Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Devivo, Douglas G. and Karger, Barry L.(1970) 'Studies in the Flotation of Colloidal Particulates: Effects of Aggregation in the Flotation Process', Separation Science and Technology, 5: 2, 145 — 167

To link to this Article: DOI: 10.1080/00372367008057956

URL: http://dx.doi.org/10.1080/00372367008057956

SEPARATION SCIENCE, 5(2), pp. 145–167, April, 1970

Studies in the Flotation of Colloidal Particulates: Effects of Aggregation in the Flotation Process

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Summary

An experimental investigation is reported of the effects of several solution parameters on the flotation of colloidal kaolin and montmorillonite using ethylhexadecyldimethylammonium bromide. The parameters examined were the zeta potential of the surfactant-particulate species, the concentration of selected cations, pH, and the ratio of initial surfactant concentration to initial particulate concentration. Two apparatuses were used to assess the affect of aggregation on flotation; one employed bubbles of 1–2 mm average diameter to effect the flotation, while the other used bubbles of about 0.2 mm. In the large bubble system, aggregation adversely affected the flotation of the particulates. For the small bubble (0.2 mm) system, the affect of aggregation on the flotation of particulates was contrary to that in the large bubble (1–2 mm) system. These observations are explained in terms of bubble sizes and their attachment to the particulate species during the flotation process. Studies also showed that several cations and pH variations cause little interference. A general discussion is given relative to the application of the process to large-scale clarification of turbid waters.

INTRODUCTION

Separation processes utilizing selective adsorption at gas–liquid interfaces from bubbles generated in aqueous media have found a number of applications over the past few years. These processes, which have the generic name of adsorptive bubble separation processes, have recently been reviewed and their applications discussed in two articles

(*1, 2*). A nomenclature scheme for these methods was published in 1967 (*3*). Foam separation is a category of the nomenclature scheme pertaining to separations utilizing a foam. Foam separation methods can be subdivided into foam fractionation and flotation, the former dealing with the removal of soluble species and the latter dealing with the removal of particulate species. Foam fractionation has been used to separate radioactive metal ions (*4*), nonbiodegradable detergents (*5*), and many other soluble ionic species. Ore flotation, a subdivision of flotation, has been used for many years in the dressing of metallic ores. In this application we are concerned with heterogeneous systems containing macrosized solids of a crystalline nature (*6, 7*).

Although a great deal has been published on ore flotation, very few studies have been concerned with the flotation of colloidal-size particulates (colloid flotation). Clanton et al. (*8, 9*) reported qualitative studies on several sols, while Jaycock and Ottewill (*10, 11*) were among the first workers to present an extensive investigation of the flotation of a colloidal system. These latter authors studied the effect of adsorption of cationic surfactants and electrokinetic properties on the extent of flotation of silver iodide. Workers in the Soviet Union have applied flotation to the removal of colloidal metal oxides from aqueous sols. Colloids have been separated both in the pure form (*12, 13*) and with adsorbed and occluded isotopes and impurity elements (*14–17*). A 99.4% removal of ^{134}Cs, present in microquantities, was accomplished by sorption on $K_2Cu_3[Fe(CN)_6]_2$ followed by flotation of the ferrocyanide using gelatin as a foaming agent (*14*). Skrylev and Mokrushin (*18*) fitted a first-order rate equation to the removal of colloidal ferric hydroxide, manganese dioxide, and mixed ferrocyanide particulates using gelatin as the surface-active agent.

Grieves and co-workers have successfully applied flotation to several colloidal systems and suspended solids including ferric and stannic oxides (*19, 20*), kaolin clay (*21*), and active carbon (*22*). In each of the above studies an oppositely charged surfactant was used to effect flotation of the colloid or suspended solids. The species to be separated was thus concentrated via a mobile foam generated in the bulk by sparging with air. The studies dealt with the effects of feed colloid concentration, gas rate, and pH. Grieves and co-workers have also reported a study of the rate of removal of positively and negatively charged colloidal ferric oxide from aqueous suspensions (*23*). The rate of removal of the colloid was correlated with the quantities of surfactant and particulates in the residual suspension. Negatively charged particulates were removed at a rate directly proportional to the surfactant to particulate concentration ratio in the residual suspension and a power function greater than one of the residual concentration of particulates. In contrast to negatively charged ferric oxide, the rate of removal of positively charged ferric oxide was dependent upon an exponential function of the initial surfactant concentration.

