe, it fails to adhere in firing. The remedy in such cases is to add fluxes [258] or to decrease the proportion of constituents which are present in too great amount to exert their best fluxing action.[259] Some of the additions made for other purposes are also fluxes, such as borax, soda ash, etc. The refractoriness of an excess of zinc oxide may explain the following observations:

Purdy [260] says: "To zinc many ascribe all the responsibility for the manifestations of crawling." Later he says that it may be due to too high zinc oxide. Stephani [261] says beading in the kiln

---

[254] Private notes on lectures by Edward Orton, jr., at Ohio State University; 1905.

[255] J. Landw., **54**, p. 345; 1906.

[256] Fackt. Trans. Am. Cer. Soc., **11**, p. 615; 1909.

[257] Purdy, ibid., **5**, p. 162; 1903.

[258] Seger, Collected Writings, p. 589. Private notes on a lecture by R. T. Stull; 1905. Bourry, Treatise on Ceramic Industries, p. 236; 1901.

[259] Stull, Trans. Am. Cer. Soc., **12**, p. 764; 1910.

[260] Purdy, ibid., **4**, p. 70; 1902.

[261] Ibid., **11**, p. 615; 1909.

may be prevented by replacement of zinc oxide by magnesia. Eleod [262] overcame flaking by calcining a portion of glaze containing all the zinc oxide.

Purdy [263] stated that "BaO (used as barium carbonate) is more potent than CaO (used as whiting) in producing flakes."

Seger [264] added glaze to an engobe to increase its adhesion to the fired body.

Stull [265] has explained in detail the remedies for the various defects of engobes. From his cases 16 and 24 it appears that some engobes sinter onto the ware, and then if subjected to still higher temperatures the additional fire shrinkage causes them to craze or flake off if not very firmly attached by the fluxes.

H. MISCELLANEOUS APPLICATIONS

A few miscellaneous applications of the principles discussed in this paper are included; some are no more than suggestions, but they are given for what they are worth.

21. WATER PURIFICATION

Clays may be present as an impurity of water supplies, or they may be used as a means of removing other impurities, such as mineral bases that produce incrustations in boilers.

This twofold rôle is readily explicable on the views advanced in this paper. Roughly speaking, when the clay content of a river is high the soluble salt content is low, and when the soluble salt content is high the clay content is low. As the lowest amount of soluble salts and highest proportion of suspended matter come at the high-water stage of a river, the suspension might be and usually is attributed to the extra carrying power of water with the increased velocity that accompanies a high stage. But with a high stage the water of a river is greatly diluted. A sufficient degree of dilution, it has been shown (p. 55), will enable even still water to hold in solution or suspension very decided amounts of soluble clay colloids. The solvent action at least supplements the mechanical tendency to suspension.

---

[262] Ibid., 11, p. 174; 1909.

[263] Trans. Am. Cer. Soc., 11, p. 169; 1909.

[264] Collected Writings, pp. 624, 627, 629.

[265] Trans. Am. Cer. Soc., 12, pp. 763, 764; 1910. See also Bourry, Treatise on Ceramic Industries, pp. 295–298, 315–316; 1901.

Atterberg [266] said:

Spring waters in general contain some salt and therefore are usually clear, even when they come from clayey soils. The waters of mines and streams are, on the other hand, weaker in salts and always turbid with clay particles.

Schloesing [267] said:

It is then to the presence or to the absence of these salts that it appears natural to attribute the limpidity or the troubled character of the filtered liquid.

Further: [268]

There are rivers that are habitually turbid with soil, among others the Garonne and the Loire; analysis shows that their waters are too poor in salts of the alkaline earths. According to M. H. Sainte-Claire Deville, the content of lime and magnesia of our principal rivers are, on the average, the following:

	Seine	Rhone	Garonne	Loire
	mg	mg	mg	mg
Lime (per liter)	104.0	63.4	36.1	27.0
Magnesia (per liter)	1.3	4.5	1.6	2.9

These figures, approaching those given above as necessary to produce coagulation, show that the water of the Seine ought to deposit its soil in a few hours; those of the Rhone in a sensibly longer time; those of the Garonne and of the Loire do not clear.

Public water supplies should contain 70 to 80 mg of lime per liter in order to clarify spontaneously in sedimentation basins.

(*a*) USE OF COAGULANTS TO REMOVE CLAYS

The natural settling of a turbid water is usually too slow a process for economical work at purification plants. To many waters which exhibit permanent turbidity are added salts of those bases which form insoluble precipitates with clay sols; for instance, addition of lime or alum effects a rapid sedimentation.

