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SILICIC ACID, ITS INFLUENCE AND REMOVAL IN WATER PURIFICATION

BY

OTTO MITCHELL SMITH

B. S. Drury College, 1907
M. S. University of Illinois, 1918

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

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SILICIC ACID, ITS INFLUENCE AND REMOVAL IN WATER PURIFICATION.

By Otto Mitchell Smith.

INTRODUCTION.

Little attention has been paid to the presence of silicic acid in natural waters except in cases where its content is quite high. It is universally present but usually in amounts less than 100 parts per million. It is more prevalent in the surface waters of the Mississippi Valley[16] especially on the western watershed. It is found in as large amounts as 1,163 parts per million at Cesenate, Italy,[46] 1,230 parts per million at Deep Rock Springs, Oswego, N. Y.,[13] and 923 parts per million at the Yellowstone National Park.[37]

Silica in solution usually occurs as colloidal silicic acid and[32] in combination with the basic elements. Its presence in water used for steam purposes has always been considered detrimental and conducive to the formation of a hard flinty scale. Besides forming an undesirable scale, A. Goldberg[21] believes silicic acid is responsible for many boiler disturbances. When the acid is distilled with water solutions of nitrates and chlorides, nitric and hydrochloric acid are liberated.

Turbidity in water is generally caused by the suspensions of very finely divided mineral matter, mainly clay. Clay may be defined as a mixture of minerals of which the most representative members are the silicates of aluminium, iron, the alkalies and alkaline earths. The hydrated aluminium silicate, kaolin. $(Al_2O_3,2SiO_2,2H_2O)$ is the most abundant compound.

There are many cases in the literature emphasizing the difficulties of clarifying water containing finely dispersed clay particles. Fuller[20] in 1898 found at times a turbidity which was difficult to coagulate with an abnormal consumption of alum. Ellms,[17] Black and Veatch,[7] and Catlett[12] show the difficulties in the treatment of such water.

THEORETICAL AND HISTORICAL PART.

As silicic acid and clay suspension are considered as sol and suspensoid respectively a brief discussion of the general properties of colloids is pertinent. Burton[11] defines a colloid solution "as a suspension, in a liquid medium, of fine particles which may be graded down from those of microscopic to those of molecular dimensions; these particles may be either homogeneous matter, solid or liquid, or solutions of a small percentage of the medium in an otherwise homogeneous complex. The one property common to all such solutions is that the suspended matter will remain almost indefinitely in suspension in the liquid, generally in spite of rather wide variations in temperature and pressure; the natural tendency to settle, due to the attraction of gravitation, is overbalanced by some other force tending to keep the small masses in suspension."

With the development of the ultra microscope and the investigations of Zsigmondy and Siedentopf[53] it is possible to show that there is a continuous gradation in the size of particles of the disperse phase from 1.70×10^{-7} cm. in diameter to that of visible organisms and this leads to the belief that there is a gradation in size from the smallest of these particles to the molecules.

Tyndall[47] (1869) found that small particles could be revealed by the lateral diffusion of a beam of light traversing a solution. Applying this method Linder and Picton[29] were able to grade the sizes of particles of colloidal arsenous sulfide.

Wiedemann[51] (1852) and Quincke[39] (1861) confirmed the discovery of Reuss that a liquid would move across a diaphragm or through a capillary tube towards one of the electrodes when a current is passing. The migration of sols in the electric field was first observed by Linder and Picton. As suspended particles carry electrostatic charges, it seems logical to conclude that as result of these charges, suspended particles whose masses are small enough are equally distributed throughout the liquid, and prevented from ever settling because of the mutual repulsion of the charges. Such a solution is called a sol in contradistinction to the jelly-like form called a gel. When the dispersion of relatively insoluble particles is not so great as to become macroscopically invisible—such a system is termed a suspension. The change of an irreversible hydrosol to an amorphous precipitate wherein there is no Brownian movement is known as coagulation.

Schultz,[43] and Linder and Picton[29] showed that the coagulating power depends upon the valency of the metal ion and according to later workers, equivalent solutions containing monovalent, bivalent and trivalent metallic ions would possess, whatever the nature of the anion, coagulating powers in the ratio of $1:35:1023$ which is nearly represented

by the formulae $1:x:x^2$. In 1899 Hardy[22] found that the concentration of the acid necessary for coagulation of electronegative particles and of alkali for the coagulation of electropositive particles is determined by the laws of ordinary chemical equilibrium.

Burton,[10] adding graduated amounts of aluminium sulfate $Al_2(SO_4)_3$ to a negative sol, found that there was a decrease and even a reversal of the charge. Thus if one is able to pass from a negative sol to a positive sol there must be a point of zero potential—"isoelectric point." Hardy[23] suggests that the coagulation of colloids by electrolytes takes place when the particles have their charges neutralized by the adsorption of oppositely charged ions of an electrolytic solution and at the isoelectric point. His previously published conclusions were[24] that the conditions which determine coagulation are: (1) concentration of colloid, (2) temperature, (3) the nature of the ion, and (4) that the action is additive if the ions are of the same valency and "subtractive" if of different valencies, as the one inhibits the other.

Crum, [15] Linder and Picton, [29] and Whitney and Ober,[50] have established the fact that during the process of coagulation a portion of the electrolyte is always adsorbed by the coagulum and that amount is proportional to the electrochemical equivalents of the anion.

Lottermoser,[28] Blitz,[9] and Billitzer[5] demonstrated that colloids of opposite sign precipitate each other; that there is an optimum of precipitating action shown for certain proportions of colloid and that, if in any case these favorable proportions are exceeded on either side, no precipitation occurs; and that the direction of migration of the whole under the influence of the electric current is the same as that of the colloid in excess. This leads to the subject of protective colloids. Many organic colloids when added in comparatively minute quantities to suspensoids have the power of preventing the coagulation of the system.

PROPERTIES OF SILICIC ACID AND CLAY SUSPENSIONS.

Silicic Acid.

This colloid possesses the properties common to its class. In concentrated solutions it is unstable, but below 1 per cent it is stable for years. It has not been prepared free from electrolytes; its molecular weight is about 49,000. Billitzer[4] and Fleming[19] found it amphoteric, carrying a negative charge in akaline and a positive charge in acid solutions. Fleming's data, converted into terms of hydrogen ion concentration, indicate that the isoelectric point lies between a P_h value of 13.6 and 13.9, which is not in accordance with facts. It exhibits the Tyndal effect and is precipitated by electrolytes and positive colloids. The

coagulation from dilute solution is irreversible. Hardy[25] determined that the coagulating power of electrolytes, which precipitate a solution of about 1/120 normal silicic acid, varies with the cation, the anion having little effect. Of these aluminium sulfate was the most active and sodium salts least. It is also coagulated within a short time by copper sulfate, cadmium nitrate, calcium, barium and strontium chlorides and carbonates, barium hydroxide, concentrated solutions of ammonium sulfate, dilute solutions of egg albumin, glue, basic dyestuffs, carbon dioxide gas and graphite.

Pappada[35] found that neutral salts only act at great concentrations but accelerate gelation (coagulation) according to the lyotope series.

$$SO_4 > Cl > NO_3; \text{ and}$$
$$Ca > Rb > K > Na > Li$$
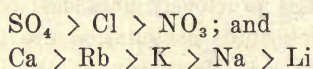
Silicic acid hydrosols do not act as a protective colloid for colloidal gold, but F. Kuspert[34] found that real protective action occurs at the moment the silicic acid is being precipitated. Silicic acid is precipitated in insoluble compounds by many chemical reagents, but this phase of the subject is not here discussed.

Properties of Clay Suspensions.

Clay suspensions are impure suspensoids. That they carry a negative charge is shown by Ellms[17] and Count Schwerin.[44] Very dilute suspensions exhibit the Tyndal effect. Ultra-microscopic observations have shown that the parties probably have a diameter of 1.7 x 10^{-7} cm. or less. According to Mayer, Schaffer and Terroine,[30] the addition of a trace of alkali decreases the size of negative suspended particles. Ashley[1] reviewing the work of many investigators came to the conclusion that the colloids in clay are non-crystaline, hydrated, gelatinous aluminium silicates; organic colloids; gelatinous silicic acid and hydrated ferric oxide; that aluminium hydrate, $Al(OH)_3$, is rarely present; and that the colloids of clay may carry into suspension solid particles that are wholly non-colloidal, according to the ordinary ideas, which particles may stabilize the clay sol. The work of Van Bemmelen[48] and Parmelee[36] indicates that the longer clay substance is washed the more colloidal it becomes; and that bodies are gradually hydrolyzed from crystaline compounds to soluble colloids.

Ionic Reactions.

A. Lottermoser[28] considers that "the hydrosol condition is only possible if one of the reacting ions ($I^- + Ag^+$, $Fe^{+++} + 3OH^-$, $SiO_2 + 2H^+$) remains up to a certain minimum amount in excess; than on

exceeding this limit the gel formation begins and becomes complete if equivalent amounts of the reacting ions are brought together. The hydrosol condition is bound up with the presence of certain ions in the colloid."

If sodium carbonate or an acid be added to a clay which has just enough calcium, Ca, to keep the colloid matter in the gel form, it may react according to the following equations:

$$Ca \; Gel + Na_2CO_3 = CaCO_3 + Na_2 \; Gel \; or$$

$$Ca \; Gel + H_2SO_4 = CaSO_4 + H_2 \; Gel.$$
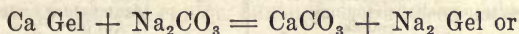
Foerster[18] first perceived the nature of the action of sodium carbonate on the clay gel. The chemical reactions of the colloidal matter in clay are remarkably similar to those of fats and soaps, the conditions of solubility and insolubility are parallel, but the colloidal matter of clay is more readily acted upon. Thus in a general way the salts of the fatty acid and the sodium, and ammonium sols of clay colloids are soluble in water. The free fatty acid and the acid gels are insoluble in water. The bivalent and trivalent bases form insoluble salts with soaps and insoluble gels with clays. Ashley[1] says "The proof of these conceptions is that they are not inconsistent with known facts about clays; that they have proved a most helpful and suggestive guide in planning investigations, and that they have never misled."

Effect of Electrolytes in Clay Suspensions.

Much valuable information is available in the ceramic research on the action of salts on clay suspensions. The effect of the salt varies with (1) the clay; (2) its previous mechanical treatment; (3) its age; (4) concentration; (5) degree of dispersion; (6) and the presence of colloids. The same electrolyte will have widely different effects, coagulating at one concentration and dispersing at another.

The work on slips by Rohland,[40] Mellor and Green and Baugh,[31] Weber,[49] Audley,[3] Kerr and Fulton,[33] Back,[6] Ashley,[2] Thomas,[45] and Bleininger,[8] shows that sodium, potassium and lithium hydroxides, carbonates, silicates and sulfides generally have a high dispersive or stabilizing power while the most active coagulating agencies are the salts of bivalent and trivalent metals. In Table 1 substances have been classified according to their action on clay slips:

TABLE 1—ACTION OF VARIOUS SUBSTANCES ON CLAY SLIPS.

Dispersing.	Irregular.	Neutral.	Usually coagulating.	Coagulating.
Univalent ions in the presence of high hydroxyl ion concentration Alkali salts of weak acids Strongly dissociated salts in small concentration (?) K₂SO₄, KHSO₄, KNO₃ Tannin Gallic acid Water glass Increasing addition tends to coagulate the slip	Na₂SO₃ Na₂SO₄ HgSO₄ MgSO₄ Na₃PO₄ Na(C₂H₃O₂) Ammonium gallate NaCl HCl Water glass Effect is to make the slip thinner CuSO₄ NH₄OH K₂SO₄Al₂(SO₄)₃.24 H₂O Small amounts thicken and increasing amounts thin the slip	alcohol dilute solutions of NaCl	Grape sugar Humic acid Borax NH₄Cl CaCl₂ CaSO₄ Ammonium urate Aniline Methyl amine Ethyl amine	Bivalent and trivalent ions in the presence of high concentration of hydroxyl ions. Bivalent ions in the presence of mono and bivalent ions

This arrangement seems to confirm Hardy's conclusions that the dispersion or coagulation of a negative sol varies inversely with the valency of the cation, and that the action of anion obeys the regular ionic laws.

The above data are obtained from concentrated clay suspensions where the ultimate end is the formation of a stable fluid slip of the highest clay content. In water purification on the other hand, the aim is the removal of a very small amount of clay from a large amount of water. It is clearly evident from a study of dilute clay suspensions and colloidal silicic acid, that the physical state of the substances and their chemical properties must be taken into consideration, together with the factors which influence them, i. e. (1) degree of dispersion; (2) the presence of the protective colloids and absorbed substances; (3) magnitude and kind of electric charge; (4) the liquid or dispersing medium; (5) the ionic content of the liquid; (6) the concentration; (7) the temperature, and (8) the speed of reaction of added substances.

