Clays and Clay Minerals, Vol. 43, No. 4, 478–481, 1995.

INSTABILITY OF SiO_2 COLLOIDS AND SORPTION OF Ca^{2+} IONS

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Abstract—SiO_2 sols were made unstable by addition of Ca^{2+} ions. The resulting states of instability were classified as gelation, flocculation, and precipitation by means of observation, by checking the Tyndall effects on the supernatant or suspending solution, as appropriate, and by measuring the apparent densities of flocculated mass. The concentrations of free Ca^{2+} ions left in solution were measured by means of a Ca^{2+} ion selective electrode. The amounts sorbed onto SiO_2 particles were then calculated by material balance. It was found that while the amount sorbed dictates the limit of stability, the SiO_2 concentration in the mixture is an important factor deciding the state of instability. Depending on the SiO_2 concentration, there were two distinct flocs with the apparent floc density of 6 ± 1 and 12 ± 1 mg SiO_2/ml.

Key Words—Ca^{2+} induced instability, Ca^{2+} sorption, Flocculation, Gelation, Precipitation, Silica colloids, Two distinct flocculates.

INTRODUCTION

Extensive studies have been devoted to the stability of SiO_2 sols in the presence of various electrolyte cations. A recent paper by Milonjic (Milonjic 1992) contains an effective summary of the history of such studies. A majority of the works seems to conclude that it is the amount of electrolyte cations sorbed, not the surface charges that is the key quantity in dictating stability of SiO_2 sols. In all the studies, the attention has been focused on the limit of stability, and nothing was said about the resulting state of instability.

In dealing with problems associated with tailings, however, the state, in which a destabilized sol results in, is also important (Cheng *et al* 1991) When the conditions (the concentration of cations, the value of pH, etc.) cross the limit of stability, they could take various states of instability. The entire volume of sol may turn into gel (gelation), or coagulated particles sink leaving finer particles dispersed (precipitation). Or, a volume of gel-like mass may form leaving a clear supernatant solution above it (flocculation) (van Olphen 1991). Gelation is a special case of flocculation. A gel is a macroscopically homogenous mass with elasticity. The particles are agglomerated to form a floc which occupies the entire volume of an available space. The difference between flocculation and precipitation lies in the mode of particle agglomeration. For precipitation, particles coagulate to form larger particles, which sink to the bottom of the test tube. The density of the precipitates is very close to that of particles themselves. In this case, finer particles may remain in the suspending liquid, which can be detected by the Tyndall effect. In flocculation, the particles organize themselves into a visible floc, with some orders of magnitude larger volume than precipitates. The supernatant liquid above the floc is clear with no particles, which can be checked by the lack of the Tyndall effect. The boundary between the floc and the supernatent can be sharp or gradual with some gradient in particle concentration. Stable sols are such that particles are suspended evenly throughout the entire solution, which causes the Tyndall effect. This scheme of classification is not universal. In fact, there is none accepted universally at present. In this work, however, we use the above classification scheme, though somewhat arbitrary, for convenience.

In the present work, we address the state of instability explicitly, when stability of a SiO_2 sol is broken by addition of Ca^{2+} ions. We noted that the SiO_2 concentration in the mixture is an important factor dictating the state of instability. What follows is a preliminary report of a qualitative work.

EXPERIMENTAL

40 wt. % SiO_2 sols used were Ludox HS-40 donated by Canada Colors and Chemicals Ltd. The primary particles were specified as 120 Å in diameter and it was confirmed by small angle x-ray scattering technique (Xu *et al* unpublished). The specification for the sample of Ludox HS-40 indicated that it contained 0.41 wt. % of titrable alkali as Na_2O. It follows then that there is 3.4×10^{-4} mol of Na^+ ions/g of SiO_2 surfaces. Our own results indicated $(4.0 \pm 0.4) \times 10^{-4}$ mol/g. The concentration of SiO_2 particles were found to be 40.1 wt. % by gravimetry.

20.00 ml solutions were made of a stock solution of Borax buffer (0.05 M), and those of $CaCl_2$ of various concentrations and appropriate amounts of SiO_2 sol.