The reagent chosen should form a coagulum of minimum solubility and a soluble reaction product with a minimum of undesirable properties. For example, the effect of alum in coagulating the sodium sol may be written

$$\underset{\text{(soluble)}}{Al_2SO_4} + \underset{\text{(soluble)}}{\text{Na sol}} \rightarrow \underset{\text{(insoluble)}}{\text{Al gel}} + \underset{\text{(soluble)}}{Na_2SO_4}$$

[266] Landw. Vers. Sta., 69, pp. 93–143; 1908.

[267] Encyclopedie Chimique, M. Fremy. Tome X. Applications de Chimie Organique. Contribution a l'Etude de la Chimie Agricole, par M. Th. Schloesing. Paris, Vve Ch. Dunod, Editeur, Quai des Augustins, 49; 1888. Du sol, p. 62.

[268] Ibid., p. 65.

Some reagents, while forming the desired insoluble coagulum, give poisonous soluble reaction products or are themselves poisonous, and hence may not be used (e. g., lead nitrate).

In practice it is necessary to leave some soluble salt in the water in place of the clay sol removed. In substantially all turbid waters there are present bases which, under proper conditions, can coagulate clay sols;[269] but to effect satisfactory clarification, it is necessary always to add a sufficient excess of reagent.

(*b*) USE OF CLAY TO REMOVE BASES

Clay has also been used for many years to remove bases such as iron from water supplies. The reaction involved is again a simple exchange of bases, altogether analogous to the reaction with alum mentioned above. If we assume that a partial removal of the soluble iron salts is sufficient, the water will probably be clear at the end of the process; but if an excess of soluble clay is used the water will be left turbid. Incidentally it may be noted that turbidity of quiet water is an indication that the water contains a very small proportion of soluble salts.

If good mechanical stirring arrangements are available, an acid clay might be added to a water containing iron salts without producing permanent turbidity; this may be illustrated by the following scheme:

$$\underset{\text{(soluble)}}{FeSO_4} + \underset{\text{(insoluble)}}{H\ gel} \rightarrow \underset{\text{(insoluble)}}{FeGel} + \underset{\text{(soluble)}}{H_2SO_4}$$

J. G. Roest [270] found 1.5 per cent potter's clay sufficient to precipitate suspended matter from the waste waters of pulp mills. The precipitate has an appreciable value as a fertilizer.

It is a common practice to use kaolin as a precipitant where, in most cases, the less expensive, more plastic clays would be more effective, since the colloid content is the active agent.

22. ADDITION OF ACID DISINFECTANTS TO MODELING CLAYS

In preparing modeling clays, it is sometimes desirable to add a disinfectant (for use in public schools, etc.). In such cases a compound of acid nature is to be preferred, in order that the plasticity shall not be lessened by the addition.

---

[269] For example, see R. B. Dole: The Quality of Surface Water in the United States. I. Analyses of Water East of the 100th Meridian. U. S. Geological Survey, Water-Supply Paper 236, 1909.

[270] Chem. Weekblad, 6, pp. 106–109; Chem. Zentr., 1909, I, 796; C. A., 4, p. 3110; 1910.

23. USE OF SOAP FOR CLEANSING

On a previous page (p. 75) are given the results of a series of experiments on the effect of soap on clays. From these the practical conclusion, as applied to laundry work, is that a given soap will do the best work with dirt of the nature of clay on cloth when a particular concentration of soap in water is used. A less concentration will be ineffective in loosening dirt. A greater concentration, as when soap is rubbed on a badly soiled spot, though reaction takes place, is not at first effective because of salting out; but when the cloth is rinsed out in pure water the concentration is thereby diminished, and so passes momentarily through the strength giving the strongest solvent effect. Practical experience has shown that a mixture of solvents is often more effective than soap alone, for example; gasoline in the soapy water assists with greasy dirt; borax, soda, etc., are of value in particular cases.

24. CLEANING BRICK FRONTS

The cleaning of the fronts of brick buildings is often a vexatious problem in smoky cities. According to the British Clayworker,[271] the "present foolish custom of sandblasting brick fronts" leaves all brick, excepting the very hardest sorts, in such condition that they are soon dirtier than before. "A soap wash, followed by an acid solution," would serve the purpose better, and at one-fifth of the amount expended. These conclusions were verified by means of a series of comparative tests made on the walls of the old Arsenal buildings at the Pittsburg Testing Plant. Cold solutions (0.5, 1, 2, 5, and 10 per cent) of a common laundry soap (Colgate's Octagon) were used, and the conditions of application were made as uniform as possible. From these tests it appears that the 1 per cent solution gives the best results, as in this case nearly all of the soot was removed, and the bricks had nearly regained their original red color. The effect of adding kerosene to the 1 per cent soap solution was also tried; but it was found that even with 1 per cent kerosene added the results were not so good as with the soap solution alone.