METHODS OF EXPERIMENTATION, MATERIAL AND APPARATUS.

Briefly, the experimental work has developed along three lines: (1) the removal of silicic acid from solutions by electrolytes and colloids; (2) the effect of electrolytes on dilute clay suspensions, and (3) the effect of silicic acid on the coagulation of clay suspensions by alum in the presence of electrolytes.

Regeants.

Washed potters' clays were used in making the suspensions. No attempt was made to obtain the clay in a high state of purity. Those clays which remained in longest suspension were Tennessee Ball Nos. 3 and 1, number three being the best. Ashley[1] rates Tennessee No. 3 as having a relative colloid content of 95 to 100 per cent. The clay was freed from large particles and soluble salts by washing with distilled water and running the suspension through a Sharples super-centrifuge; the desired end was a suspension nearly like that in surface waters but as free as possible from electrolytes.

Characterization of Suspensions.

	By turbidimeter.	By weight.	Coefficient of fineness.
Tennessee No. 1 Ball	400*	325*	0.75
Tennessee No. 3 Ball	400	330	0.82

The No. 3 clay stood in contact with water in ordinary glass bottles over one year before being used. Kahlbaum's, Merck's, or analyzed chemicals were used without further purification. Colloidal silicic acid was prepared as directed by Graham and dialyzed with parchment paper until there remained only a trace of chloride. Determination of hydrogen ion concentrations was by the colorimetric method of Clark and Lubs.[14] Standards and indicators were made as directed using ordinary distilled water. The accuracy of the solutions was determined by checking against fresh permanent standards prepared by Clark and Lubs. The accuracy of the readings is within $\pm$ 0.1 pH value.

Measurements of Turbidity.

Standards for determining turbidities were prepared from the original clay suspensions and checked with a standardized turbidimeter. Turbidities were not read closer than 7 per cent. Fine particles of various sizes in suspension do not settle uniformly leaving a clear supernant liquid but are deposited in layers or zones. According to Wiley's formulae, which is determined for particles between 0.0001 and 0.02 millimeters in diameter, the rate of fall is proportional to the square root of the diameter of the particle that is $D = 0.0255 V.$[2]

Those particles of approximately the same diameter will settle together leaving a turbid suspension of finer particles above. In a suspension one can observe two or three of these zones of widely different turbidities and rates of sedimentation. Within a zone the turbidity is

* Expressed in parts per million.

fairly uniform, but different zones vary as much as 100 per cent within a vertical distance of ½ inch.

If the turbidity of an undisturbed suspension be taken at regular intervals at a fixed point, it will be noticed that the numerical values will be nearly constant for some time, then within a brief interval of time will change markedly as particles from a higher zone traverse the field of view. This phenomenon is well shown in many of the figures. As it was necessary to determine the turbidity of a suspension without disturbing the liquid, the following method was devised. A stereopticon equipped with a 500 watt lamp was adjusted to yield a slightly diverging cone of light. Two screens each having four holes 3/16 inches in diameter were inserted in the path of this beam. The holes in each screen were in a vertical row arranged in pairs. The centers of the holes were ½, ¾, and 2¼ inches below the surface of the liquid in the sample bottles. One screen was placed 1½ inches in front of and 1½ inches to the side of the other screen so that the standard and the unknown could be observed together. The observations were made at right angles to the beam of light.

The 100 cc. samples were contained in 4-ounce French square flint bottles, 1⅜ inches square; the depth of the liquid was 2⅝ inches. For turbidities below 100 parts per million the ordinary method of comparing with standards in similar bottles was used. In the coagulation of the suspensions, the reagents were added in sufficient concentrations to give a reaction before the natural occurrence of sedimentation of particles.

All results are expressed as turbidities in parts per million, and milligram equivalents per liter, except in the case of colloidal silicic acid which is in parts of SiO_2 per million.

EXPERIMENTAL PART.

In dealing with the action of electrolytes on colloids a method of determining the amount of colloids present is greatly to be desired. A search of the literature revealed only one method that seemed applicable. This was devised by Rohland[41] and improved upon by Ashley.[1] It depends upon the amount of dye adsorbed by the colloid and is fairly successful in estimating the adsorptive or colloidal power of concentrated clay suspension, but is not reliable when applied to dilute suspensions of clay. Further work along this line is needed. The refractive index and viscosity were investigated, but variations were too slight to be serviceable. There appeared to be no correlation between the hydrogen ion concentration and the degree of coagulation. Kataphoresis experiments only measure the sign and not the magnitude of the charge.

Later in the work it was found that silicic acid exerted a marked influence and an endeavor was made to find a method of separating it from the clay. Several[38,52] have been given but none of sufficient selective action to be of value at these dilutions.

An attempt was made to filter the silicic acid from a suspension by a Berkefeld army filter No. 3 with the following results:

Silicic Acid.

added.	recovered.
298*	155
129	84

This confirms the work of Linder and Picton.[29] The silicic acid is evidently coagulated by contact with the walls of the filter.

INFLUENCE OF ELECTROLYTES ON THE PRECIPITATION OF SILICIC ACID FROM DILUTE SOLUTIONS.

The amount of colloidal silicic acid in a solution containing no suspensoids is easily obtained by the usual method of analysis. In the determinations of silica, SiO_2, one evaporation was made, as on a second evaporation only a few tenths of a milligram additional was obtained.[27] The errors due to the manner of adding the reagents and their different concentration was reduced to a minimum by making the methods of manipulation as uniform as possible.

TABLE 2—SILICIC ACID IS NOT PRECIPITATED FROM 5 CC. OF A SOLUTION CONTAINING 625 PARTS PER MILLION SiO_2 BY THE FOLLOWING SALTS:

Reagent.	Temperature ca 23° C.		Reagent.	Time 6 hours.	
	No. cc. used.	Highest concentration.		No. cc. used.	Highest concentration.
0.1 N NaCl	12	.07N	0.2 N BaCl₂	8	.06N
0.1 N Na₂CO₃	12	.07N	1.0 N CaCl₂	4.2	.05N
0.1 N NaHCO₃	12	.07N	0.5 N Al₂(SO₄)₃	12	.07N
0.1 N Na₂SO₄ and K₂SO₄	12	.07N	0.1 N FeCl₃	11	.07N
0.1 N Na₃PO₄	8	.06N	0.1 N FeSO₄(NH₄)₂SO₄	12	.07N
0.1 N Mg(HCO₃)₂	12	.07N	0.1 N FeCl₂	10	.07N
0.1 N MgSO₄	12	.07N	0.1 N AlCl₃	12	.07N

From a solution containing not less than 184 nor more than 625 parts per million of SiO_2, silicic acid is not precipitated by the reagents given in Table 1, but is precipitated from 5 cc. of a solution containing 625 parts per million of SiO_2, by the following:

* Expressed as parts per million.

Temperature ca 23°C.   Time: 5 minutes.

5.5 cc. ....0.18 N   NaOH   .099 N concentration
.6 cc. ....0.018 N $Ca(OH)_2$ .0019 N concentration
.4 cc. ....0.26 N $Ba(OH)_2$ .0019 N concentration
2.6 cc. ....(.6 mg) colloidal Fe   .0045 N concentration

This experiment indicates that bivalent ions have a precipitating value fifty times that of monovalent ions. Trivalent ions according to the formulae 1:x; x^2 should have a coagulating value of 2,500 times that of the univalent, or fifty times that of the bivalent ions. Qualitative experiments with more dilute solutions indicate that the ratio between bivalent and trivalent to be about one to four. Colloidal iron is only one-half as efficient as calcium hydroxide. The more dilute a solution the less marked is this precipitating effect of the cations.

Very dilute solutions —30 or 40 parts per million of SiO_2—are not precipitated by sodium hydroxide, and rather high concentration of calcium hydroxide to silicic acid are necessary to obtain a precipitate within six hours. At these concentrations the reactions no doubt are ionic, and precipitates of calcium silicates are thrown down. Since the hydroxides of calcium and barium precipitate silicic acid, it is desirable to know the effect of added univalent and bivalent ions upon the amount of calcium hydroxide needed.

To 5 cc. of a dialyzed silicic acid solution, containing 625 parts per million of SiO_2 there was added 0.5 cc. of a 0.1 normal solution of the electrolytes and the silicic acid was precipitated by the addition of calcium hydroxide. The results are given in Table 3.

TABLE 3—THE EFFECT OF THE ADDITION OF VARIOUS ELECTROLYTES ON THE PRECIPITATION OF COLLOIDAL SILICIC ACID* BY CALCIUM HYDROXIDE.

Temperature ca 23°C.			Time 5 minutes.
Reagent.			$Ca(OH)_2$ required.
0.0 cc.	0.2 N	$Ca(OH)2$	0.6 cc.
0.5 cc.	0.1 N	$BaCl_2$	0.3 cc.
0.5 cc.	0.1 N	$MgSO_4$	0.3 cc.
0.5 cc.	0.1 N	$CaCl_2$	0.3 cc.
0.5 cc.	0.1 N	$NaHSO_4$	0.3 cc. ⎫ in excess re-
0.5 cc.	0.1 N	H_2SO_4	0.35 ⎬ quired to
0.5 cc.	0.1 N	$KHSO_4$	0.3 cc. ⎭ neutralize
0.5 cc.	0.1 N	NaCl	0.6 cc.
0.5 cc.	0.1 N	Na_2SO_4	0.7 cc.
0.5 cc.	0.1 N	K_2SO_4	0.7 cc.
0.5 cc.	0.1 N	Na_2SO_4	0.6–0.7 cc.

* 5 cc. of silicic acid containing 625 parts per million of SiO_2 were used.

The following compounds complicate the precipitation by reacting with the Ca. ions:

Na_2CO_3 Na_3PO_4 $Ca(HCO_3)_2$

$NaHCO_3$ $Mg(HCO_2)_3$
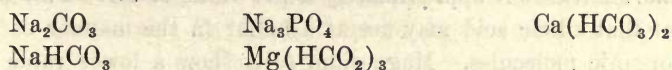
This experiment proved, as expected, that the precipitating value of the cation depends upon its valence and that hydroxyl had some influence at these concentrations. Neutral salts of the univalent cations were not present in sufficient amount to influence the results. In cases where the solution was acid or there was formed an insoluble calcium precipitate, the concentration of calcium ion is that necessary to combine with the anion plus an amount sufficient to produce precipitation. This is shown in the reactions of sulfuric acid and calcium hydroxide.

To measure the effect of the hydroxylion on the reaction, the pH value was determined, the results of which are given in Table 4.

TABLE 4—THE CONCENTRATION OF HYDROGEN ION NECESSARY BEFORE SILICIC ACID* IS PRECIPITATED BY $Ca(OH)_2$ IN THE PRESENCE OF SALTS.

Salts.	pH value.
0.18 N NaOH	9.5
0.01 N $Ca(OH)_2$	9.2
0.02 N NaOH	9.2
colloidal Fe	off color

Precipitation of silicic acid by $Ca(OH)_2$ in presence of 0.5 cc. of 0.1 normal salt solutions:

Salts.	pH value.
0.1 N $CaCl_2$	9.2
0.1 N $MgSO_4$	8.6
0.1 N H_2SO_4	9.2
0.1 N NaCl	9.3
0.1 N $NaHSO_4$	9.0
0.1 N $NaHCO_3$	9.2
0.1 N Na_2SO_4	9.4
0.1 N Na_2CO_3	9.4
0.1 N Na_3PO_4	9.3
10 cc. $CaSO_4$ saturated soln	9.2
0.1 N $Mg(HCO_3)_2$	8.8
0.1 N $MgSO_4$	8.6
0.1 N $AlCl_3$	below 7.5 when precipitation occurred
0.1 N $Al_2(SO_4)_3$	below 7.5 when precipitation occurred
Average	9.0

* 5 cc. of a solution containing 625 parts per million of SiO_2 were used.

The different systems of salt, silicic acid and calcium ions have different normalities but approximately a pH value of 9.0. This points to the fact that silicic acid may act as a buffer in the manner of large complex organic molecules. Magnesium salts show a lower value than calcium which is probably due to the precipitation of magnesium hydroxide which obscured the true end point. It was not possible to determine hydrogen ion concentration of iron salts with indicators. The quantitative removal of silicic acid by calcium hydroxide, barium hydroxide and chloride, aluminium sulfate and colloidal iron was tried on a water from Albuquerque, N. M., the analysis of which is given in Table 5.

TABLE 5—ANALYSIS OF SAMPLES OF WATER FROM ALBUQUERQUE, NEW MEXICO.

Residue.*		479.1 p. p. m.	$\frac{N}{1000}$ equivalents
Silica	SiO_2	82.6	
Non volatile		0.3	
Al_2O_3 Fe_2O_3		0.2	
Iron	Fe	.03	
Manganese	Mn	0	
Calcium	Ca	69.6	3.473
Magnesium	Mg	14.0	1.145
Sodium and potassium	Na & K	76.8	3.257 sum 7.875
Ammonia	NH_3	0.06	
Carbonate	CO_3	84	2.800
Sulfate	SO_4	175.3	3.647
Chloride	Cl	46.5	1.311
Nitrate	NO_3	1.6	.026 sum 7.784
Nitrite	NO_2	0.0	Difference .091
Phosphate	P_2O_5	0.0 Error	of analysis −0.58 per cent.