Table 1. $SiO_2 - Ca^{2+}$ system, state of stability/instability and sorption, $[Ca^{2+}]_{sorbed}$. The stability/instability label: st, stable sol.; prec., precipitation. f-I or f-II; flocculation, with apparent density in ( ) in units of mg SiO_2/mL. gel; gellation, with apparent density in ( ) in units of mg SiO_2/mL. The nominal amount of sorption is placed below the stability/instability label in units of 10^{-4} mol/g SiO_2.

	Nominal amount sorbed, $[Ca^{2+}]_{sorbed}$ (10^{-4} mol/g SiO_2)							
$[Ca^{2+}]_{tot}$ (mM)	1	2	3	4	5	6	8	10
$[SiO_2]$ (mg/mL)								
(A) 30	st. 0.3	st. 0.6	st. 0.9	gel(30) 1.2	gel(30) 1.5	gel(30) 1.7	gel(30) 2.2	gel(30) 2.6
(B) 10	st. 0.8	f-I(14) 1.4	f-I(12) 1.9	f-I(12) 2.3	f-I(12) 2.7	f-I(12) 3.1	f-I(12) 3.8	f-I(13) 4.4
(C) 9	st. 0.9	st. 1.6	f-I(11) 2.3	f-I(12) 2.9	f-I(12) 3.5	f-I(12) 3.9	f-I(12) 5.1	f-I(11) 6.1
(D) 6	st. 1.0	f-I(10) 1.8	f-I(11) 2.3	f-I(11) 3.0	f-I(11) 3.4	f-I(11) 4.0	f-I(11) 5.2	f-I(10) 5.9
(E) 3	prec. 1.7	f-II(7) 3.4	f-II(7) 4.8	f-II(7) 6.4	f-II(6) 7.7	f-II(6) 9.2	f-II(6) 12.4	f-II(6) 16.1
(F) 2	prec. 2.2	f-II(6) 4.2	f-II(6) 5.8	f-II(6) 7.8	f-II(6) 10.0	f-II(6) 11.9	f-II(6) 16.0	f-II(6) 20.1
(G) 1.8	prec. 2.3	f-II(6) 4.5	f-II(6) 6.2	f-II(6) 7.9	f-II(6) 10.5	f-II(6) 12.7	f-II(6) 17.1	f-II(6) 21.4
(H) 1	prec. 3.1	f-II(5) 5.6	f-II(5) 8.3	f-II(5) 11.3	f-II(5) 14.2	f-II(5) 17.2	f-II(5) 23.4	f-II(4) 30.0
(J) 0.9	prec. 4.1	f-II(6) 8.8	f-II(5) 13.3	f-II(5) 18.3	f-II(5) 22.3	f-II(5) 26.7	f-II(5) 36.8	f-II(5) 47.7
(K) 0.6	prec. 4.8	f-II(6) 8.7	f-II(6) 12.3	f-II(6) 16.8	f-II(6) 21.8	f-II(6) 27.5	f-II(6) 38.2	f-II(6) 49.0
(L) 0.18	prec. 16.7	f-II(5) 33.3	f-II(5) 48.7	f-II(5) 66.7	f-II(5) 88.9	f-II(5) 109.	f-II(5) 143.	f-II(4) 188.
(M) 0.06	prec. 33.3	prec. 68.3	prec. 108	prec. 153	prec. 231	prec. 250	prec. 367	prec. 450

$CaCl_2 \cdot 2H_2O$ (American Scientific & Chemicals) was used for preparing Ca^{2+} stock solutions. The concentrations of the resulting mixtures were for Borax fixed at 0.01 M, for the total Ca^{2+} ions from 1 mM to 10 mM, and for SiO_2 particles from 0.06 mg/ml to 30 mg/ml. The value of pH was constant at 9 throughout this study.

The mixtures were stirred by a magnetic stirrer for about an hour and allowed to stand for a day. The mixture was stirred thoroughly again and the EMF of the mixture was determined by a Ca^{2+} ion selective electrode. The imprecision was about ±0.3%. The electrode was purchased from Fisher Scientific. The species present in these solutions, i.e., Na^+, borate, and possibly dissolved SiO_2 (Iler 1979a), are not listed as interfering species in the accompanying catalogue.