[271] British Clayworker, 19, Brickbuilder, 25, 1910.

25. POLISHING PLATE GLASS

Plate glass is polished with water and rouge, an iron oxide prepared by calcining sulphate of iron. It is found in practice that the rouge does not work well unless it has a certain acidity, and that much of it is carried off by the waste waters from the polishing process. Now the water used with the rouge dissolves the alkali from the freshly exposed face of the glass; so that it is easily conceivable that the alkali first neutralizes the acidity of the rouge, then reaches such a concentration as to cause the suspension and loss of the rouge. This suggests that by a continuous supply of acid during glass polishing, the alkali could be kept neutralized; the rouge would then be kept in a coagulated condition, and so would not be wasted so readily by outflowing water. It may, on the other hand, be true that the rouge now flowing away would not be of value for longer periods of use and that a more rapid attack by acid would give an inferior polish. However, the practicability of the suggestion could easily be tested.

26. FULLER'S EARTH

Fuller's earth may be defined as clay of especially high absorptive powers or colloid content. There are many varieties, and the possibilities of improving or regulating it are many. As its action is in many cases an exchange of bases, the first idea is to see to it that one's earth has the base best adapted to the specific purpose in view, either by selecting it or by treating with salts.

If it is not sufficiently porous for most effective working, it may be made so by heat treatment. This sets the colloids without destroying their reactivity in most cases. The structure of the gels of certain fuller's earths, however, is so much altered even by drying out at ordinary temperature as to make them worthless. This accounts for the differences of opinion noted in technical literature concerning the desirability or uselessness of heating fuller's earth. The silicate and the humus colloids are probably unharmed by heat, while the iron hydroxide, alumina, and silica colloids probably lose in activity. The point is worth investigation.

A concentrated fuller's earth may be prepared from any clay by dissolving out the colloid matter and recoagulating it. It is

possible that some clay washing plants may obtain an artificial fuller's earth as a by-product by coagulating the clay waters that ordinarily refuse to settle on standing, and now run to waste.

27. KAOLIN AND FULLER'S EARTH AS ANALYTICAL REAGENTS

Various clays have been employed as absorbents in agricultural analysis, e. g., kaolin in the determination of tannin in tanning extracts and liquors [272] and in tea,[273] and in the determination of alcohol in flavoring extracts;[274] fuller's earth, for the determination of caramel in vinegar,[275] vanilla,[276] etc.

In each case unexplained difficulties occur in practice, and the methods are looked upon with more or less suspicion. This is but natural, as the action of the clay in each case resides in a colloid constituent present in unknown amount (high with the fuller's earths, low with kaolins) and combined with more or less easily replaceable bases.

It would therefore seem advisable that for such determinations the same amount of colloid matter (as determined by the malachite green oxalate test, for example) should be taken each time, rather than equal weights of clay; further, that by treatment with appropriate salt solutions, those bases giving more favorable action should be put into the colloid matter.

According to Jennison: [277]

> When a solution of a dyestuff, more particularly the basic colors, is added to starch, clay, green earth, etc., a certain amount of coloring matter is taken up.

He does not consider the action as due to any chemical attraction, and condemns the colors produced as fugitive, lacking fullness and brightness. Hundeshagen, however, has found some dyes to be very strongly held by minerals. Further on Jennison [278] states that lakes formed with less than the theoretical amount of tannic acid are fugitive; yet a stable, satisfactory, though duller color, is obtained by using the theoretical amount. We have

---

[272] U. S. Dept. Agr., Bur. Chem., Bull., **99**, pp. 123, 124, 1906.
[273] Ibid., **107**, p. 150, 1907.
[274] Chemist and Druggist, p. 178, 1904. J, Ind. Eng. Chem., **1**, p. 94, 1909.
[275] J. Am. Chem. Soc., **29**, p. 75, 1907. U. S. Dept. Agr., Bur. Chem., Bull., **105**, p. 23, 1907.
[276] Ibid., **132**, pp. 55–58, 1910.
[277] Francis H. Jennison: The Manufacture of Lake Pigments from Artificial Colors. London: Scott, Greenwood & Co., p. 73; 1910.
[278] Ibid., p. 74.

observed that a dyed clay is brilliant or dull according to the whiteness or darkness of the original clay. We consider the formation of a clay lake as truly that of a chemical compound as is the formation of a tannic-acid lake. Jennison also says: [279]

> The formation of lakes from basic colors is dependent on the combination of the amido or basic group or groups in the color molecule with various acids producing insoluble salts of the coloring matters.