* NOTE.—Owing to reaction between fixed alkalies and silica on evaporation and heating, the residue is too low.

The reagents were added in excess (but the amount of this excess unfortunately was not recorded) and the reaction carried out at a pH value of 8.5 to 10. Five different treatments were tried. The amount of calcium and barium compounds were those necessary for softening and removing sulfates.

1. $Ca(OH)_2$ and heating to 90°C. removed 37 per cent leaving 52 ppm. in soln.

    $Ba(OH)_2$ and heating to 80°C. removed 36 per cent leaving 53 ppm. in soln.

2. $Ca(OH)_2$, filtration and adding

    $Al_2(SO_4)_3$ removed 30 per cent leaving 58 ppm. in soln.

    $AlCl_3$ + NaOH removed 84 per cent leaving 13 ppm. in soln.

    $FeSO_4(NH_4)_2SO_4$ removed 37 per cent leaving 51 ppm. in soln.

3. $Ca(OH)_2$, $Ba(OH)_2$, $BaCl_2$, filtration and adding
   colloidal Fe removed 38 per cent leaving 31.6 ppm. in soln.
   excess $Ba(OH)_2$ removed 44 per cent leaving 36.0 ppm.
   in soln.
   $AlCl_3$ + NaOH removed 91 per cent leaving 5.0 ppm.
   in soln.
4. $Al_2(SO_4)_3$ and $Ca(OH)_2$ removed 34 per cent leaving 55 ppm.
   in soln.
5. Treatment with colloidal Fe removed 26 per cent leaving 61
   ppm. in soln.
   $Al(OH)_3$ cream removed 44.6 per cent leaving 38 ppm.
   in soln.

It is evident that the most efficient precipitants are the trivalent ions in an excess of hydroxyl ions. According to the theory of coagulation, the optimum conditions for precipitation of negatively charged silicic acid should be (1) an amount of trivalent cations or positively charged colloids to exactly neutralize the negative charges, (2) a minimum amount of cations, protective or stabilizing colloids, and (3) a pH value approaching the isoelectric point. Just what conditions must be defined in order to locate the isoelectric point, chemists have not yet discovered. Fleming[19] designated it in terms of normality of the solution, but it seems preferable to express it as hydrogen ion concentration.

The above tests indicate that the optimum pH value for the precipitation of silicic acid is approximately 9.0. According to theory this should be the location of the isoelectric point. In order to determine this value more accurately and in the absence of bivalent cation, aluminium hydroxide was precipitated in the silicic acid solution by sodium hydroxide and aluminium chloride.

The silicic acid used was prepared by bringing a solution of sodium silicate to a pH value of 6.5 by the addition of hydrochloric acid. This solution contained 4 mols of SiO_2 to one mol of NaCl. Two dilutions were used: 87 and 232 parts per million of SiO_2. To the silicic acid solution were added water to produce the proper dilution, aluminium cloride and $N/10$ sodium hydroxide, which was added drop by drop with constant shaking. These solutions were shaken at frequent intervals during 48 hours. By that time the reaction was practically complete. The solution was filtered and silicic acid determined in the filtrate. It was noticed in precipitating aluminium from a solution of aluminium chloride, silicic acid and sodium chloride, that the manner of adding the reagents and the relative ratio of aluminium to silicic acid markedly influenced the character and amount of the precipitate. Table 6 shows this very strikingly.

TABLE 6—RELATIONSHIP BETWEEN THE AMOUNT OF SILICIC ACID PRE-
CIPITATED AND THE CHARACTER OF THE PRECIPITATE.

SiO$_2$—Content 87 parts per million—Temp. ca 23°C—Time 48 hrs.

Milliequivalents of Al.	SiO$_2$ p. p. m. precipitated.	SiO$_2$ p. p. m. in Soln.	pH	Remarks.
1.75	8	79	7.1	Faint turbidity.
1.75	3	84	7.5	Clear.
2.91	2	85	7.5	Faint turbidity.
2.91	4	83	7.5	Faint turbidity.
4.37	51	36	6.8	Fair precipitate.
5.87	65	22	7.0	Well flocked.
5.87	35	52	7.6	Faint turbidity opalescent filtrate.
7.28	75	12	7.0	Well flocked.
7.28	45	42	7.6	Turbid.
8.73	80	7	7.1	Well flocked.
8.73	81	6	7.6	Well flocked.

Poor removal of silicic acid is associated with a turbid colloidal solution and a sticky gelatinous precipitate which is very difficult to filter, while a good removal is usually obtained when the precipitate is well floculated and settles quickly; the resulting clear solution exhibits little Tyndal effect. In the absence of silicic acid a flocculent precipitate of aluminium hydroxide was produced in a dilute solution of AlCl$_3$ by N/10 NaOH, or in a dilute solution of Na(OH) by 0.0003N AlCl$_3$, regardless of the manner of adding reagent, or presence of NaCl. If the above solution contained 87 parts per million of SiO$_2$, as colloidal silicic acid, on adding N/10 NaOH drop by drop, a precipitate formed at the end of one hour depending upon the amount of AlCl$_3$ in the solution, but if an equivalent amount of N/10 or stronger NaOH was added all at once, no precipitate formed. Such a solution showed a very strong Tyndal effect and gradually deposited a slight fine precipitate. One solution was made from which a very little precipitate settled at the end of a month. Apparently the system was less stable the higher the concentration of NaOH and the more suddenly it was added and mixed. The same effect was produced when sodium carbonate or acid carbonate was used instead of hydroxide.

With calcium hydroxide an excellent precipitate formed regardless of the manner of adding the reagent. There is evidently some complex substances formed under these conditions, which are intimately connected with a sodium ion and the silicic acid. Perhaps the silicic acid, in the presence of sodium ions, is acting as a protecting colloid preventing in some manner passage of aluminium hydroxide from the colloid into the crystaline condition. In any event, a recognition of this fact is quite valuable in obtaining well flocked precipitates.

A high ratio of silicic acid to aluminium tends to produce colloidal solutions while the reverse ratio produces nicely flocked precipitates.

The magnitude of the Tyndal effect is inversely related to the removal of the silicic acid and the character of the flock or precipitate.

Thus in plotting the curves, Figures 1 and 2, from Tables 7 and 8 respectively, only the higher concentrations of aluminium were used.
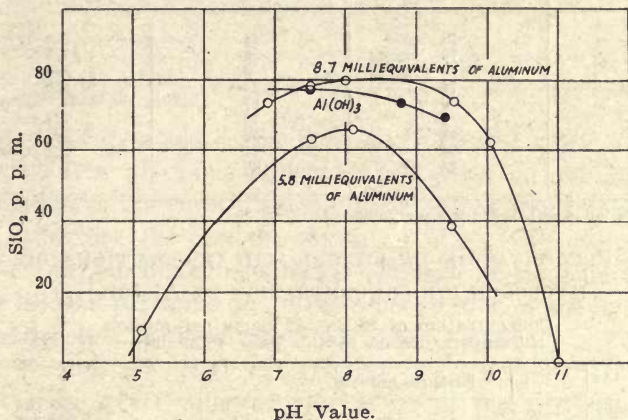
Figure 1.—Comparison between the pH value, the precipitation of silicic acid and the amount of Al(OH)$_3$ in the solid phase.
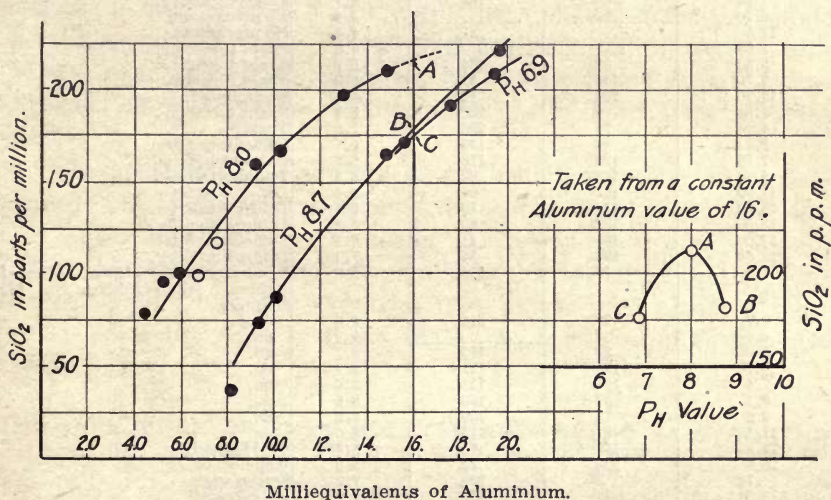
Figure 2.—Comparison between the pH value, the precipitation of silicic acid, and the amount of Al(OH)$_3$ in the solid phase.

The lower values are inaccurate because of the formation of colloidal solutions. There is shown in Figure 1 a third curve plotted from the data in Table 9. Values for this curve were obtained by precipitating the aluminium with ammonia in the absence of silicic acid.

TABLE 7—REMOVAL OF SILICIC ACID* BY ALUMINIUM HYDROXIDE OF VARYING HYDROGEN ION CONCENTRATION.

Milliequivalents of Al.	Temperature ca 23°C.	Time 48 hours.		
	SiO$_2$ precipitated.	SiO$_2$ in solution.	pH	
8.73	73	14	6.8	
8.73	79	8	7.5	
8.73	79	8	8.0	
8.73	74	13	9.6	
8.73	0	87	11.	no ppt.
5.82	9	78	5.2	colloidal.
5.82	63	24	7.5	
5.82	65	22	8.2	colloidal.
5.82	38	49	9.5	

* Concentration of SiO$_2$ is 87 parts per million.

TABLE 8—PRECIPITATION OF SILICIC ACID IN SOLUTIONS OF VARYING HYDROGEN ION CONCENTRATION BY Al (OH)$_3$.

Concentration of SiO$_2$—232 parts per million
Temperature ca 23°C.   Time 48 hours.

Milli-equivalents of Al.	Parts per millions.			Remarks.
	SiO$_2$ precipitated.	SiO$_2$ in solution.	pH value.	
1.94	50	182	4.7	Slight turbidity.
9.70	----------------	----------------	4.4	No precipitate.
17.5	----------------	----------------	4.4	No precipitate.
1.94	----------------		6.0	Slight turbidity.
5.82	98	134	5.9	Slight turbidity.
9.70	149	83	6.0	Slight turbidity.
11.70	220	12	6.1	Precipitated.
1.94	4	228	6.7	Slight turbidity.
4.03	26	206	7.0	Turbid.
5.82	96	136	6.7	Difficult to filter.
7.76	120	112	6.4	Well precipitated.
9.70	142	90	6.5	Well precipitated.
11.70	167	65	6.6	Difficult to filter.
13.60	173	59	6.7	Difficult to filter.
15.50	172	60	6.8	Difficult to filter.
17.50	191	41	6.9	Difficult to filter.
19.40	208	24	7.2	Difficult to filter.
3.0	17	215	9.8	Tendency to be colloidal. Filtered through Blue Ribbon No. 589 Filters.
3.7	21	211	8.8	do.
4.4	5	----------------	9.2	do.
5.9	57	175	8.7	do.
6.7	101	131	8.7	do.
7.4	101	131	8.6	do.
8.1	37	195	8.8	do.
9.2	73	159	8.5	do.
11.1	87	145	8.6	do.
14.8	167	65	8.8	Well flocked.
20.6	220	12	8.9	Well flocked.
.74	3	229	7.2	Settles well.
1.5	47	185	7.8	Well flocked.
2.2	61	171	7.8	Well flocked.
3.0	59	173	7.0	Well flocked.
3.7	81	151	8.0	Well flocked.
4.4	79	153	8.0	Well flocked.
5.2	95	137	7.4	Well flocked.
5.9	99	133	7.6	Well flocked.
6.7	99	133	7.6	Well flocked.
7.4	129	103	8.4	Well flocked.
9.2	159	73	7.4	Well flocked.
11.1	167	65	8.6	Well flocked.
13.0	197	35	8.6	Well flocked.
14.8	209	23	8.2	Well flocked.
18.5	197	35	7.6	Well flocked.

TABLE 9—EFFECT OF THE HYDROGEN ION CONCENTRATION ON THE PRECIPITATION OF ALUMINIUM HYDROXIDE.

	Temperature ca. 28°C.		Time 48 hours.	
Ph value	6.8	8.0	6.8	9.4
Al in solution	1.5*	0.5	12	17.3
Character of flock	good	good	good	gelatinous

* Expressed as parts per million.

