

CCCCV.—*The Influence of Alkalis on the Coagulation of Silica and Clay Suspensions by Alkali Chlorides.*

By HENRY BOWEN OAKLEY.

MANY studies have been made on the coagulation of clay suspensions and silicic acid sols by electrolytes, but hardly any systematic observations have been made on the influence of the reaction of the medium on the results, although Bradfield (*J. Amer. Chem. Soc.*, 1923, 45, 1243) has shown that this factor has a great influence on the coagulation of clay, as on most other aqueous colloidal systems.

In continuance of the comparison of the properties of clay and silica made in these laboratories, a comparative study of the coagulation of a fine suspension of the latter substance was also made. The results suggested that silica on which small quantities of alumina had been precipitated might behave like clay in its coagulation by mixtures of alkali-metal chlorides and hydroxides. This proved to be the case when certain conditions were observed, and the general results lend further support to the view that the reactions involved in the absorption of alkalis by clay and its coagulation are of a chemical nature. The experiments recorded in this paper are confined to the alkali-metal and calcium chlorides and hydroxides.

*Description and Preparation of Clay.*—The clay used in these

experiments was No. 10195, prepared from a heavy cotton soil by decantation from 0.05% sodium carbonate. It was flocculated by dilute hydrochloric acid ( $N/100$ ) and purified to a high resistance by dialysis. The molecular ratio  $\text{SiO}_2 : \text{Al}_2\text{O}_3$  was about 4. The clay was practically identical with No. 6640 described by Joseph and Hancock (J., 1924, **125**, 1888) and contained 0.15% of humus. It may be objected that the process of purification may largely alter the characteristics of clay; this is certainly true in that an "acid" clay has very different properties from the same clay combined with a base, but there is no evidence that the process of purification alters the clay in any other way.

#### EXPERIMENTAL.

*The Nephelometric Method of Measuring the Concentration of Clay Suspensions.*—In some of the experiments the amount of clay remaining in suspension in the various tubes after 1 hour was estimated by comparison with a standard suspension of clay in a Klett nephelometer. Preliminary experiments showed that, contrary to expectation, neutral flocculants even in excess did not affect the turbidity if the suspension was stirred immediately before the measurement was made. The addition of alkalis, however, produced a very marked decrease in turbidity, the effect apparently being dependent only on the nature of the alkali and not on its concentration. The following table shows the effect produced by hydroxides and carbonates, the turbidity of a 0.1% purified clay suspension being taken as unity and used as standard.

	Ba.	Ca.	$\text{NH}_4$ .	K.	Na.	Li.
Hydroxide .....	0.95	0.93	0.84	0.81	0.58	—
Carbonate .....	—	—	0.82	0.84	0.64	0.50

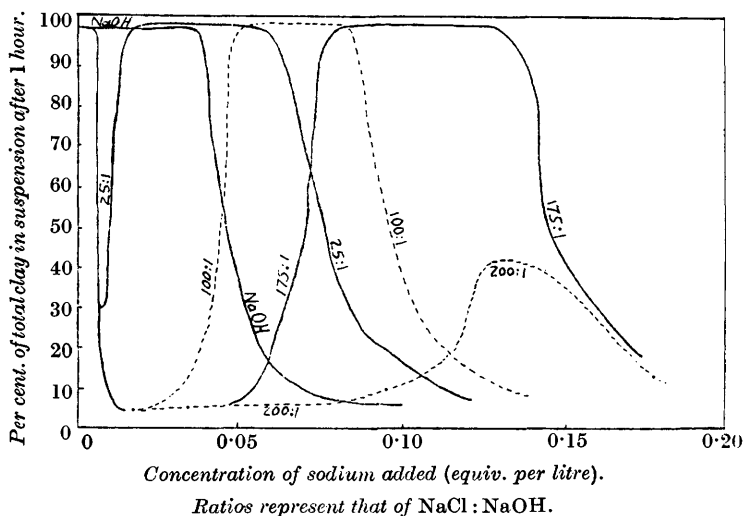
The order is approximately that of the Hofmeister series. This decrease in turbidity was allowed for in measuring the concentration of alkaline suspensions by using an alkaline standard.

