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Filtration and Electrophoretic Mobility Studies of Flocculated Silica Suspensions

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Under conditions of controlled pH, investigations have been conducted into the behavior of the electrophoretic mobility (ζ -potential) of a crystalline silica suspension flocculated by (1) aluminum perchlorate, (2) a polyethylenimine, and (3) both reagents used in conjunction. The findings of this study have been correlated with the results of refiltration measurements with respect to the amount of polymer necessary to optimize the filtration rate compared to the amount of polymer necessary to lower the electrophoretic mobility to zero. The effect of pH on the mobility and filtration rate of crystalline and amorphous silica suspensions has been investigated. Exploratory observations on the crystalline silica-polyacrylamide system have also been included.

Introduction

Previous investigations, conducted in these laboratories,²⁻¹³ have been directed toward verifying that the refiltration rate is a reproducible, quantitative measure of the effectiveness of high polymers in flocculating colloidal dispersions. This project, initiated for the Atomic Energy Commission in 1950 by La Mer and Smellie, was published in a series of six papers.²⁻⁶ It culminated in the discovery of a filtration law dependent upon the eighth power of the polymer concentration. This new filtration law was subsequently tested and verified for both clay and phosphate slime suspensions. Later, Healy and La Mer, under U. S. Public Health Service grants, studied flocculation from the standpoint of adsorption, modifying the original theory to consider adsorption by only a fraction of the segments of the polymer molecule.⁷⁻¹⁰ In the course of this work, studies of the flocculation of calcium phosphate suspensions further substantiated the eighth power filtration law.

Research by the present authors has tested the refiltration law on another solid, amorphous silica, while, at the same time, determining the effect of varying the solid content of the silica suspensions being flocculated.^{11,12} Recently, changes in the flocculation behavior, induced by varying the particle size and the crystalline nature of the silica, have been studied.¹³ Silica was selected as the substrate in preference to kaolinite, montmorillonite, or Fuller's earth, because the complications of ion exchange are less prominent.¹⁴

Many investigators have evaluated coagulant and flocculant¹⁵ effectiveness by observing the behavior of

the electrophoretic mobility of the suspensions being flocculated.¹⁶⁻²¹ This paper compares results from filtration studies with those from mobility determinations for two flocculating agents operating on silica dispersions.

The optimum flocculant concentration, P_m , is that amount of material which produces a maximum rate (minimum time) of refiltration. This paper is concerned with comparing the value of P_m obtained from refiltration experiments with the amount of flocculant which reduces the absolute value of the electrophoretic mobility to zero, P_m^* .

To avoid becoming embroiled in a discussion of the physical meaning of ζ -potential, the results of this research have been reported in terms of the observable quantity, the electrophoretic mobility. Where values of ζ -potential are presented, they have been calculated from the simple Helmholtz-Smoluchowski equation

$$ZP = EM \cdot 4\pi \frac{V_t}{D_t} \quad (1)$$

without corrections such as those advocated by Henry, Booth, and Overbeek.²² Here ZP is the ζ -potential of the suspended particle, EM the electrophoretic mobility, V_t the viscosity of the suspending liquid, and D_t the dielectric constant of the suspending liquid. For water at 25°, eq. 1 becomes

$$ZP = 12.85EM \quad (2)$$

when ZP is expressed in mv. and EM is in $\mu/\text{sec.}/\text{v.}/\text{cm}$.

The system we subjected to the measurements described above consisted of crystalline silica, aluminum perchlorate (an inorganic flocculant), and ET-494, a cationic polyethylenimine (an organic flocculant). Exploratory investigations demonstrated that both the silica-ET-494 and silica-aluminum perchlorate systems, when subjected to filtration measurements, exhibited reproducible optimum polymer concentrations at solid contents low enough (<0.04% by weight) to permit mobility determinations. Data were collected at different values of pH.