A study of data and curves indicates: (1) that silicic acid is best precipitated at a pH value of 8.0 to 8.5, which is probably a closer approximation to the truth than the former value of 9.0 obtained with calcium hydroxide, (2) that the amount of silicic acid precipitated follows closely the amount of aluminium hydroxide in the solid phase, and (3) that below a pH value of 4.0 the concentration of the hydrogen ion shifts the reaction so far to the right in the equation.

$$H^+ + AlO_2^- + H_2O \leftrightarrows Al(OH)_3 \leftrightarrows AlO^+ + HO^- + H_2O$$

and that above a pH value of 11.0 so far to the left that the solid aluminium hydroxide phase is unstable and disappears.

In the region below these curves the tendency to form colloidal solutions is quite marked, and the gelatinous nature of the precipitate and the magnitude of the Tyndal effect generally varies inversely with the amount of aluminium ions added to the system, and directly as the hydrogen ion concentration departs in either direction from a pH value of 8.25.

The precipitation of silicic acid by aluminium sulfate may be explained: (1) by the neutralization of the charge on the silicic acid complex by the aluminium ion, resulting in a precipitation of silicic acid, (2) by the neutralization of the negatively charged silicic acid by positively charged aluminium hydroxide, (3) by the solid aluminium hydroxide adsorbing silicic acid, and (4) by the formation of an insoluble chemical compound.

THE INFLUENCE OF ELECTROLYTES AND SILICIC ACID ON THE COAGULATION OF CLAY SUSPENSIONS.

The next step was to determine the effect of silicic acid and the commonly occurring electrolytes on the coagulation of a clay suspension with aluminium sulfate.

Reagents were added to one hundred cubic centimeter portions of a clay suspension and thoroughly mixed by shaking for one minute. The sample was then allowed to remain perfectly quiet and the turbidity of the liquid determined at appropriate intervals at a point 1/2-inch below its surface.

The electrolytes used were sodium hydroxide, acid carbonate, carbonate and chloride; magnesium bicarbonate, and sulfate; calcium hydroxide, chloride and bicarbonate; barium hydroxide, Merck's dialyzed iron and sulfuric acid.

The effect of electrolytes on the stability of a dilute clay suspension is similar to that observed with clay slips. The results of adding increasing amounts of sodium hydroxide is first dispersion followed by coagulation.[2] In Tables 10 and 11 and Figures 3 and 4 it is shown that the coagulative powers of calcium and barium hydroxide are practically the same, and that the ratio of aluminium to calcium and barium ions is about five to one. Data from many of the tables have been collected and shown in graphic form in Figures 6 and 7. The salts arranged according to their efficiencies as coagulants are: aluminium sulfate, calcium and barium hydroxides, calcium chloride, magnesium sulfate and magnesium bicarbonate. Sodium chloride has little effect until its concentration becomes so great as to salt out the clay. Sulfuric acid has no apparent effect up to concentration of 0.35 milliequivalents but higher concentrations coagulate. (See Table 16 and Figure 5.) Sodium hydroxide, carbonate, acid carbonate and sulfate have at first a stabilizing influence followed by a coagulating effect. The coagulating effect of anions seems to be an inverse function of their valencies.

The effect of added salts on the coagulation of clay suspensions by aluminium sulfate is shown in Tables 12 to 20, Figures 8 to 15.

TABLE 10—THE EFFECT OF VARYING STRENGTHS OF NaOH ON THE RATE OF COAGULATION OF CLAY BY $Al_2(SO_4)_3$.

Tenn. No. 3 Ball Clay—Temperature ca 23° C.
Milliequivalents of NaOH added.

Milliequivalents of Al.	0.00		0.049		0.09		0.18		0.36	
	Turbidity.									
	1 hr.	1½ hrs.	1 hr.	2 hrs.	1 hr.	2 hrs.	1 hr.	2 hrs.	1 hr.	1½ hrs.
0.0	420	420	420	400	420	400	450	400	450	400
.02	420	400	------	------	420	360	------	------	------	------
.06	400	400	------	------	400	360	450	420	------	------
.09	150	75	420	400	350	375	420	420	------	------
.13	125	75	150	100	175	50	300	240	400	400
.17	125	50	100	90	275	150	200	75		
.18	100	50	100	85	375	175	200	40	350	350
.37	100	------	100	85	450	350	400	400		
.55	125	50	100	80	300	250	420	375	75	60
.74	------	------	------	------	------	------	------	------	400	275
.92	150	60	100	75	240	100	420	125	300	200
1.11									75	75
1.29	150	75	90	50	200	50	350	100	300	125
1.47									250	90
1.66	------	------	------	------	150	50	------	------	190	90
2.03	------	------	------	------	------	------	------	------	125	50

TABLE 11—COMPARISON OF $Ca(OH)_2$, $Ba(OH)_2$, COLLOIDAL FE AND $Al_2(SO_4)_3$ AS COAGULANTS.

Tenn. No. 3 Ball Clay—Temperature ca 23° C.
Milligram equivalents.

$Al_2(SO_4)_3$.	Turbidity.	$Ca(OH)_2$.	Turbidity.	$Ba(OH)_2$.	Turbidity.	Fe.	Turbidity.
.02	400	.26	400	.13	400	.38*	400
.06	400	.43	390	.66	400	3.9	400
.09	400	.60	350	.79	375	4.6	350
.13	375	.69	350	1.05	100	6.1	200
.17	50	.86	150	1.32	60	6.9	100
.37	40	1.03	100			8.1	40
		1.38	50			9.2	40
		1.72	50				

* Parts per million.

TABLE 12—EFFECT OF Na_2CO_3 ON THE COAGULATION OF A CLAY SUSPENSION BY $Al_2(SO_4)_2$.

Tenn. No. 1 Ball Clay—Temperature ca 24° C.
Milliequivalents of Na_2CO_3 added.

Milliequivalents of Al.	0.5		1.0	
	Turbidity.			
	1½ hrs.	14 hrs.	1½ hrs.	14 hrs.
0	400+	150	400+	150
.30	125	10	400	150
.45	125	0	125	10
.60	175	0	65	0
.75	400	0	125	0
.90	400	0	100	0

TABLE 13—EFFECT OF $NaHCO_3$ ON THE COAGULATION OF A CLAY SUSPENSION BY $Al_2(SO_4)_3$.

Tenn. No. 1 Ball Clay—Temperature ca 24° C.

Milliequivalents of Al.	Milliequivalents of $NaHCO_3$ added.							
	.03		0.6		1.0		1.5	
	1½ hrs.	13 hrs.	1½ hrs.	13 hrs.	1½ hrs.	13 hrs.	1½ hrs.	13 hrs.
0	400+	325	400	400	400	300	400+	300
.03	400+	275	400	375			400+	250
.06	400+	150	400	300	400	200		
.09	400	150	400	275			400+	250
.12	350	75	300	100	350	200	400	150
.15	275	75	225	65		5		
.18	125	50	175	50	125	40	250	150
.24	60	10	180	10	100	10	75+	25
.30	60	10	75	10	60	10	75+	10
.36			60	5	60	5	60	5
.42			60	0	60	5	75	5
.48			65	0	60	0	50	0
.54			65	0	60	0	60	0
.60					60	0	60	0
.66							60	0
.78							60	0
.90							50	0

TABLE 14—ACCELERATING EFFECT OF Na_2SO_4 ON THE COAGULATION OF CLAY SUSPENSION BY $Al_2(SO_4)_3$.

Tenn. No. 3 Ball Clay—Temperature ca 24° C.
Milliequivalents of Na_2SO_4 added.

Milli-equivalents of Al.	1		2		3		4	
	Turbidity.							
0	1*	24	1	24	1	24	1	24
.0	400	350	400	350	400	150	400	40
.03	375	150					400	25
.06	350	35					200	0
.09	350	10	125	0			60	0
.12	25	0	60	0			50	0
.15			50	0				
.18			40	0				

* Time expressed in hours.

TABLE 15—EFFECT OF NaCl ON THE COAGULATION OF CLAY SUSPENSIONS BY ALUM.

Tenn. No. 3 Ball Clay—Temperature ca 24° C.—Tenn. No. 1 Ball Clay.
Milliequivalents of NaCl added.

Milli-equivalents of Al.	1		3		10		1		2	
	Turbidity.									
0	1*	24	1	24	1	24	1½	12	1½	12
.0		200		150		150	400	300	400	250
.03	400	150	350	10	50	0	400	200	400	200
.06	350	15	175	0	50	0	100	100	400	60
.09	100	0	50	0	50	0	90	0	80	0
.12	25	0	40	0	50	0	80	0		

* Time expressed in hours.

TABLE 16—THE EFFECT OF VARYING STRENGTHS OF H_2SO_4 ON THE RATE OF CLAY BY $Al_2(SO_4)_3$.

Tenn. No. 3 Ball Clay—Turbidity 420—Temperature Ca 23° C.
Milliequivalents of H_2SO_4 added.

Milli-equivalents of Al.	0.0		0.049		0.09		0.18		0.36	
	Turbidity.									
	1 hr.	2 hrs.	1 hr.	2 hrs.	1 hr.	1½ hr.	1 hr.	1½ hr.	1 hr.	1½ hr.
0.000	420	420	420	420	420	400	420	400	420	250
.02	420	400			400	375	400	400		
.06	400	400	375	200	370	310	290	150	360	350
.09	150	75			200	60	240	100	150	90
.13	125	75	150	50	150	60	140	60	100	60
.17	125	75								
.18	100	50	150	50	140	50	75	50	150	50
.37			100	60	125	50	75	50	200	50
.55	125	50			100	50	50	50	200	50
.74										
.92	150	60								

TABLE 17—EFFECT OF MgSO₄ AND Mg(HCO₃)₂ ON THE COAGULATION OF CLAY SUSPENSIONS BY $Al_2(SO_4)_3$.

Tenn. No. 1 Ball Clay—Temperature ca 24° C.
Milliequivalents of MgSO₄ added.

Milliequiva- lents of Al.	1		2		3	
	Turbidity.					
	1½ hrs.	14 hrs.	1½ hrs.	14 hrs.	1½ hrs.	14 hrs.
0	400	100	350	50	325	15
.009					400	15
.018	-----	-----	200	25	175	10
.030	150	10			150	0
.036	-----	-----	125	10	125	0
.060	150	0	125	0	100	0
.090	125	0	125	0	-----	-----
.120	125	0	100	0	-----	-----

TABLE 18—MILLIEQUIVALENTS OF Mg(HCO₃)₂ ADDED.

Milliequiva- lents of Al.	1		2		3	
	Turbidity.					
	1½ hrs.	14 hrs.	1½ hrs.	14 hrs.	1½ hrs.	14 hrs.
0	400	150	400	85	350	65
.009	-----	-----	-----	-----	350	30
.018				80	300	25
.030	350	125	350	35	275	20
.045	-----	-----	-----	-----	250	15
.060	250	25		10	125	15
.090	175	15	150	0	-----	-----
.120	125	10	-----	-----	-----	-----

TABLE 19—EFFECT OF CaCl₂ THE COAGULATION OF CLAY SUSPENSIONS BY $Al_2(SO_4)_3$.

Tenn. No. 1 Ball Clay—Temperature ca 24° C.
Milliequivalents of CaCl₂.

Milliequiva- lents of Al.	1		2		3	
	Turbidity.					
	1½ hrs.	14 hrs.	1½ hrs.	14 hrs.	1½ hrs.	14 hrs.
0	400	125	185	10	175	10
.009	-----	-----	-----	-----	175	10
.010			185	5	175	5
.030	300	25	180	0	200	0
.045	-----	-----	-----	-----	175	0
.060	175	10	175	0	125	0
.090	125	5	175	0	-----	-----
.120	175 (?)	0	175	0	-----	-----

TABLE 20—EFFECT OF Ca(HCO$_3$)$_2$ ON THE COAGULATION OF CLAY SUSPENSIONS BY Al$_2$(SO$_4$)$_3$.

Tenn. No. 1 Ball Clay—Temperature ca 23° C.
Milliequivalents of Ca(HCO$_3$)$_2$.