If, then, the colloid-acid radicals of good colored clays are dissolved by suitable deflocculants, and decanted from the crystal sediments, they should give pure lakes on adding first the dye and then sufficient acid to neutralize the alkali bases present. The coagulum may be treated by usual methods to incorporate it with oil, etc.

28. PAINTS

Natural pigments, such as ochre or sticky hematite, for example, may be deflocculated, decanted from the gritty sediment, coagulated, and incorporated with oil. Such a process, by its avoidance of grinding, may prove of economic importance in paint manufacture.

Zachariah Cartwright [280] has a clearly conceived patent for preparing "solutions or pseudosolutions" of hydrated oxides, such as those of iron, manganese, chromium, and the like, ordinarily insoluble in water, consisting in mixing the finely powdered oxide with an aqueous solution of soap. The oxides are insoluble in solutions containing 10 per cent or more of soap. Around 5 per cent is a "critical" point; weaker solutions dissolve or suspend the oxide; 1 per cent and 0.5 per cent give solutions of great permanency. The permanency may be increased or the solution protected against excess of alkali by adding sugar, etc., to prevent precipitation. This solution may be used for dyeing fabrics, etc. "Fixing agents such as gum may be incorporated with the oxide solution and the latter may then be evaporated down to any required degree of concentration." The 1 per cent solution may be decanted from impurities, such "totally insoluble" substances as silica, etc., and then coagulated, preferably by acid, though excess of alkali may be used. When 5 per cent soap solution is used, there is obtained a temporary or "time

[279] Ibid., p. 76.

[280] British Patent 24842 (Nov. 18, 1908).

solution," from which everything is precipitated in two hours. In this case the impurities fall first, then the least hydrated oxides, and in succession, the more highly hydrated oxides. These form a distinct layer upon the impurities, and may be readily scraped off. As the colors of the hydrated iron oxide vary from deep red to light yellow with the degree of hydration, it is possible to match any desired sample by watching the progression of shades from dark red to yellow, interrupting the sedimentation and decanting when the color matches the sample. Seven per cent is the maximum amount of oxide that it is advisable to suspend, on account of impairing fluidity. After precipitating the decanted solution with acid, it is washed and dried, when it is ready for the market.

In conclusion, it would seem that the idea of the exchange of bases and the other ideas advocated in this paper might be of service in connection with questions of fertility and its dependence on the nature of the soil, the fertilizers used, etc. For instance, lime or any other reagent from a fertilizer might have the effect of putting into solution bases which are combined with the clay colloids; according to the composition of the resulting soil solution, the effect would be stimulating to vegetation or the reverse.

I. ACKNOWLEDGMENTS

In this investigation I have been very fortunate in having the unfailing support and helpful suggestions of my chief, Mr. A. V. Bleininger, and the hearty good will of my associates, especially Mr. W. E. Emley, who assisted me for some months, and Mr. S. E. Young, who spent a shorter period on the work.

WASHINGTON, November, 1911.[281]

[281] Final revision of manuscript completed at this date.