*The Flocculation of Clay by Mixtures of the Chlorides and Hydroxides of the Alkali Metals.*—Following Bradfield (*loc. cit.*), a series of mixtures was prepared,  $N$  with respect to sodium, containing sodium chloride and sodium hydroxide in ratios ranging from 2 : 1 to 200 : 1. Each mixture was added in increasing amounts to a series of large boiling-tubes. Water was added to make the volume up to 45 c.c., and then 5 c.c. of a 1% suspension of purified clay (10195) were added at 5-minute intervals to each tube. These were shaken a dozen times by hand, and after standing undisturbed for 1 hour, 10 c.c. were withdrawn with a pipette 3.5 cm. below the surface. The height of each column of liquid was about 7 cm.

The amounts of clay in these samples were estimated in the nephelometer, and when required, the  $p_H$  of a further sample was also measured electrometrically with a Clark's cell.

Some of the results are plotted in Fig. 1. The ordinates represent the percentage of the total amount of clay remaining in suspension after 1 hour and the abscissæ the total concentration of the sodium. The interesting effect is observed that the curves for mixtures in which the ratio of chloride to hydroxide is 25 to 1 or more show a pronounced maximum and minimum, the range of the latter increasing with increasing ratio of chloride to hydroxide, until with pure sodium chloride the maximum has disappeared completely. This

FIG. 1.

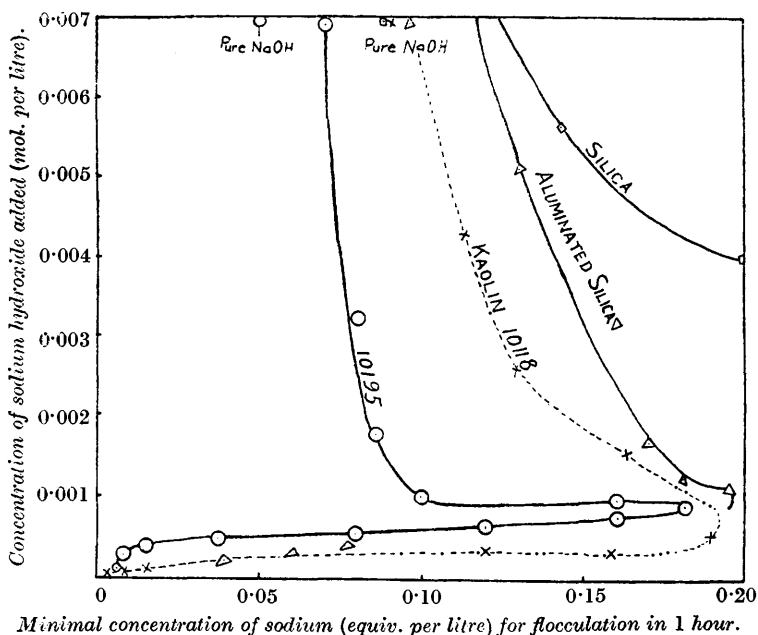


phenomenon has been observed with different clays and only fails when the initial reaction of the suspension is alkaline (*Nature*, 1926, **117**, 624). It is also shown with a more limited range of mixtures by kaolin, but here the ratio of chloride to hydroxide must not be less than 250 to 1. The same phenomenon is shown with lithium, potassium, and also calcium at much lower concentrations and for mixtures in which the ratio of calcium chloride to calcium hydroxide varies from 1 : 1 to 3 : 1.

The following scheme compares the effects of mixtures of potassium, sodium, and lithium chlorides with their respective hydroxides in which the ratio of chloride to hydroxide is 100 : 1. A minus sign indicates no flocculation in 1 hour, and a plus sign indicates that less than 30% remains in suspension after 1 hour.