About 7 ml portion of the mixture was transferred into a 10 ml test tube and was allowed to stand for about a month. The state of instability as classified above was then determined by observation and also using the Tyndall effect. A 0.5 mW He-Ne laser was used for this purpose. The apparent volumes of flocs and gels were determined by means of the volume marks on the same test tube to within 0.1 ml. For the case of diffuse boundary, about the middle of the the gradient zone is taken to be the boundary. The apparent density was then calculated using the total weight of SiO_2 particles and the apparent volume. It was later observed that the state of instability and the apparent floc density stayed the same within the unceraінty stated above after 6 months.

RESULTS AND DISCUSSION

Table I summarizes the observations. After about a month from preparation, the state of each mixture appeared to have settled. Some stayed as stable sols, while others clearly developed visibly turbid floc which occupied a fair portion of test tube. The supernatent liquids above these flocs were all clear without the Tyndall effects. For the series with the highest SiO_2 concentration, series A, gelation occurred at higher concentrations of Ca^{2+}. The entire test tube became a homogeneous turbid elastic mass. The series of the lowest SiO_2 concentration, series M, appeared transparent, but the Tyndall effect was clearly evident for the mixtures of low Ca^{2+} though less than that for zero Ca^{2+}. As the Ca^{2+} concentration increases, the Tyndall effect diminishes to zero when $[Ca^{2+}]_{total} > 4$ mM. This series were judged as precipitation. In the series with SiO_2 concentrations between these two extremes, the mixture was either stable or precipitation at lower concentrations of total Ca^{2+}. The latter case was judged by the fact that the Tyndall effect diminishes as Ca^{2+} concentration increased, while for the former case it seemed the same as for zero Ca^{2+} mixture. For higher concentrations of Ca^{2+}, there were visible flocs. For such cases, the apparent volume of each floc was estimated within ±0.1 ml, and the apparent density was calculated using this and the total amount of SiO_2 particles. For all the flocculation cases studied, the supernatent liquids did not contain any SiO_2 particles, judging from the lack of the Tyndall effect. For the gelation case, the apparent gel density is the same as SiO_2 concentration as prepared, since the volume of gel is that of the entire mixture. As is evident from Table I, there appear to be two distinct kinds of flocs, with different apparent densities, 6 ± 1 mg/ml, floc(I), and 12 ± 1 mg/ml, floc(II). When the apparent density is plotted against SiO_2 concentration at a fixed value of total Ca^{2+} concentration, a clear step is evident, as shown in Figure 1 for $[Ca^{2+}]_{total}$ = 6 mM. This sudden change in density resembles the volume-phase transition of acrylamide gels (Hirotsu *et al* 1987). In the present case, the transition, if indeed it is, seems to be driven by the concentration of SiO_2 particles.

Among other possible factors that governs such a sharp density change of floc, sorption of Ca^{2+} on SiO_2 particles may play an important role, besides dictating the limit of stability (Milonjic 1992). For the purpose of estimating the amount of sorption, we made an attempt at measuring the free Ca^{2+} concentration in suspending solution by Ca^{2+} ion sensitive electrode. There are the total of four different kinds of colloidal situations, stable, precipitation, flocculation and gelation, in all of which the EMF must be measured under a similar situation. Thus, all the samples were stirred just before the EMF measurement. In this way, the EMF values are under the condition that all the particles are forced to disperse homogeneously. The EMF readings were converted to the concentration of free Ca^{2+} ions in solution using the calibration curve, which was previously obtained with a series of standard Ca^{2+} in the same buffer without SiO_2 particles suspending. The concentration of free Ca^{2+}, $[Ca^{2+}]_{free}$, thus determined was found less than the original Ca^{2+} concentration as prepared. The difference was more for the sample with a higher SiO_2 concentration. The decrease in $[Ca^{2+}]_{free}$ in the presence of SiO_2 particles can be due to sorption of Ca^{2+} ions onto SiO_2 particles and/or to the so-called "dispersion effect" (van Olphen 1991a). This comes from the Donnan potential the reference electrode registers depending on whether the reference electrode is in contact with suspension or supernatent solution. Since we have to deal with all four situations and all the cases but one has a supernatant solution, it is not immediately obvious how to assess the dispersion effect applicable generally to all the cases. We, thus, tentatively assume that the apparent decrease in $[Ca^{2+}]_{free}$ is due only to sorption onto SiO_2 particles.