PUBLICATIONS ISSUED BY THE BUREAU OF STANDARDS, DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

1. The Effect of Preliminary Heat Treatment upon the Drying of Clays (53 pp.) ..... *A. V. Bleininger*
2. The Strength of Reenforced Concrete Beams. Results of Tests of 333 Beams (first series) (200 pp.) ..... *R. L Humphrey and L. H. Losse*
3. Tests of Absorptive and Permeable Properties of Portland Cement Mortars and Concretes, Together with Tests of Damp Proofing and Waterproofing Compounds and Materials (127 pp.) ..... *Rudolph J. Wig*
4. The Effect of Added Fatty and Other Oils upon the Carbonization of Mineral Lubricating Oils (14 pp.) ..... *C. E. Waters*
5. The Effect of High-Pressure Steam on the Crushing Strength of Portland Cement Mortar and Concrete (25 pp.) ..... *R. J. Wig*
6. The Determination of Chromium and Its Separation from Vanadium, in Steels (6 pp.) ..... *J. R. Cain*
7. The Testing of Clay Refractories, With Special Reference to Their Load Carrying Capacity at Furnace Temperatures (78 pp.) ..... *A. V. Bleininger and G. H. Brown*
8. A Rapid Method for the Determination of Vanadium in Steels, Ores, etc., Based on Its Quantitative Inclusion by the Phosphomolybdate Precipitate (20 pp.) ..... *J. R. Cain and J. C. Hostetter*
9. The Density and Thermal Expansion of Linseed Oil and Turpentine (27 pp.) ..... *H. W. Bearce*
10. The Melting Points of Fire Bricks (— pp.) ..... *C. W. Kanolt*
11. Comparison of Five Methods Used to Determine Hardness (27 pp.) . *R. P. Devreis*
12. Action of the Salts in Alkali Water and Sea Water on Cements (157 pp.) ..... *P. H. Bates, A. J. Phillips, and Rudolph J. Wig*
13. The Evaporation Test for Mineral Lubricating and Transformer Oils (13 pp.) ..... *C. E. Waters*
14. Legal Specifications for Illuminating Gas (31 pp.) ... *E. B. Rosa and R. S. McBride*
15. Surface Insulation of Pipes ..... *B. McCollum and O. S. Peters*
16. The Manufacture of Lime ..... *W. E. Emley*
17. The Function of Time in the Vitrification of Clays ..... *G. H. Brown and G. A. Murray*
18. Electrolysis in Concrete ..... *E. B. Rosa, Burton McCollum, and O. S. Peters*
19. Physical Testing of Cotton Yarns (31 pp.) ..... *W. S. Lewis*
20. Determination of Sulphur in Illuminating Gas (46 pp.) ..... *R. S. McBride and E. R. Weaver*
21. The Dehydration of Clays (23 pp.) ..... *G. H. Brown and E. T. Montgomery*
22. The Effect of Overfiring Upon the Structure of Clays ..... *A. V. Bleininger and E. R. Montgomery*
23. The Technical Control of the Colloidal Matter of Clays (118 pp.) ..... *H. E. Ashley*
24. Determination of Phosphorus in Steels Containing Vanadium (11 pp.) .... *J. R. Cain and F. H. Tucker*

CIRCULARS

No. 2. Measurement of Length and Area, Including Thermal Expansion.
No. 3. Verification of Standards of Mass.
No. 4. Verification of Standards of Capacity.
No. 5. Testing of Clinical Thermometers.

No. 6. Fees for Electric, Magnetic, and Photometric Testing.
No. 7. Pyrometer Testing and Heat Measurements.
No. 8. Testing of Thermometers.
No. 9. Testing of Glass Volumetric Apparatus.
No. 10. Legal Weights (in pounds) per Bushel of Various Commodities.
No. 11. The Standardization of Bomb Calorimeters.
No. 12. Verification of Polariscopic Apparatus.
No. 13. Standard Specifications for the Purchase of Incandescent Lamps.
No. 14. Samples of Analyzed Irons and Steels—Methods of Analysis.
No. 15. A Proposed International Unit of Light.
No. 16. The Testing of Hydrometers.
No. 17. Magnetic Testing.
No. 18. Standard Gauge for Sheet and Plate Iron and Steel.
No. 19. Standard Density and Volumetric Tables.
No. 20. Testing of Electrical Measuring Instruments.
No. 21. Precision Measurements of Resistance and Electromotive Force.
No. 22. Standard Specifications for Transformers, Oil-immersed, Self-cooled, 60-cycle, 2200 Volts.
No. 23. Standardization of Electrical Practice in Mines.
No. 24. Publications of the Bureau of Standards.
No. 25. Standard Analyzed Samples—General Information.
No. 26. Analyzed Iron and Manganese Ores—Methods of Analysis.
No. 27. The Testing and Properties of Optical Instruments.
No. 28. The Determination of the Optical Properties of Materials.
No. 29. Announcement of a Change in the Value of the International Volt.
No. 30. Lime: Its Properties and Uses.
No. 31. Copper Wire Tables.
No. 32. State and Municipal Regulations for the Quality, Distribution, and Testing of Illuminating Gas.
No. 33. United States Government Specification for Portland Cement.
No. 34. The Relation of the Horsepower to the Kilowatt.
No. 35. Melting Points of Chemical Elements.
No. 36. The Testing and Properties of Electrical Condensers.
No. 37. Electric Wire and Cable Terminology.
No. 38. The Physical Testing of Mechanical Rubber Goods.
No. 39. Specifications for and Measurement of Standard Sieves.
No. 40. Sodium Oxalate as a Standard in Volumetric Analysis.
No. 41. Testing and Properties of Textile Materials.
No. 42. Metallographic Testing.
No. 43. The Metric Carat.
No. 44. Polarimetry.
No. 45. The Testing of Materials.