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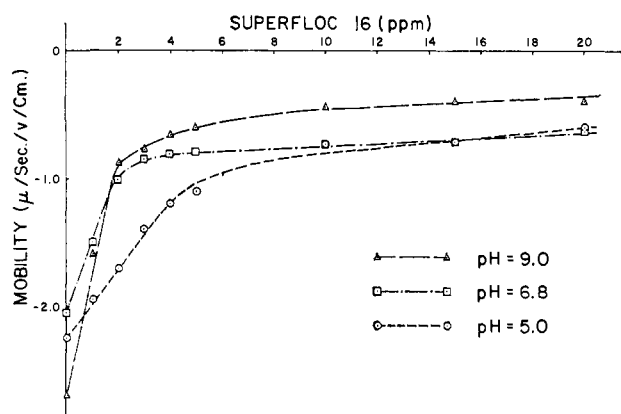


Fig. 1.—Mobility of a 0.4 g./l. of crystalline silica suspension as a function of added Superfloc 16 at constant pH.

Originally, it was planned to study the above system with Superfloc 16, a weakly anionic polyacrylamide with less than 1% COOH, as the organic flocculant instead of ET-494. However, preliminary experiments at several values of pH showed that: (1) below solid contents of 0.5 g./100 g. of water, the optimum polymer concentration obtained from filtration experiments was zero p.p.m. of Superfloc 16; (2) with increasing dosage of Superfloc 16, the absolute value of the electrophoretic mobility *decreased* asymptotically toward zero (see Fig. 1).

Experimental

Instrument Calibration.—The refiltration procedure for these experiments was identical with that described previously.¹¹ An accurate knowledge of the volume between the etched lines of the collecting cylinder (52.7 ml.) was the only calibration involved.

The final pH values of the various suspensions were determined with a Beckman Zeromatic pH meter, which had been calibrated using appropriate buffer solutions. The results were reproducible to 0.05 of a pH unit.

The electrophoretic mobility determinations were made with a Zeta-Meter, a recently developed, commercial microelectrophoresis apparatus. This instrument was calibrated: (1) by direct measurement of the critical physical and optical dimensions, and (2) indirectly, by determining the mobility of Fuller's earth particles as a function of pH. The results agreed with the previously published data of Black and Hamrah^{17b} obtained with a Briggs microelectrophoresis cell. Both methods of calibration gave satisfactory agreement with expected values and confirmed the reliability of the Zeta-Meter as an instrument for measuring electrophoretic mobility.

Materials.—Crystalline silica was a sample marketed by Pennsylvania Glass Sand Corp. under their product name 5-μ Min-U-Sil; 98% of this material had a diameter less than 5 μ. The surface area of the sample was 20,600 cm.²/g.; the average particle size based on the surface mean was 1.1 μ.

Amorphous silica (99.5% through 325 mesh) was preparation 19 of Whittaker, Clark, and Daniels, used previously by us.^{11,12} ET-494, a product of Dow Chemical Research, is a cationic polyethylenimine with an approximate molecular weight of 50,000.

Superfloc 16, manufactured by American Cyanamid, is a weakly anionic polyacrylamide (1% COOH) of molecular weight 3–5 million.

Aluminum perchlorate, hydrated with 9 moles of water, was supplied by K & K Laboratories. This salt was selected for use, because it is known to be completely dissociated even in dilute solution. Furthermore, the perchlorate anion does not penetrate the aluminum coordination sphere readily.

Mobility Measurements.—Suspensions for mobility measurements were prepared by mixing 0.04 g. of silica with 60 ml. of water in a 100-ml. beaker at a fixed speed with a magnetic stirrer for 3 min. Sufficient dilute acid (0.01 N HCl) or base (0.01 N NaOH) was then added to ensure that the final pH of the suspension would have the desired value. Agitation was continued for