The success of these studies in the application of flotation to the removal of colloidal particulates made it seem worthy to examine the flotation of kaolin and montmorillonite in more detail. The purpose of this paper, thus, is to study the effect of a variety of parameters on the rate of flotation of the clays, with special emphasis on the role of zeta potential on this rate. It can be noted that these two species of clays contribute to the turbidity of water in many areas of the world and thus are a major problem in water treatment. The application of flotation to the clarification of water containing colloidal kaolin or montmorillonite appears feasible and advantageous in specialized applications such as military field use or in specialized industrial separation problems. Specialized instances are emphasized because of the economic restrictions on the flotation process owing to the surfactant requirement.

EXPERIMENTAL

Apparatus

A schematic diagram of the first flotation apparatus is given in Fig. 1. Nitrogen gas was passed through, in series, two gas saturator bottles filled with deionized water; a glass-wool water droplet trap; a constant differential flow controller; and a calibrated rotameter. The gas was sparged through a 50–60-μ pore-size glass frit located at the base of the column and the foam produced travelled up the column. A side exit arm on the column was located 19 cm above the initial sol level and led into a heat exchanger where the foam was collapsed and drained into a large beaker.

The second flotation cell used was a modification of one first described by Sebba (*24*) and is shown in Fig. 2. The cell was constructed of Pyrex and had the following characteristics: 9 cm diameter, 2 liter capacity, 7 cm diameter sintered glass frit of 5–10 μ porosity. Samples were withdrawn by inserting a pipet into the cell through the top opening.

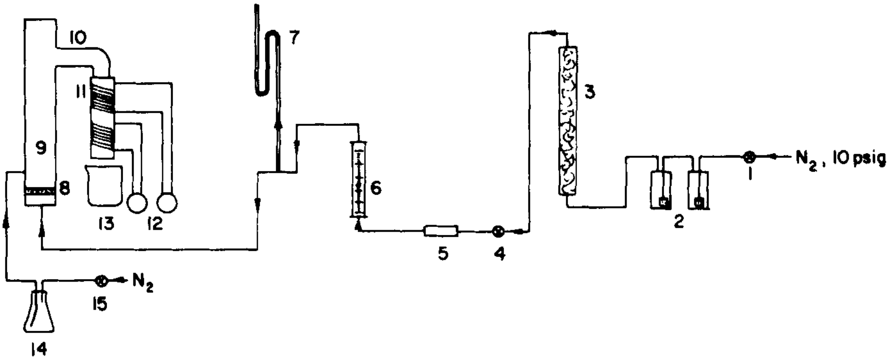

FIG. 1. Plexiglas flotation column apparatus. (1) Needle valve; Swagelok no. IRS4. (2) 500 ml. gas saturator bottles filled with deionized water. (3) Water droplet trap; 1 m × 3 cm o.d., packed with glass wool. (4) Needle valve; Swagelok no. IRS4. (5) Constant differential flow controller; Moore Products Co., Model 63 BU-L. (6) Calibrated rotameter; Kontes Glass Co., no. K-626500. (7) Mercury manometer. (8) Porous glass frit; 8 cm diameter, 50–60 μ pore size; Kontes Glass Co. (9) Flotation column; Plexiglas, 90 cm × 10 cm o.d. (10) Exit arm; Plexiglas, 5 cm o.d. (11) Heat exchanger; stainless steel, 60 cm × 6 cm o.d., two tandem coils of no. 22 Chromel wire. (12) Variac controls for heat exchanger coils. (13) Collapsed foam collector; 200 ml beaker. (14) Surfactant injection system; 500 ml vacuum flask with ¼ in. o.d. stainless steel tubing. (15) Needle valve; Swagelok no. IRS4.

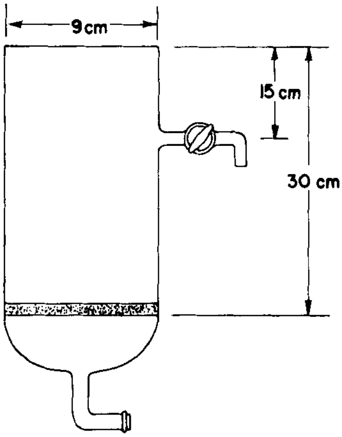

FIG. 2. Pyrex flotation cell with 5–10 μ pore size frit.