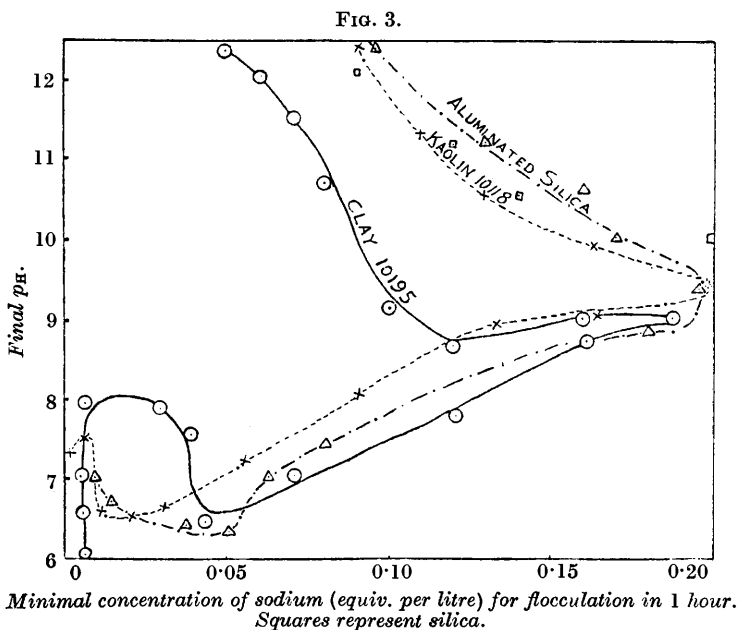
Conc. of metal, $\times 10^3$ .	K.	Na.	Li.	Ca (conc. $\times 10^4$ ). CaCl <sub>2</sub> : Ca(OH) <sub>2</sub> = 2 : 1.
2	—	—	—	—
3	+	—	—	—
5	+	—	—	—
7	+	+	—	—
10	+	+	+	—
20	+	+	+	—
30	+	+	+	—
40	±	—	—	—
50	—	—	—	—
60	—	—	—	—
80	+	—	—	+
100	+	±	—	+
140	+	+	—	—
180	+	+	+	—
200	+	+	+	+

FIG. 2.



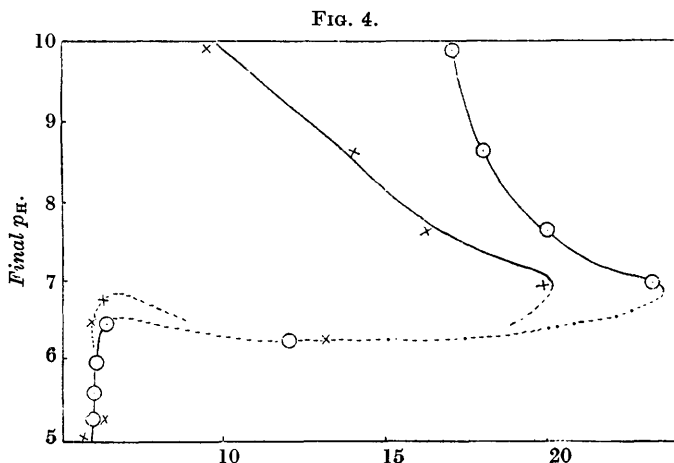
It will be noticed that the flocculating power and the first zone of coagulation decrease in passing from potassium to lithium. This phenomenon was not observed by Bradfield (*loc. cit.*), who worked on the finest fraction of clay separated by means of a supercentrifuge. His suspension, although acid, had not been treated with *N*/100-hydrochloric acid before purification, as in the present work, and his observations were made after the suspensions had been standing for 24 hours.

The influence of the alkalinity on the minimal concentration of kation required to flocculate clay in 1 hour can best be summarised by plotting these quantities. In Fig. 2, the concentration of hydroxide added is plotted against this minimal concentration, and in Fig. 3 the final  $p_H$  is similarly plotted. The minimal concentration is defined, for the purpose of these curves, as that concentration which allows for the 20 and 40% of the clay to remain in suspension after 1 hour. The results for kaolin and for silica on which a small quantity of aluminium hydroxide has been precipitated are also included in these diagrams, and will be discussed later. The most



important characteristic of these curves is that the minimal concentration of sodium required for flocculation rises very rapidly on the addition of small quantities of alkali, and reaches a very pronounced maximum when the concentration of alkali added is 0.009N or when the  $p_H$  is 9. This for a 0.1% suspension corresponds to the amount of sodium this clay can absorb without beginning to break down into soluble silicates and aluminates (Oakley, this vol., p. 2819). A curious feature of the curves in Fig. 3 is the sudden drop in the  $p_H$  and its subsequent rise with increasing concentrations of sodium, and this in spite of the steadily increasing concentrations of alkali as shown in Fig. 2. Although the measurements in this

neighbourhood are admittedly difficult to repeat, there is no doubt of the reality of the effect which has been observed in each of the three substances studied. The fall in  $p_H$  is due to increased absorption of sodium with increasing sodium-ion concentration accompanied by the liberation of an equivalent quantity of hydrogen ions. The combination of the clay with sodium is accompanied by an increase in the concentration of sodium ions required to flocculate it in a given time. That sodium chloride has a very large effect in decreasing the  $p_H$  of clay suspensions is shown by the following figures. The effect is far greater than that produced on sodium silicate which is in true solution, and it is generally agreed that this is due to the



Added concentration of calcium required for flocculation in 1 hour (equiv. per litre  $\times 10^4$ ) (circles). Specific conductance ( $\times 10^5$ ) at  $20^\circ$  (crosses).

combination of sodium with the clay acid, with the liberation of an equivalent quantity of free acid.