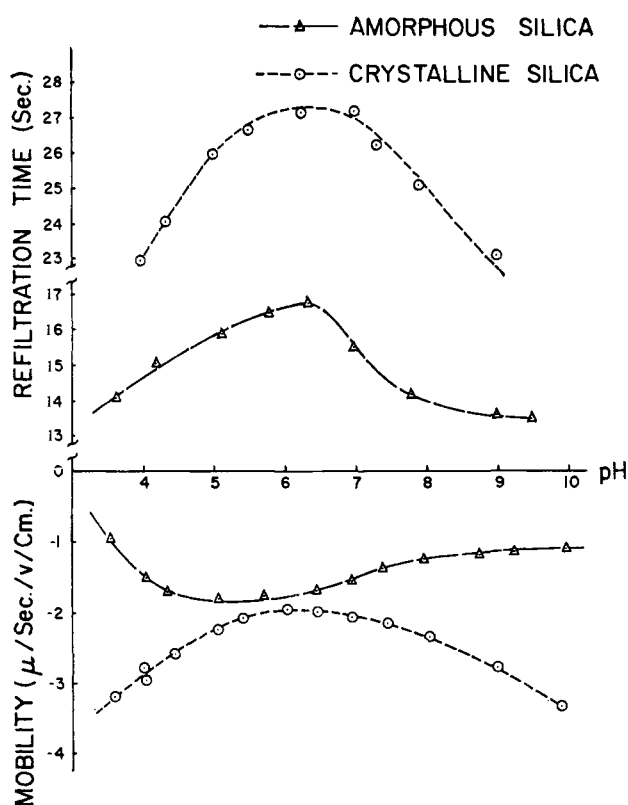


Fig. 2.—Mobility and refiltration time for a 0.4 g./l. of crystalline silica or amorphous silica suspension as a function of pH.

2 min. At the end of this time, an aliquot of 0.001 M aluminum perchlorate, diluted to 20 ml. with water, was added to the suspension; and after 2 min. of further mixing, an aliquot of 0.005% by weight polymer solution, diluted to 20 ml. with water, was added. Agitation was discontinued 2 min. later. Electrophoretic mobility determinations on these suspensions were then made in accordance with the directions in the Zeta-Meter manual, with special care being taken to avoid bubble formation and turbulence in the cell.

Filtration Measurements.—Suspensions for filtration measurement were prepared in an analogous manner, except that 0.2 g. of silica was added to 300 ml. of water, while aliquots of aluminum perchlorate and polymer were each diluted to 100 ml. with water. Both the apparatus and the procedure for filtration measurements have been discussed in detail elsewhere.¹¹ Minor modifications were made by: (1) substituting a Millipore assembly for the Büchner funnel in order to accommodate a large volume of suspension in a single portion, and (2) replacing the Whatman No. 2 filter paper used previously by a glass fiber substitute. Both changes were necessitated by the difficulties encountered in filtering silica suspensions of extremely low solids content. The procedure of adding the aluminum salt before the polymer in both the refiltration and mobility determinations was selected arbitrarily. The order of addition of reagents will be discussed in a later paper.

Results

The filtration rate and mobility curves for the crystalline silica alone, as a function of pH, are shown in Fig. 2. Due to the unexpected nature of the results obtained, the determinations were repeated with an *amorphous* silica sample. These have also been included for comparison.

All of the filtration rate curves for the aluminum perchlorate-silica and ET-494-silica systems exhibited sharp minima typical of those encountered previously^{4,11} and need not be discussed further in this text.

Figure 3 presents the electrophoretic mobility as a function of added flocculant and shows the behavior

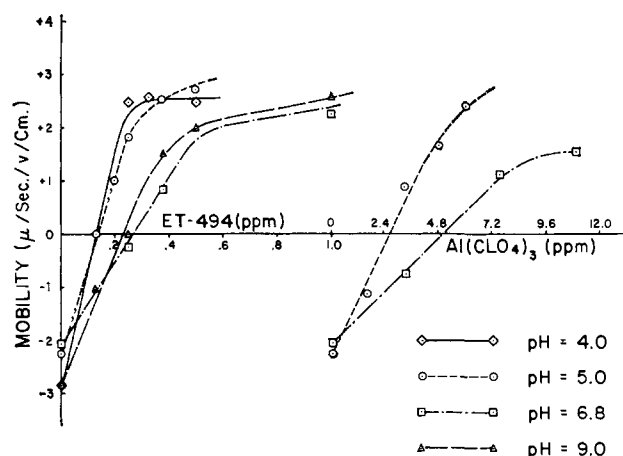


Fig. 3.—Mobility of a 0.4 g./l. of crystalline silica suspension as a function of added flocculant at constant pH.

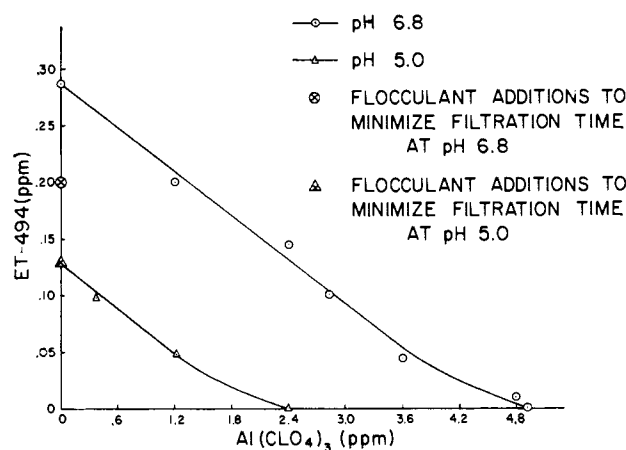


Fig. 4.—Path of zero mobility in a three-dimensional electrophoretic mobility plot at constant pH.