	0		1		0		2	
Milliequiva-lent of Al.	Time in hours and turbidity.							
	1½	13	1½	13	1½	13	1½	13
0	325	----------	325	125	200	----------	200	25
.009	----------	----------	----------	----------	200	175	75	10
.018	----------	----------	----------	----------	150	10	50	5
.030	325	125	200	15	150	0	40	0
.045	----------	----------	----------	----------	125	0	25	0
.060	325	70	75	10	----------	----------	----------	----------
.090	75	10	50	5	----------	----------	----------	----------
.120	50	0	50	0	----------	----------	----------	----------
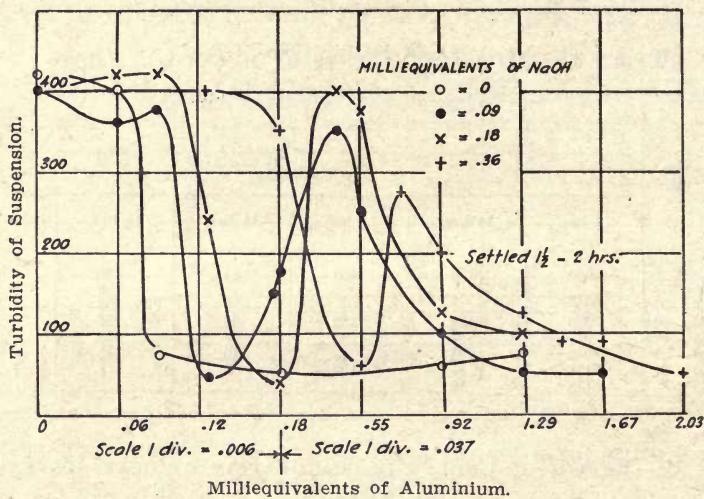
Figure 3.—Effect of NaOH on the coagulation of a clay suspension by Al$_2$(SO$_4$)$_3$.
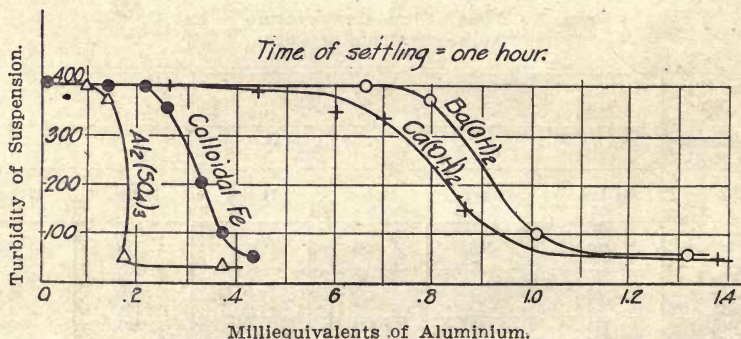
Figure 4.—Comparison of Al$_2$(SO$_4$)$_3$, colloidal Fe, Ca(OH)$_2$, Ba(OH)$_2$ as coagulants.
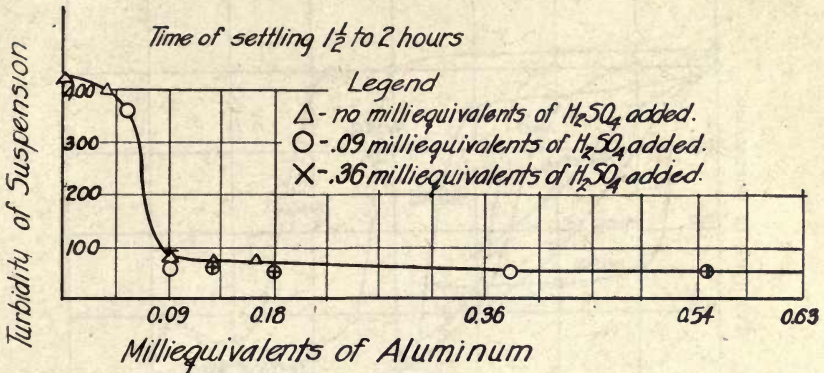
Figure 5.—Effect of H_2SO_4 on the coagulation of clay suspension by $Al_2(SO_4)_3$.
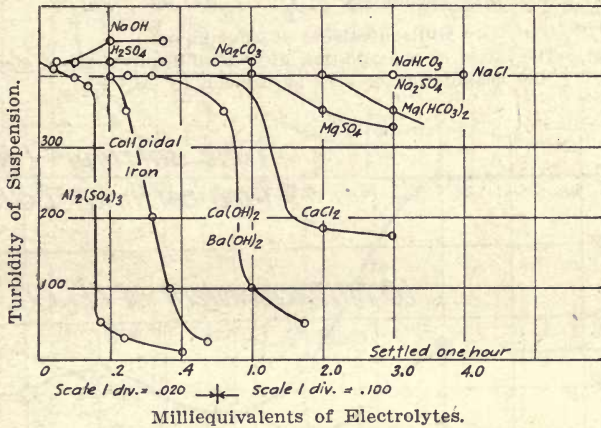
Figure 6.—Effect of electrolytes on the coagulation and settling of clay suspensions.
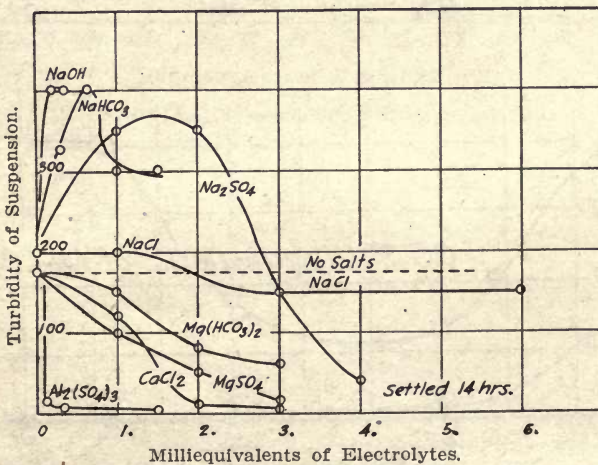
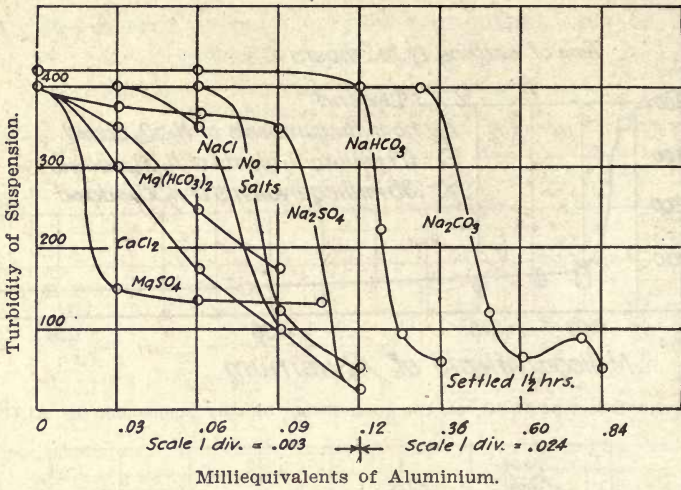Figure 7.—Effect of electrolytes on the coagulation and settling of clay suspensions.

Milliequivalents of Aluminium.

Figure 7 "A".—The effect of the addition of one milliequivalent of electrolytes on the coagulation of clay suspension by $Al_2(SO_4)_3$.
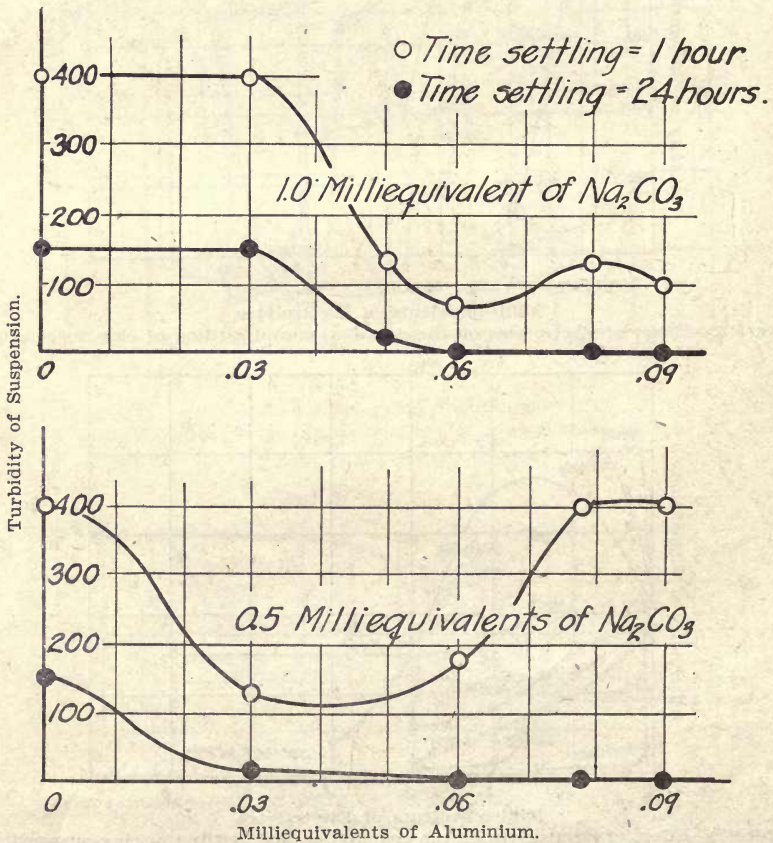

Milliequivalents of Aluminium.

Figure 8.—Effect of Na_2CO_3 on the coagulation of clay suspensions by $Al_2(SO_4)_3$.
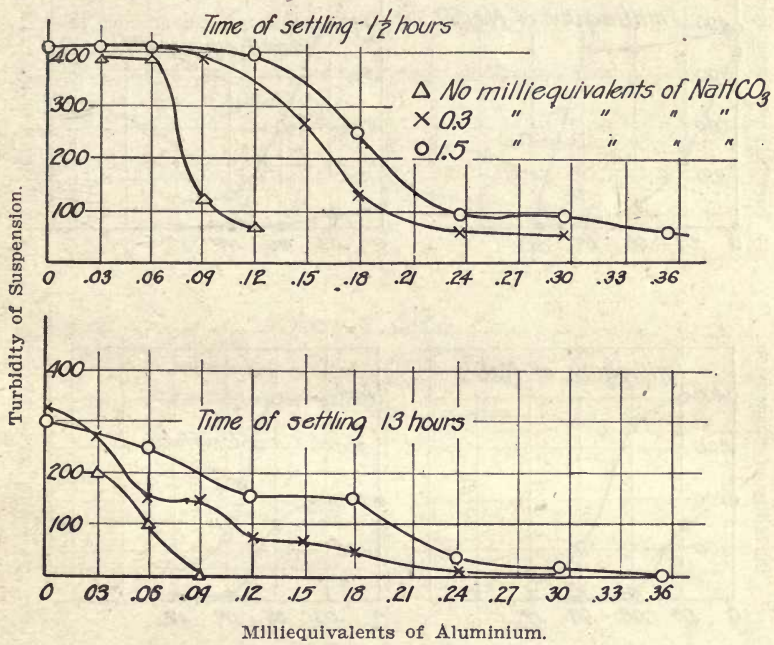
Figure 9.—Effect of NaHCO$_3$ on the coagulation of clay suspension by Al$_2$(SO$_4$)$_3$.

Milliequivalents of Aluminium.
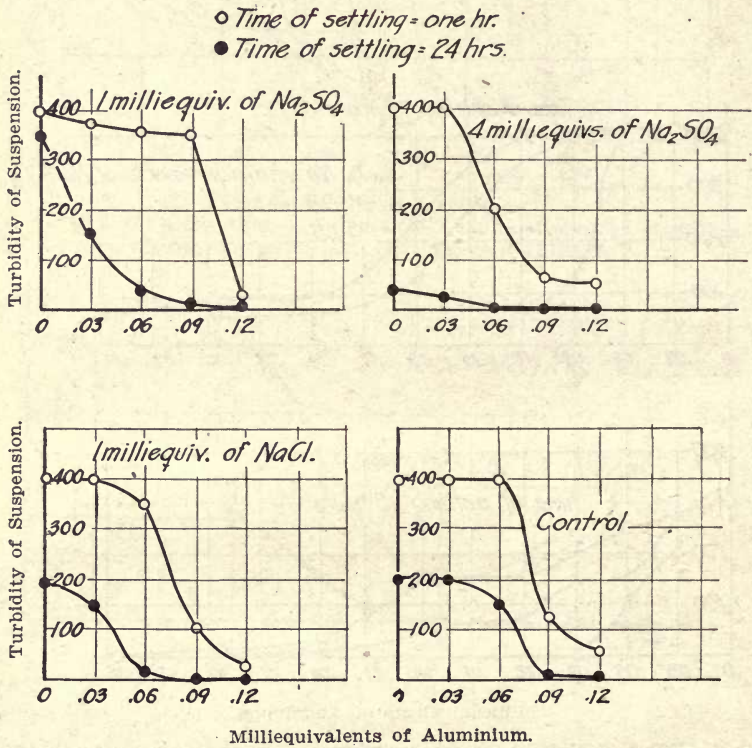
Figure 10.—Effect of Na₂SO₄ and NaCl on the coagulation of clay suspension by Al₂(SO₄)₃.
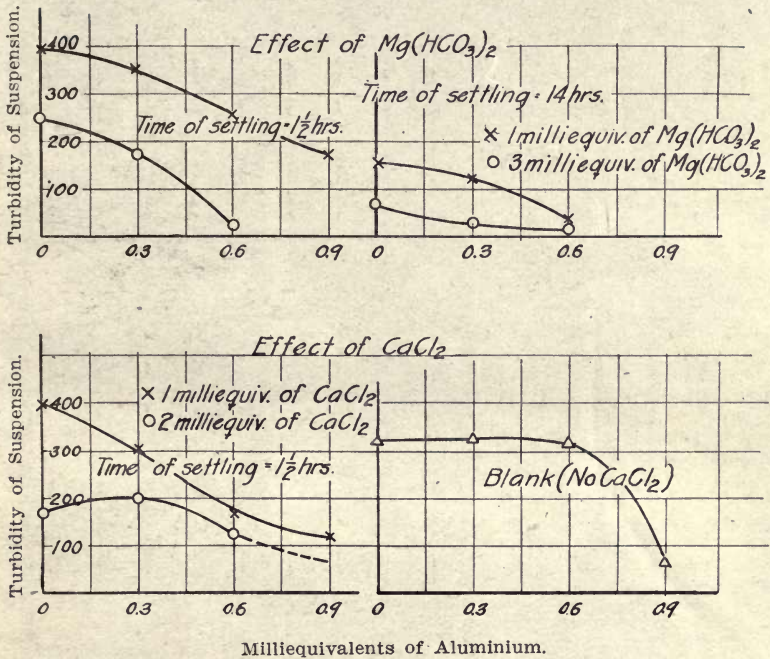
Figure 11.—Effect of $Mg(HCO_3)_2$ and of $CaCl_2$ on the coagulation of clay suspension by $Al_2(SO_4)_3$.