The lowering of  $p_H$  by the addition of neutral salt.

1% Clay suspension.		Sodium silicate ( $\text{SiO}_2 = 0.02M$ ).	
No NaCl.	$N/2$ -NaCl.	No NaCl.	$N/2$ -NaCl.
10.70	9.30	10.72	10.39
10.01	7.85	9.90	9.62
9.40	7.00	9.40	9.00
8.60	6.30	—	—

*The Flocculation of Clay by Calcium Chloride and Hydroxide.*—These results are plotted in Fig. 4; as with sodium, the minimal concentration of calcium required for flocculation shows a sudden increase to a maximum with the addition of small quantities of calcium hydroxide, but here the concentrations are about 1/10 of

those for sodium, and the  $p_H$  at the maximum is 7 instead of 9. The curve for the specific conductivity shows that the decrease in the minimal concentration above a  $p_H$  of 7 is even more marked than that indicated by the other curve, which shows the initial concentration of calcium added. As with sodium, the results indicate that the combination of the clay with calcium in the initial stages is accompanied by an increase in the concentration of calcium ions required to flocculate it in 1 hour. This is directly opposite to the results obtained by Comber (*J. Agric. Sci.*, 1920, **10**, 425) and confirmed by Kermack and Williamson (*Nature*, 1926, **117**, 824), who found that clay was more readily flocculated by calcium in an alkaline medium. The discrepancy is due to the fact that these workers used more concentrated solutions and consequently much higher rates of flocculation than those described in this paper. This is clearly shown by the following results (*Nature*, 1926, **118**, 661) for the time required to flocculate a 0.1% suspension in solutions of calcium hydroxide and chloride at various concentrations.

Conc. of Ca <sup>++</sup> ions.	Time required for flocculation.		
	Ca(OH) <sub>2</sub> .	CaCl <sub>2</sub> .	2Ca(OH) <sub>2</sub> + CaCl <sub>2</sub> .
0.001	7 hours	14 mins.	6 hours
0.002	28 mins.	10 "	32 mins.
0.003	2 "	7 "	12 "
0.004	1.5 "	6 "	4.5 "
0.005	1.5 "	6 "	3.5 "
0.010	1.5 "	6 "	1.5 "
0.014	1.5 "	6 "	1.5 "

It is shown below that a suspension of silica is only coagulated by calcium chloride or sodium chloride in an *alkaline* medium. I suggest that the reason why clay is coagulated more readily in an alkaline medium only when the concentration of the alkali is above a certain value is that at these higher concentrations some of the clay is broken down into silicates (Oakley, *loc. cit.*) and thus behaves in flocculation like silica.

*The Effect of Alkalies on the Flocculation of Silica.*—Smith (*J. Amer. Chem. Soc.*, 1920, **42**, 461) noticed that silicic acid is coagulated by sodium and calcium hydroxides at concentrations of 0.1 and 0.002, respectively, but not at all by the chlorides at a concentration of 0.07. These results have been confirmed for a silica suspension. The silica used in these experiments was purified by repeated treatments with hot concentrated hydrochloric acid, washed by decantation, and dialysed to a high specific resistance. It was then reduced to a finely divided state by repeated grinding in a wet condition in an agate mortar and sedimentation. In this way, a 1% suspension was obtained which remained in suspension for 2 hours. The following table gives the minimum concentration of

sodium required to cause coagulation of a 0.1% suspension in 1 hour, various mixtures of sodium chloride and sodium hydroxide being used. The experiments were made in test-tubes, the volume being 10 c.c., and 1 c.c. of the 1% suspension being added last.

The flocculation of silica by sodium chloride and hydroxide mixtures.

NaCl : NaOH.	Conc. NaOH, × 100.	Conc. Na, × 100.	$p_H$ .	NaCl : NaOH.	Conc. NaOH, × 100.	Conc. Na, × 100.	$p_H$ .
0 : 1	9.0	9	12.21	300 : 1	0.14	42	9.21
10 : 1	1.2	12	11.13	500 : 1	0.11	55	8.73
25 : 1	0.56	14	10.53	1000 : 1	0.07	70	8.20
50 : 1	0.40	20	10.06	2000 : 1	0.045	90	7.27
100 : 1	0.26	26	9.77	1 : 0	0.00	100	No
200 : 1	0.18	37	9.54				flocc.