TABLE I

pH	ET-494 needed for		—For optimum filtration—		Al(ClO ₄) ₃ needed for		—For optimum filtration—	
	Zero mobility (p.p.m.)	Optimum filtration (p.p.m.)	EM (μ/sec./v./cm.)	ZP (mv.)	Zero mobility (p.p.m.)	Optimum filtration (p.p.m.)	EM (μ/sec./v./cm.)	ZP (mv.)
4	0.1 (?)	0.10	0	0
5	.13	.13	0	0	2.64	3.24	+0.60	+7.0
6.8	.28	.20	-0.65	-7.5	4.92	3.84	-0.65	-7.5
9	.22	.20	- .20	-2.5
	± .02	± .02	± .02	±0.2	±0.02	±0.02	±0.02	±0.2

exhibited by both the ET-494-silica and aluminum perchlorate-silica systems at the pH values studied.

Table I summarizes and compares the results from filtration experiments with those from electrophoretic mobility studies. At a given pH, the mobility corresponding to the optimum concentration of flocculating agent determined from filtration experiments was read from the appropriate curve in Fig. 3. Based on the value thus obtained, a ζ -potential was calculated and included in columns 5 and 9.

In order to determine if any synergistic effects accrued from the simultaneous presence of *both* aluminum perchlorate and ET-494 in the system, a surface was generated with the aluminum perchlorate concentration as abscissa, the ET-494 concentration as ordinate, and electrophoretic mobility (or filtration time) as the coordinate in the third dimension. Figure 4 shows the path of zero mobility in the three-dimensional mobility surface at pH values of 5 and 6.8. The area above this line corresponds to the region of positive mobility, while that below the line represents negative mobility. The points of minimum filtration time in the three-dimensional filtration time surface at pH values 5 and 6.8 have also been indicated.

Discussion

The ability of a weak *anionic* polymer (Superfloc 16) to reduce the strongly negative mobility of a suspended colloid (silica) is an interesting observation which parallels the findings of Healy.²³ A tentative explanation of this phenomenon is apparent if it can be assumed that, during the process of flocculation, a sufficient fraction of the surface area of the solid is covered by adsorbed polymer. Under these conditions, the colloidal particle, with its weakly anionic surface coating, would be expected to behave like a suspended particle of appreciably lower negative surface charge.

(23) T. W. Healy *J. Colloid Sci.*, **16**, 609 (1961).

An analogous explanation has been offered for suspended particles whose negative ζ -potentials in the presence of aluminum or ferric salts change both sign and magnitude.^{19,20,24}

In just what way the negative polymer adsorbs on the negative solid surface is not understood at this writing. Undoubtedly, the presence of even minute impurities in either the polymer structure or the silica surface would have a greatly magnified effect on the short range chemical interactions which overpower the long range electrostatic forces in adsorption and bridging reactions at small distances.

The *ineffectiveness* of Superfloc 16 in flocculating suspensions of less than 0.5 g./100 g. of water defies explanation at the present time. It should be mentioned, however, that this finding parallels the recently published results of Ockershausen and Peterman,²⁵ who found that a cationic polymer, which successfully coagulated 100 p.p.m. of montmorillonite in tap water, was not effective in floc production and turbidity removal in a 10 p.p.m. suspension.

Figure 2 demonstrates the dependence of the filtration rate and electrophoretic mobility of suspended silica upon the value of pH. From this plot, it can be seen that the isoelectric point of the amorphous silica probably lies between pH 2 and 3, which agrees with the previous research of Losenbeck²⁶ who found the isoelectric point in this same range depending upon the concentration of SiO₂. In the basic pH range, however, present data indicate that the mobility approaches a constant value of $-1 \mu/\text{sec.}/\text{v.}/\text{cm.}$

At present, the dependence between the electrophoretic mobility of the crystalline silica and the pH defies explanation; and under the circumstances the

(24) W. Stumm and J. J. Morgan, *J. Am. Water Works Assoc.*, **54**, 971 (1962).