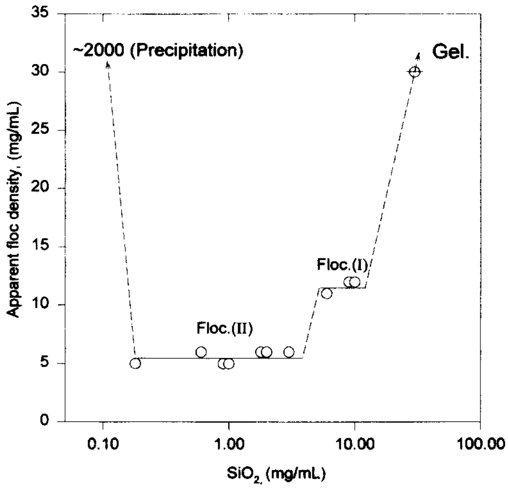

Figure 1. The apparent floc density against SiO_2 concentration, at $[Ca^{2+}]_{total}$ = 6 mM.

The amount sorbed was calculated from total Ca^{2+} material balance, and is listed in Table I. Note that this amount sorbed is nominal only, since it may contain yet unknown systematic error, due to the dispersion effect. As is evident for series (A) to (D) in Table I, the amount sorbed, though nominal, seems to take about 1.4 to 1.6 × 10^{-4} mol/g SiO_2 at the boundary

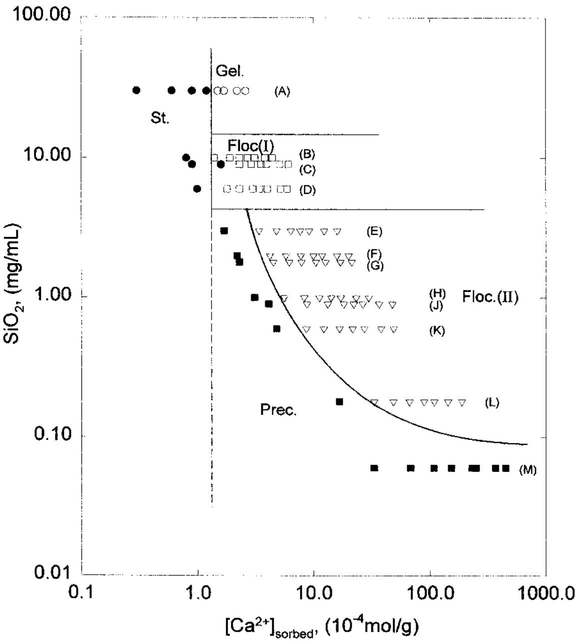

Figure 2. Stability/Instability Diagram for SiO_2-Ca^{2+}. The abscissa is the amount Ca^{2+} sorbed, $[Ca^{2+}]_{sorbed}$ (10^{-4} mol/ml), and the ordinate is the total concentration of SiO_2 particles, (mg/ml). St, stable sol; Gel, gelation; Floc(I), flocculation (I); Floc(II), flocculation (II); Prec., precipitation. See the text for detail.

between stable and gelation or flocculation(I). Assuming Ca^{2+} replaces two Na^+ ions, the above threshold value is about the same as the total surface cations. This is consistent with the earlier conclusion that the amount of Ca^{2+} adsorbed plays the key role in destabilizing SiO_2 colloids. (Milonjic 1992).

Figure 2 shows the stability/instability diagram plotted in the field of the amount sorbed and the concentration of SiO_2. Thus, it is evident that while the Ca^{2+} sorbed is an important factor dictating the limit of stability of colloids, the SiO_2 particle concentration in the system determined the state of instability. This hints that SiO_2 particles and their surfaces participate actively in the chemistry of the entire system. It is clear that much more detailed study on the surface chemistry of SiO_2 particles is necessary for a fuller understanding of the nature of instability. No doubt, application of the so-called "mass titration" (Zalac *et al* 1992, Noh *et al* 1989) will be useful as a starting point of such studies.

ACKNOWLEDGMENTS

This work was supported by Alberta Oil Sands Technology and Research Authority, Alberta, Canada, University Research Programme #883. The position of guest professor for one of us (Y.K) at Center for Ceramics Research, Research Laboratory of Engineering Materials, Tokyo Institute of Technology, was supported by The Ministry of Education, Science, and Culture, Japan.

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(Received 22 July 1994; accepted 3 January 1995; Ms. 2542)