Some of these results are plotted in Figs. 2 and 3. Above a  $p_H$  of 10, the points for silica lie close to the curve for kaolin, but with a decrease in the  $p_H$  the flocculating concentration for silica continues to increase rapidly, whereas for kaolin and clay it shows a sudden decrease.

*The Flocculation of Silica by Alumina.*—It was thought that this difference in the flocculating concentrations for clay and silica might be connected with the presence of combined alumina in the former substance, and it was accordingly decided to precipitate small quantities of alumina on silica and to find out how this product behaved towards coagulation by mixtures of sodium chloride and hydroxide.

In the following experiments the effect of sodium hydroxide on the coagulation of silica by aluminium chloride was studied. The order of adding the reagents has an effect. In these experiments the 1% silica suspension was always added to the aluminium chloride solution, and the sodium hydroxide was added last. The final concentration of silica was 0.1%. The following scheme summarises the results. The sign of the charge of the resultant suspension was determined by cataphoresis in a U-tube.

Flocculation of a 0.1% silica suspension by aluminium chloride and sodium hydroxide.

$AlCl_3$ (mol. per litre).	NaOH (mol. per litre).	Sign of charge.	Whether flocculated or not.	$p_H$ .
<0.0001	0	—	Deflocculated	
0.0001	0	Neutral	Flocculated slowly	2.4
>0.0001	0	+	Deflocculated	
0.0001	<0.0002	Neutral	Flocculated slowly	
0.0001	0.0002	Neutral	Flocculated	5.3
0.0001	>0.0002	—	Deflocculated	
0.001	<0.003	+	Deflocculated	
0.001	0.003	Neutral	Flocculated	8.5
0.001	>0.004	—	Deflocculated	



Small quantities of aluminium chloride flocculate silica, but larger quantities give a stable electropositive suspension. The addition of sodium hydroxide in quantities approximately equivalent to the aluminium chloride rapidly flocculates the silica, but the  $p_H$  at which this most rapid flocculation takes place depends on the concentration of aluminium chloride. The further addition of sodium hydroxide results in the formation of a stable electro-negative suspension. I think these results are most simply accounted for by supposing the particles of the electropositive suspensions to be coated with aluminium hydroxide, which therefore imparts the properties of a suspension of this substance to the silica. Thus, like aluminium hydroxide, it is electropositive and is easily flocculated by the addition of sodium hydroxide. With the further addition of caustic soda, a surface layer of sodium aluminosilicate is formed, which, like clay, is electronegative owing to surface ionisation into sodium ions and insoluble aluminosilicate ions. This substance should therefore behave like clay with regard to flocculation by mixtures of sodium chloride and hydroxide.

*The Preparation and Flocculation of "Aluminated" Silica.*—A stock of silica coagulated with aluminium hydroxide was prepared by adding to a 1% suspension of silica, water, aluminium chloride, and then sodium hydroxide in amounts to make the final concentrations 0.5% of silica, 0.001*M*-aluminium chloride and 0.0023*N*-sodium hydroxide. To obtain coagulation, it was necessary to determine these concentrations with some care by making initial trials on small quantities. The suspension was centrifuged, the supernatant liquid decanted, and water added to the residue to make the suspension 1%. This was stable when diluted to 0.1%. The settled material was about four times as bulky as silica. A series of flocculation experiments using mixtures of sodium chloride and hydroxide was then made on 0.1% suspensions in test-tubes as with silica: the results are plotted as triangles in Figs. 2 and 3. An exactly similar series of observations was made on a pure suspension of kaolin: these results are shown as crosses in the figures. The curves for the two substances have closely similar characteristics, although the maximum in both cases is less pronounced than for clay.

Both "aluminated" silica and kaolin showed successive flocculation, deflocculation, and flocculation on the addition of increasing quantities of alkaline sodium chloride, provided the ratio of chloride to hydroxide was not less than 250 : 1. Silica, however, does not show this phenomenon. The following scheme compares the behaviour of the three substances towards flocculation by a 300 : 1 mixture of sodium chloride and hydroxide. The negative sign

indicates no flocculation and the positive sign flocculation after 1 hour. It should be mentioned that these results were obtained on a suspension of "aluminated" silica only 2 or 3 days old; a few experiments on a preparation which had been standing several months showed a change in the concentrations required for flocculation.