(25) R. W. Ockershausen and C. J. Peterman, *ibid.*, **56**, 224 (1964).

(26) O. Losenbeck, *Kolloidchem. Beih.*, **16**, 27 (1922).

lack of information about the commercial methods of manufacturing these materials and their chemical composition could only make interpretation sheer conjecture. It was noted, however, that neither adjusting the pH with 0.01 *N* H₂SO₄ nor performing the experiments in equilibrium distilled water had any measurable effect on the behavior of the mobility.

The filtration data shown in Fig. 2 indicate a marked change in the porosity of the filter cake with changing pH. At a pH of 6, the refiltration time exhibits a maximum indicating minimal porosity. The authors attribute this result to the existence of silica gel, which has been shown to form most rapidly in the pH range of 5 to 7.²⁷

Figure 3 demonstrates the behavior of the electrophoretic mobility of the crystalline silica in the presence of either ET-494 or aluminum perchlorate at various values of pH. On the whole, the mobility behavior exhibited by the silica-ET-494 and silica-aluminum perchlorate systems was entirely predictable and consistent with the results obtained by other investigators.^{17b,28} In both cases, the addition of sufficient quantities of cationic flocculant reversed the direction of colloid migration.

It is clear that in the ET-494-silica system the optimum polymer concentration indicated by zero mobility (P_m^*) passes through a maximum in the neutral pH range. In other words, more polymer is needed to reduce the electrophoretic mobility to zero at pH 6.8 than at pH values of 5 or 9. These results were confirmed by the filtration experiments which demonstrated that at pH 6.8 the amount of polymer necessary to produce a fixed rate of filtration was greater than similar quantities measure at pH values of 5 and 9.

If the results depicted in Fig. 2 at pH 5-7 can be explained in terms of limited silica gel formation, then the amount of polymer for optimum filtration must of necessity be maximized in this pH range. It is also conceivable, that in this massive state, the condition of zero mobility would be the most difficult to approach by flocculant addition. At higher and lower values of pH, electrical repulsion should increase the extent of monodispersion within the suspension, thus enabling the added flocculant to complete bonding and bridging by particle adsorption.

(27) R. K. Iler, "The Colloid Chemistry of Silica and Silicates," Cornell University Press, Ithaca, N. Y., 1955, p. 47.

(28) E. L. Bean, S. J. Campbell, and F. R. Anspach, *J. Am. Water Works Assoc.*, **56**, 214 (1964).

Table I correlates the optimum polymer concentration from filtration experiments, P_m , with the polymer concentration that reduces the electrophoretic mobility to zero, P_m^* . *The results indicate that, for the system studied, reducing the ζ -potential of the suspended particles to 0 ± 8 mv. provides optimal conditions for subsequent filtration operations.* Furthermore, this finding agrees with the results of Bean, Campbell, and Anspach,²⁸ who concluded from their studies with Delaware River water that a ζ -potential of 0 ± 8 mv. resulted in maximum turbidity reduction.

Figure 4 is a graphical representation of the three-dimensional electrophoretic mobility surface generated when both ET-494 and aluminum perchlorate are added to the silica suspension. The parallel solid lines of Fig. 4 demonstrate that the path of zero mobility is essentially linear throughout the range of joint inorganic and organic flocculant additions, the area above this line corresponding to positive mobility with that below the line indicating a region of negative mobility.

Studies of the silica-ET-494-aluminum perchlorate system were conducted at pH values of 6.8 and 5. These values of pH represent the upper and lower limits which might be encountered in commercial water purification. It is interesting to note that lowering the pH by 1.8 units halved the concentrations of ET-494 and Al(ClO₄)₃ necessary to reduce the mobility of the flocculated particles to zero. This finding coincides with the results obtained in both the silica-ET-494 and silica-aluminum perchlorate systems, which showed that more flocculant was needed to decrease the mobility to zero or produce a given filtration rate at pH 6.8 than at pH 5.

The points which represent the concentration of flocculant needed to optimize the filtration rate have also been included. At pH values of both 5 and 6.8, the addition of ET-494 *alone* was more effective than when this material was used in conjunction with aluminum perchlorate.

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