Figure 12.—The effect of NaHCO₃ on the coagulation of clay suspensions by Al₂(SO₄)₃.

0—Increasing Amounts of Al₂(SO₄)₃.

Milli-
equivs.
of
NaHCO₃

0.3

0.6

1.0

1.5
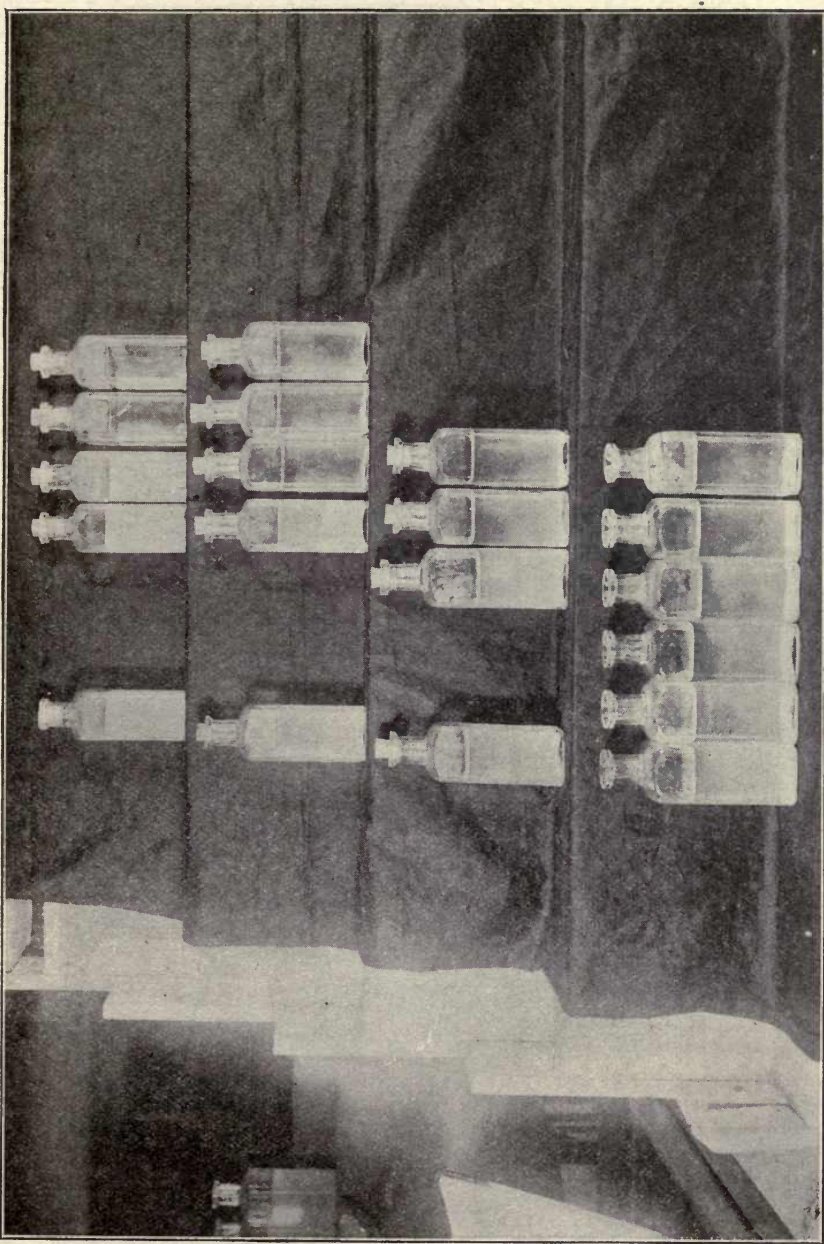
Figure 13.—The effect of $Mg(HCO_3)_2$ on the coagulation of clay suspensions by $Al_2(SO_4)_3$.

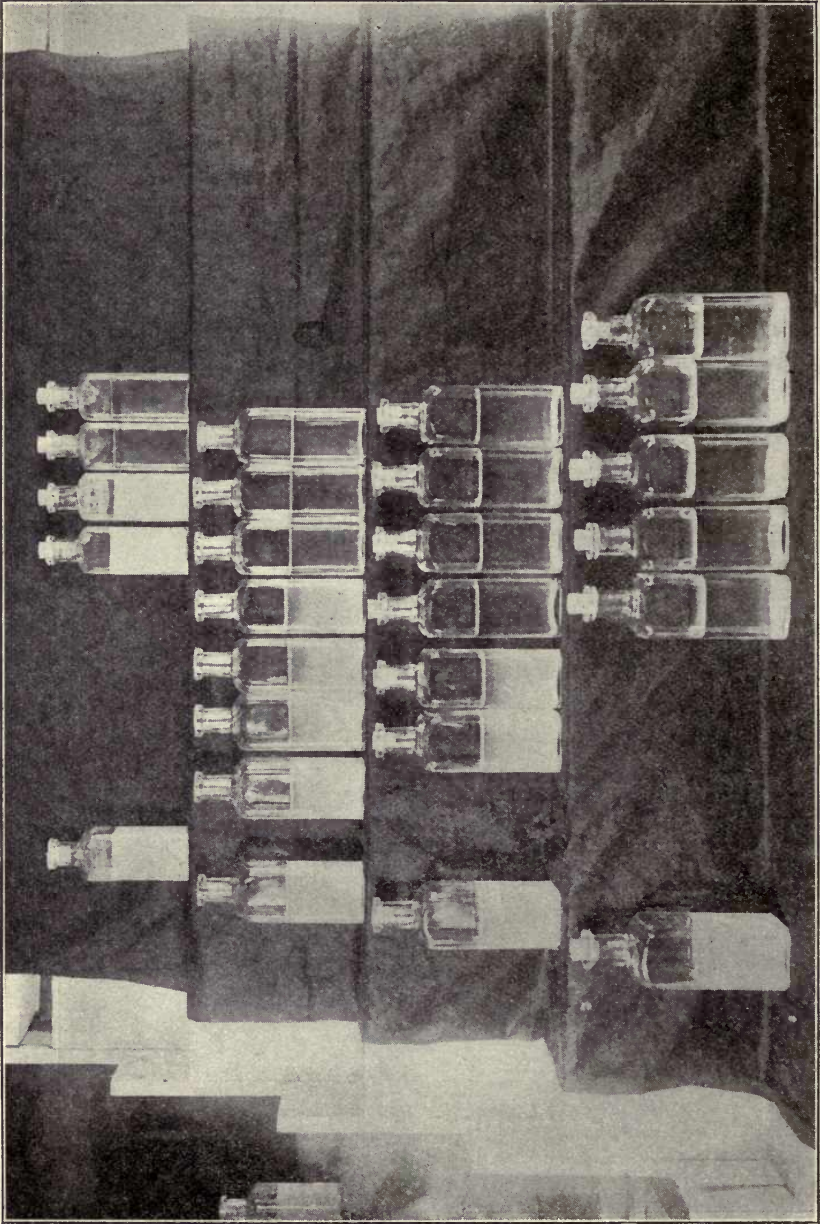0—Increasing $Al_2(SO_4)_3$.

Milliequivalents of $Mg(HCO_3)_2$

0
1
2
3

34

Figure 14.—The effect of CaCl₂ on the coagulation of clay suspensions by Al₂(SO₄)₃.
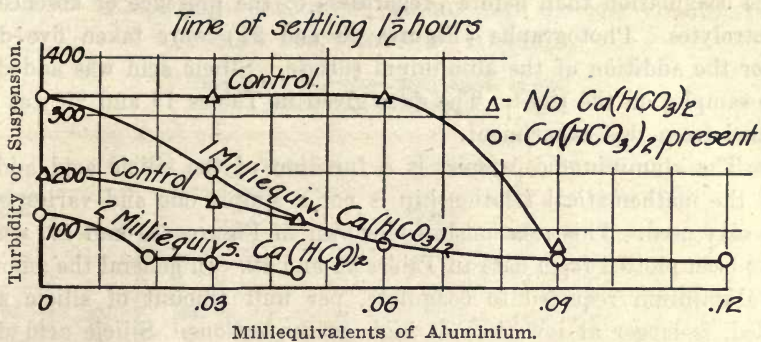
0—Increasing Amounts of Al₂(SO₄)₃.

Figure 15.—Effect of Ca(HCO₃)₂ on the coagulation of clay suspensions by Al₂(SO₄)₃.

As would be expected the presence of the trivalent and bivalent ions aid in the coagulation, sodium chloride and sulfuric acid have little effect at low concentrations, while the addition of the sodium salts causes a behavior similar to that produced by the action of sodium hydroxide (Figure 3).

As the content of sodium hydroxide is increased the amount of aluminium sulfate must be increased in order to produce coagulation and to combat the dispersive power of the sodium compound. This same effect is quite noticeable with sodium carbonate but less so with sodium acid carbonate and sulfate.

The point of coagulation is not dependent on the alkalinity of the solution. The results of these experiments are partly in accordance with work and theories of Rohland.[40,42] There seems to be no question but that coagulation is a function of the concentration of the hydroxyl ion and alkali metal ions as well as the valencies of the cation.

The monovalent ion of the alkalies is intimately connected with the dispersive or protective action of sodium salts in the coagulation of clay suspensoids and with the peculiar (Protective) effect of silicic acid in preventing the formation of aluminium hydroxide by the action of aluminium chloride and sodium hydroxide. If calcium is substituted for sodium these peculiar effects are not produced.

The effect of silicic acid on the coagulation of clay suspensions by aluminium sulfate is shown in Tables 21, 22, and 23, and Figures 15 to 19. A suspension containing 62 parts per million of dialyzed silicic acid and appropriate amounts of electrolytes were coagulated with alum and the rate of reaction compared with a suspension containing no added silicic acid. In all cases the effect of the added silicic acid was to retard the reaction, and more aluminium sulfate was required to pro-

duce coagulation than before—regardless of the presence or absence of electrolytes. Photographs (Figures 20 and 21) were taken five days after the addition of the aluminium sulfate. Silicic acid was added to the samples on the right. The data given in Tables 19 and 20 was obtained from this experiment.

The aluminium consumed is a function of the silicic acid added, but the mathematical relationship is not a simple one and varies with the clay used. This relationship is shown in Figures 15 and 17, which have been plotted from data in Tables 21 and 22. In general the amount of aluminium required to coagulate, per unit amount of silicic acid added, is larger at low than at high concentrations. Silicic acid does not seem to stabilize or disperse the clay particles, nor does its presence influence the rate of sedimentation. In this respect it differs from the alkali salts.

TABLE 21—RETARDING EFFECT OF SILICIC ACID ON THE COAGULATION OF CLAY SUSPENSION BY $Al_2(SO_4)_3$.

Tenn. No. 3 Ball Clay—Temperature ca 24°C.
Silicic Acid (SiO_2) added.

Milligram equivalents.	0 ppm.*		12.4 ppm.		24.8 ppm.		37.2 ppm.		49.6 ppm.	
	Turbidity.									
	1½**	13	1½	13	1½	13	1½	13	1½	13
.0	400	225	400	225	400	250	400	275	400	275
.03	400	150								
.06	400	125	400	175	400	250	400	275	400	275
.09	125	10	400	150						
.12	75	5	50	10	125	75	175	125	225	125
.15			50	10	50	20				
					50	10	50	20	50	25
							60	10	50	10
							50	10	40	10
									25	10

The Amount of Alum Necessary to Produce a Definite Clarification in 13 Hours in the Presence of Silicic Acid.