Conc. of Na <sup>+</sup> ion, $\times 10^3$ .	Silica.	"Aluminated" silica.	Kaolin (10118).
3	—	—	—
5	—	—	+
7	—	+	+
10	—	+	+
15	—	+	+
20	—	+	—
30	—	+	—
40	—	—	—
50	—	—	—
70	—	+	—
100	—	+	—
150	—	+	—
180	—	+	+
450	+	+	+

*Comparison of the Flocculating Powers of Sodium Hydroxide, Carbonate and Bicarbonate.*—As might be anticipated from the curves in Fig. 3, sodium hydroxide flocculates at a lower concentration than the carbonate, which in turn flocculates at a lower concentration than the bicarbonate, since this is the order of decreasing alkalinity of the three compounds. This is illustrated in the following table :

Concentration of alkali required to flocculate in 1 hour.

Clay.	NaOH.	Na <sub>2</sub> CO <sub>3</sub> .	NaHCO <sub>3</sub> .
Gezira (10195) .....	0.05	0.30	0.35
Mongalla (18107) (red) .....	0.21	0.32	0.32
Kaolin (10118) .....	0.09	0.40	0.42
Silica .....	0.09	0.42	0.95
"Aluminated" silica .....	0.09	0.25	0.60

In the present paper, I have purposely omitted any discussion of the mechanism of flocculation, owing to the absence of any really satisfactory theory of the phenomenon for colloids in general, but I think that the maxima and minima in the curves of Fig. 1 can be regarded as the outcome of two opposing factors in the stability of clay. The first factor, which tends to stabilise the suspension is the formation of a sodium compound with the clay; the extent to which this takes place will depend upon the reaction of the medium and the concentration of sodium ions, and reaches a limit between  $p_H$  9 and 10 (Oakley, *loc. cit.*). The second factor, which tends to flocculate the suspension, is the concentration of electrolyte in solution. With increasing concentrations of slightly alkaline

sodium chloride, the clay is first flocculated at a low concentration because it remains essentially an "acid clay" and contains no sodium to stabilise it. With higher concentrations, sodium is absorbed in increasing quantities until the sodium-clay complex is sufficiently lyophilic to withstand quite high concentrations of sodium chloride, but the concentration at which this second deflocculation takes place will depend on the alkalinity of the mixture used, being lower the greater the concentration of alkali until, with strongly alkaline mixtures, sodium-clay compounds are formed from the start and no minimum occurs in the flocculation curve. The deflocculated sodium clay is finally flocculated by increasing concentration of electrolyte.

With regard to the mechanism of flocculation, the theory of mutual electrical repulsion between the particles is very inadequate, as McBain has pointed out (*Colloid Symposium Monograph*, 1926, 4, 13). I think the views put forward by Duclaux (*J. Chim. phys.*, 1909, 405) on the importance of osmotic forces in colloidal solutions and suspensions offer the most hopeful starting point in the development of an adequate theory of their stability.

#### *Summary.*

1. Certain mixtures of sodium, potassium, lithium, or calcium chloride with the respective hydroxide, when added in increasing amounts to a purified clay suspension, at first flocculate, then fail to flocculate, and finally flocculate the clay again. The phenomenon is shown by kaolin and also by silica coagulated by a small quantity of alumina, but not by pure silica, and it fails only when the suspensions are alkaline. The flocculating powers are in the increasing order: lithium, sodium, potassium, calcium, the last being about 10 times as powerful as sodium.

2. There is a pronounced maximum between a  $p_H$  of 9 and 10 in the concentration of sodium or calcium chloride required to flocculate clay or kaolin. The "aluminated" silica is remarkably similar to kaolin in respect of the influence of alkalis on the concentration of sodium chloride required for flocculation, and both these substances have similar characteristics to clay with regard to flocculation.

3. Silica is flocculated by sodium or calcium chloride only when the medium is alkaline. The minimal concentration required for flocculation rises rapidly as the alkalinity diminishes.

4. Silica is flocculated by 0.0001M-aluminium chloride; greater concentrations give a stable electropositive suspension. The subsequent addition of small quantities of sodium hydroxide at first flocculates the suspension and then gives a stable electro-negative suspension.

5. Clay is more readily flocculated by calcium hydroxide than by calcium chloride at equivalent concentrations provided the concentration exceeds 0.003*N*. Below this concentration calcium chloride is the better flocculant.

I wish to express my appreciation of the helpful interest of Dr. A. F. Joseph in this work.

WELLCOME TROPICAL RESEARCH LABORATORIES,  
KHARTOUM.

[Received, June 29th, 1927.]

---