SiO₂ added.	Al₂(SO₄)₃ added to reduce turbidity to	
	100 ppm.	50 ppm.
10 ppm.	.07†	.084†
12.4 ppm.	.102	.111
24.8 ppm.	.112	.129
37.2 ppm.	.126	.153
49.7 ppm.	.129	15.3

* Parts per million.
** Time expressed in hours.
† Milligram equivalents.

TABLE 22—RETARDING EFFECT OF SILICIC ACID ON THE COAGULATION OF CLAY SUSPENSION BY $Al_2(SO_4)_3$.

Tenn. No. 3 Ball Clay—Temperature ca 24°C.
Silicic Acid (SiO_2) added.

Milligram equiva-lents.	0 ppm.*		12.4 ppm.		24.8 ppm.		37.2 ppm.		49.6 ppm.	
	Turbidity.									
	1**	24	1	24	1	24	1	24	1	24
.03	400	200	------	------	------	------	------	------	------	------
.06	400	150	------	------	------	------	------	------	------	------
.09	175	5	350	100	------	------	350	------	------	------
.12	30	5	325	50	350	50	350	100	------	------
.15	------	------	200	25	350	50	350	100	------	------
.18	------	------	75	5	350	50	350	100	------	------
.21	------	------	40	5	125	25	212	40	200	75
.24	------	------	40	5	50	10	100	30	------	------
.27	------	------	------	------	50	5	50	20	100	50
.30	------	------	------	------	50	5	40	5	------	------
.33	------	------	------	------	------	------	40	5	50	20
.39	------	------	------	------	------	------	------	------	25	15
.45	------	------	------	------	------	------	------	------	20	12
.51	------	------	------	------	------	------	------	------	20	10

The Amount of $Al_2(SO_4)_3$ Necessary to Produce a Definite Clarification in One Hour in the Presence of Silicic Acid.

SiO_2 added.	$Al_2(SO_4)_3$ added to reduce turbidity to	
	100 ppm.	50 ppm.
0	.105+	.115+
12.4 ppm.	.174	.200
24.8 ppm.	.210	.240
37.2 ppm.	.240	.270
49.6 ppm.	.270	.330

* Parts per million.
** Time expressed in hours.
+ Milligram equivalents.

TABLE 23—RETARDING EFFECT OF SILICIC ACID ON THE COAGULATION OF CLAY SUSPENSIONS BY $Al_2(SO_2)_3$ IN THE PRESENCE OF ELECTROLYTES.

Tenn. No. 1 Ball Clay—Turbidity 400 parts per million—Temperature ca 21° C—Time 3 hours.

Milli-equivalent of Al.	Milligram equivalents of salts.									
	.18 NaOH.		1.5 NaHCO₃.		2 NaCl.		2 Na₂SO₄		2 Mg(HCO₃)₂.	
	Dialyzed silicic acid, parts per million as SiO₂.									
	0	62	0	62	0	62	0	62	0	62
.03	----	----	----	----	----	350	----	----	----	400
.06	----	----	----	400	----	350	----	400	----	400
.09	----	400	----	----	350	325	75	400	----	----
.12	----	----	----	----	----	225	----	350	----	----
.15	----	400	----	----	----	----	25	25	----	350
.18	400	----	400	400	35	125	----	----	----	300
.21	25	350	----	----	----	----	10	10	----	----
.27	25	25	----	----	----	----	----	----	----	----
.30	----	----	85	400	35	15	----	----	----	----
.36	125	10	----	----	----	----	----	----	----	----
.39	----	----	65	350	----	----	----	----	----	----
.45	----	0	----	----	----	----	----	----	----	----
.60	----	----	65	300	----	----	----	----	----	----

Milli-equivalent of Al.	Milligram equivalents of salts.							
	2 MgSO₄.		0.7 Ca(OH₂).*		1.0 Ca(HCO₃)₂.		0.7 CaOH₂† 1.0 ca (HCO₃)₂.	
	Dialyzed silicic acid, parts per million as SiO₂.							
	0	62	0	62	0	62	0	62
.03	----	400	85	180	350	400	175	400
.06	50	400	85	180	100	400	----	----
.09	----	----	85	170	65	400	250	350
.12	50	150	125	170	65	400	----	----
.15	----	----	100	160	----	----	175	325
.18	25	65	----	----	----	----	----	----
.21	----	----	----	----	----	----	150	250
.27	----	----	----	----	----	----	----	----
.30	----	----	----	----	----	----	----	----
.36	----	----	----	----	----	----	----	----
.39	----	----	----	----	----	----	----	----
.45	----	----	----	----	----	----	----	----
.60	----	----	----	----	----	----	----	----

* 13 hours.
† Readings expressed as turbidities.

Milliequivalents of Aiuminium.
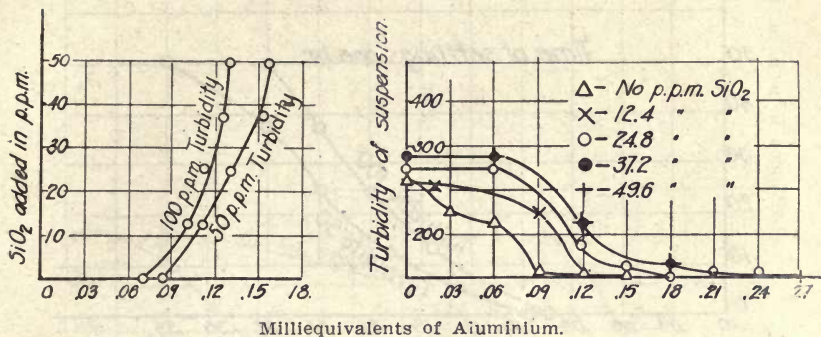
The amount of Aluminium necessary in the presence of silicic acid to produce a definite clarification.

Figure 16.—Effect of silicic acid on the coagulation of clay suspension by $Al_2(SO_4)_3$.
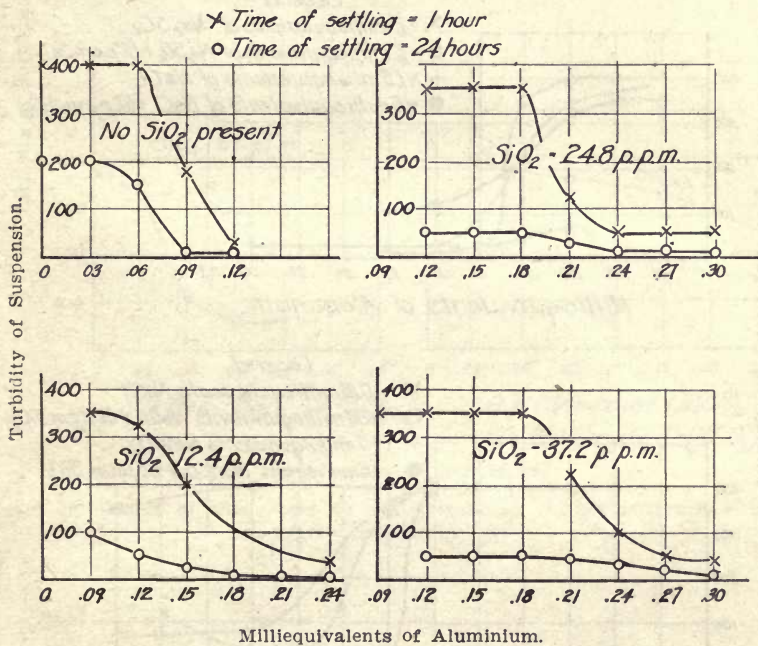

Milliequivalents of Aluminium.

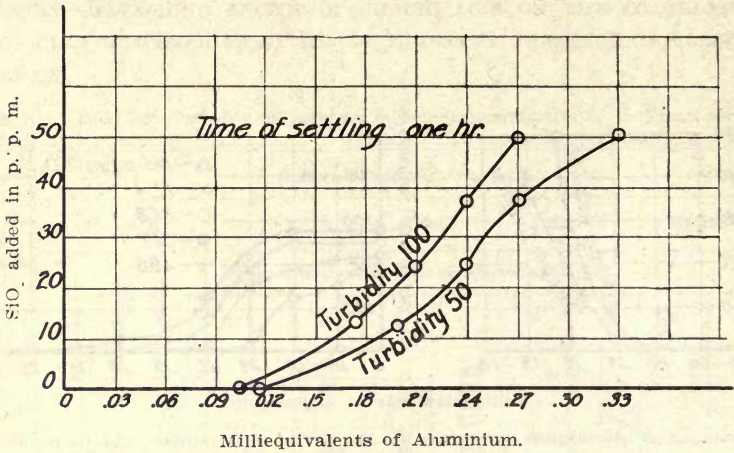Figure 17.—Effect of silicic acid on the coagulation of clay by $Al_2(SO_4)_3$.

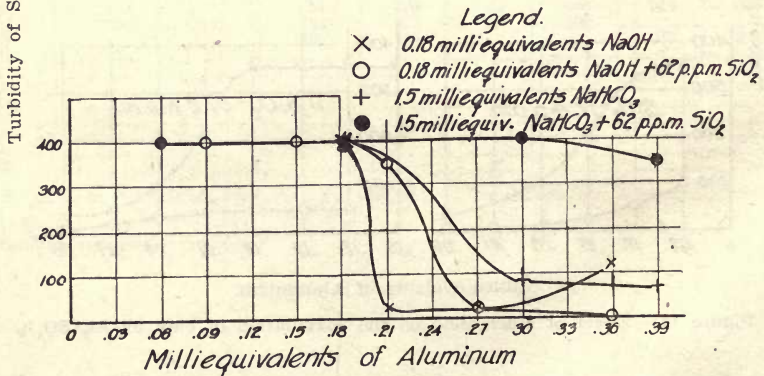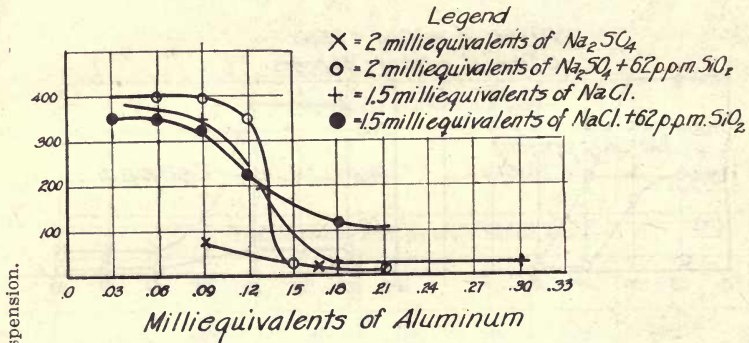Figure 18.—Al necessary to produce a definite clarification in the presence of silicic acid. Plotted from Figure 14.

Figure 19.—Effect of sodium salts on the coagulation of clay suspension by $Al_2(SO_4)_3$ in the presents of silicic acid.
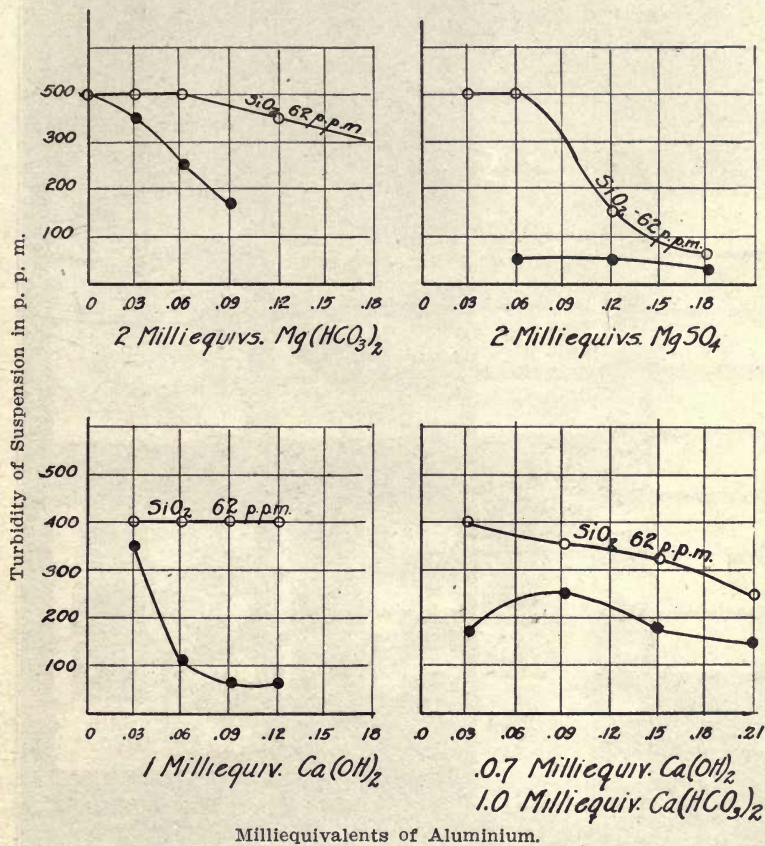
Figure 20.—Effect of silicic acid on the coagulation of clay suspensions in the presence of Electrolytes.

42

Standards of Turbidity.

Electrolyte Ca(HCO₃)₂

MgSO₄

Ca(OH)₂

Absent.   Colloidal Silicic Acid.   Present.

Figure 21.—The effect of silicic acid on the coagulation of clay suspensions by Al₂(SO₄)₃.
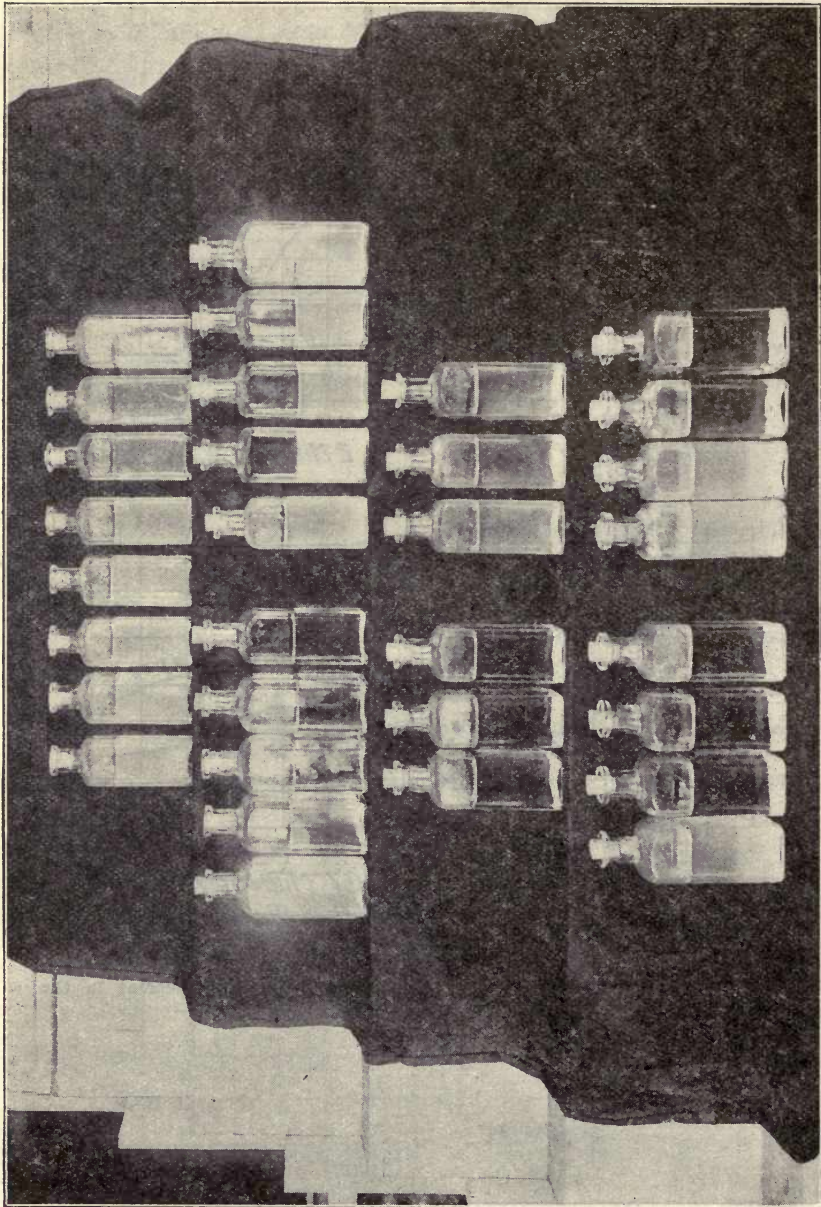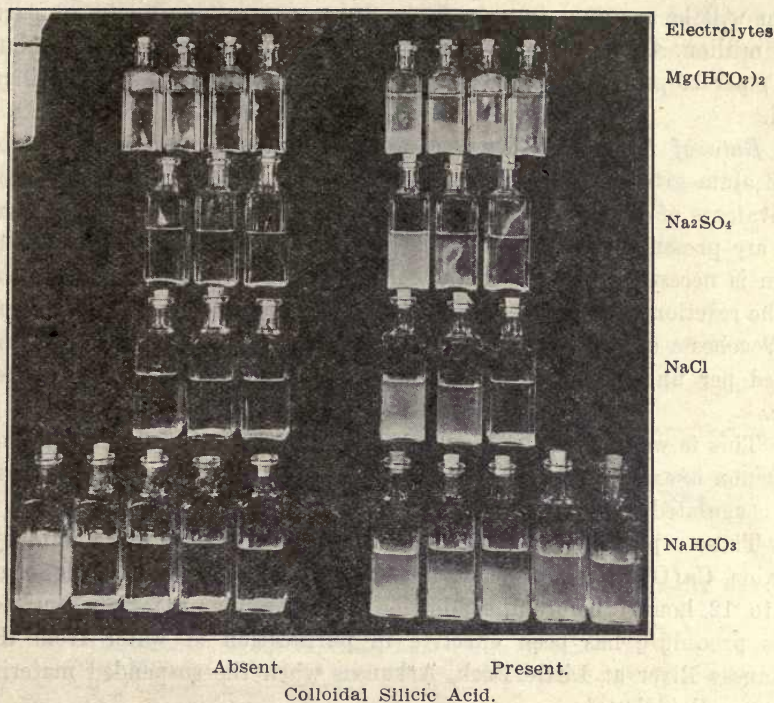
Absent.   Present.
Colloidal Silicic Acid.
Figure 22.—The effect of silicic acid on the coagulation of clay suspensions by $Al_2(SO_4)_3$.

APPLICATION.

Removal of Silicic Acid From Water to be Used for Boiler Purpose.

The experiment on a natural water already referred to indicates that silicic acid could be most economically removed by aluminium hydroxide formed in the reaction of aluminium sulfate with calcium hydroxide in a solution whose Ph value is 8.0 — 9.0, and that the precipitation is more or less directly related to the ratio of (Ca + Mg) : Na. The higher this ratio the more complete is the removal. By the proper treatment with aluminium sulfate and line it is possible to reduce the silicic acid content from 82.6 to 30 parts per million.

The Coagulation of Waters Containing Colloidal Clay.

The stability of a suspension of clay seems to be intimately connected with the amount of monovalent cations and bivalent anions present. Thus the alum needed to coagulate will be greater the larger the concentration of sodium ions except in the case when the anion is mainly chlorine. Less alum will be needed as the ratio of the Ca + Mg ions to the sodium ion increases. As the silicic acid content increases more

alum will be required to coagulate. In concentrations up to 20 parts per million, from 0.015 to 0.03 milligram equivalents of aluminium (Al) per 10 parts of SiO_2 is needed to combat the influence of the silicic acid.

Rate of Reaction.—Water containing bivalent ions when treated with alum gives a sharp, abrupt reaction, an increase of 0.3 milligram equivalents of aluminium, Al, coagulates, but when silicic acid or alkalies are present, other factors being constant, a much larger amount of alum is necessary to produce the same clarification and the abruptness of the reaction becomes less as the amount of the silicic acid and alkalies approaches a certain maximum where the magnitude of the change produced per unit amount of alum is much smaller than in the former case.

This is well shown in Figures 8, 9, 12, 14, 15, and 21. This phenomenon is exactly similar to that which occurs when "colloidal waters" are coagulated by alum and lime.

These experiments justify the addition of an excess of calcium hydroxide, $Ca(OH)_2$ and allowing it to react with the water for some time (8 to 12 hours) before the addition of the alum or ferrous sulfate. This procedure has been effective in purification of water from the Arkansas River at Little Rock, Arkansas when the suspended material is in a colloidal state.

SUMMARY.

1. Colloidal silicic acid in dilute solution can be precipitated by aluminium hydroxide.

2. Dilute solutions of dialyzed and undialyzed silicic acid behave towards electrolytes in the same manner as concentrated solutions— with the exception that proportionately more reagent is needed.

3. The optimum hydrogen ion concentration for the precipitation of the aluminium hydroxide and the removal of silicic acid by aluminium hydroxide is a concentration of 1×10^{-8}.

4. The limiting values of the hydrogen ion concentration, between which the solid aluminium hydroxide phase is present are 1×10^{-4} and 11×10^{-11}.

5. The presence of silicic acid prevents the formation of a precipitate of aluminium hydroxide, when the sodium hydroxide, equivalent to the aluminium chloride present, is added all at once. The silicic acid probably as a protective colloid prevents precipitation of the aluminium hydroxide. The presence of bivalent cations destroys this protective power.

6. The action of electrolytes on clay suspensoids is the same in dilute as in concentrated suspensions. (Slips).

7. Sodium hydroxide, acid carbonate, and sulfate stabilize or disperse clay suspensions at one concentration and coagulate at another.

8. The ratio of the coagulating power of calcium and barium hydroxide to aluminium hydroxide is about 1 to 5.

9. Coagulation of clay suspensions is aided by the bivalent and hindered by monovalent cations in the presence of acid carbonate, carbonate, sulfate and hydroxyl anions.
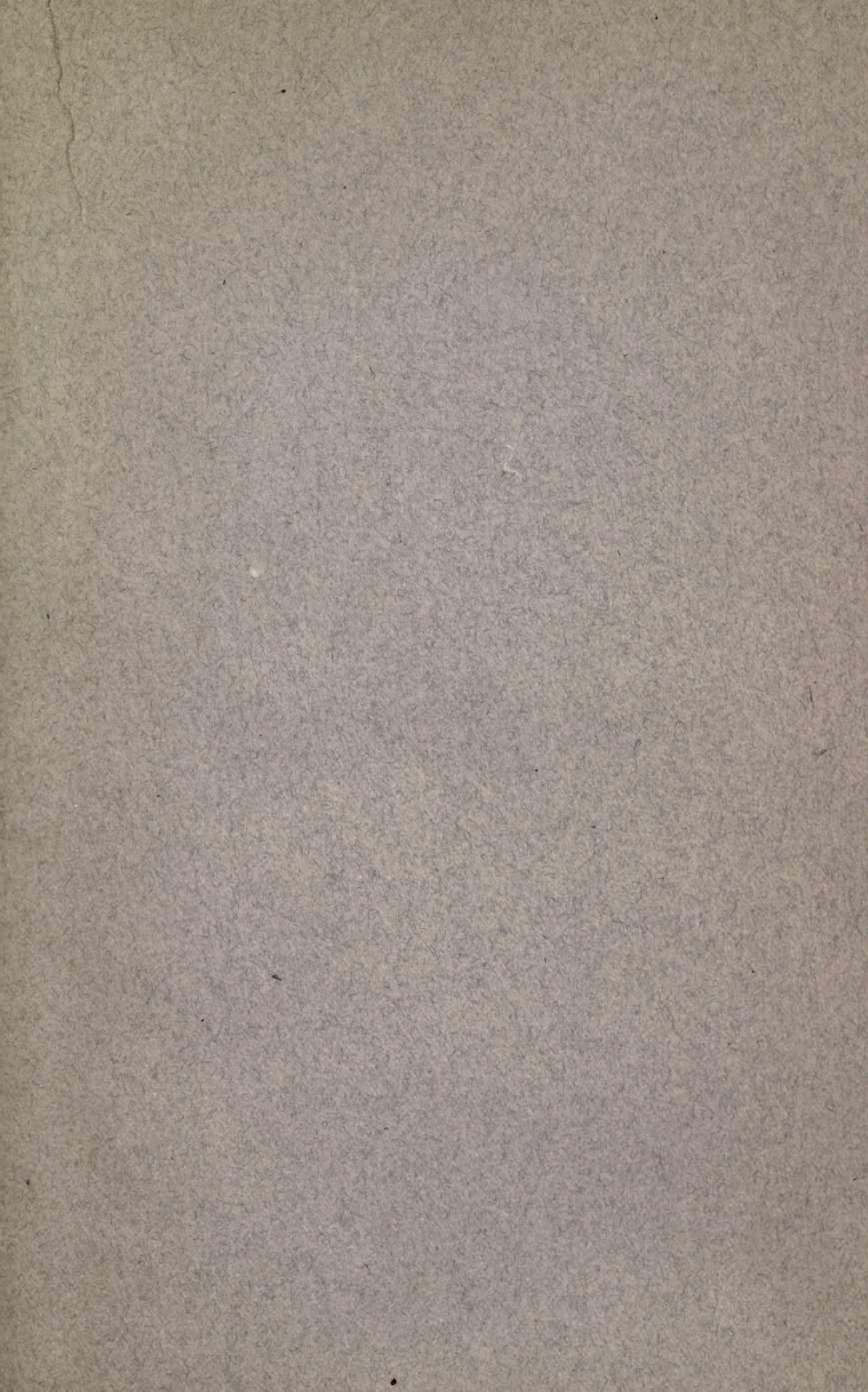
10. Silicic acid retards coagulation of clay suspensoids.

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VITA.

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