Procedure

A stock sol was prepared by dispersing 0.40 g of either kaolin or montmorillonite in 500 ml of deionized water with a Waring blender for 2 min. The sol was then allowed to stand for about 1 hr to settle out large particles, and the decanted portion was diluted to the desired concentration with deionized water. In all but a few experiments, the concentration of solids in the total initial bulk sol was 100 mg/l. At the start of each experiment, the gas flow rate through the column of the apparatus in Fig. 1 was adjusted to approximately 2000 ml/min and 3600 ml of the required sol was added to the column through an opening in the top. The gas flow was then readjusted to 2000 ± 50 ml/min and the surfactant was added to the column by gas injection of 400 ml of the required surfactant solution. This method proved superior to the previously tried method of premixing the surfactant and the sol before pouring into the column. Mixing of the surfactant and sol was extremely rapid because of turbulence caused by rising gas bubbles. Longer premixing times had no affect on the results obtained and nonequilibrium effects between particulates and surfactant did not appear important in our system. The time $\theta = 0$ was taken when the surfactant was injected into the column. Samples of the bulk sol were then drawn at 2 min intervals and analyzed first for suspended solids and then for zeta potential and surfactant concentration.

The procedure followed in the experiments with the flotation cell (Fig. 2) was the same as with the column apparatus above except that 1400 ml of the required sol was used and the surfactant solution (200 ml) was mixed directly with the sol to give a final volume of 1600 ml. The flow rate was maintained at 170 ml/min and samples were withdrawn with a pipet and analyzed in a similar manner to samples from the column apparatus.

Analyses

The initial and residual concentrations of suspended solids were determined with a Hach model 2100 laboratory turbidimeter using appropriate calibration plots. The response of the turbidimeter was linear with respect to concentration of suspended solids and corresponded to 125 Jackson turbidity units (JTU) for 100 mg/l kaolin and 36 JTU for 100 mg/l montmorillonite. The presence of surfactant did not affect the turbidity readings. Precision of these measurements was ±2%. Total surfactant concentration (free plus adsorbed) was determined by filtering a 10-ml aliquot of the residual bulk through a 0.45-μ Millipore filter; washing the retained solids with 25 ml of deionized water; and then determining the quantity of surfactant in the filtrate by a two-phase titration with tetraphenylboron (*25*). This procedure was accurate to ±0.6 mg/l. Tests with known amounts of surfactants showed that essentially all of the adsorbed surfactant was removed by the washing step. Zeta potential measurements were made on a Zeta-Meter (Zeta-Meter, Inc., New York, N.Y.). Measurements had a precision of ±3 mV.

Chemicals

The montmorillonite clay used was clay mineral standard no. 23 of the American Petroleum Institute. The sample was purchased from Ward's Natural Science Establishment, Inc., Rochester, New York. The sample was ground on an electric mortar and pestle for several hours to a mesh size greater than 200. It should be noted that the sieving step is only to remove coarse particles. Those particles passing through the screen were further disintegrated by a Waring blender. The kaolin used was a natural, air-separated, untreated clay of relatively uniform stability characteristics and size. The clay was used as received from Fisher Scientific Company. Ethylhexadecyldimethylammonium bromide (EHDA-Br) was technical grade (Eastman Chemical) and was used without further purification. Tetraphenylboron sodium (Aldrich Chemical Co., puriss. grade) and bromophenol blue (Fisher Scientific Co., certified reagent) were used as received from the suppliers.

THEORY

The removal of colloidal particulates from aqueous sols by foaming is possible because of the electrical charges on the surface of the particulates and the large surface-to-volume ratio. These two properties promote the adsorption of an oppositely charged surfactant, rendering the colloidal species surface-active. Passing gas through a porous frit into the bulk medium generates a large interfacial area on which the surface-active particulates can adsorb and subsequently be removed from the bulk.

The mechanism of interaction on ionic surfactants with colloidal particulates in the flotation process has been studied by Taggart

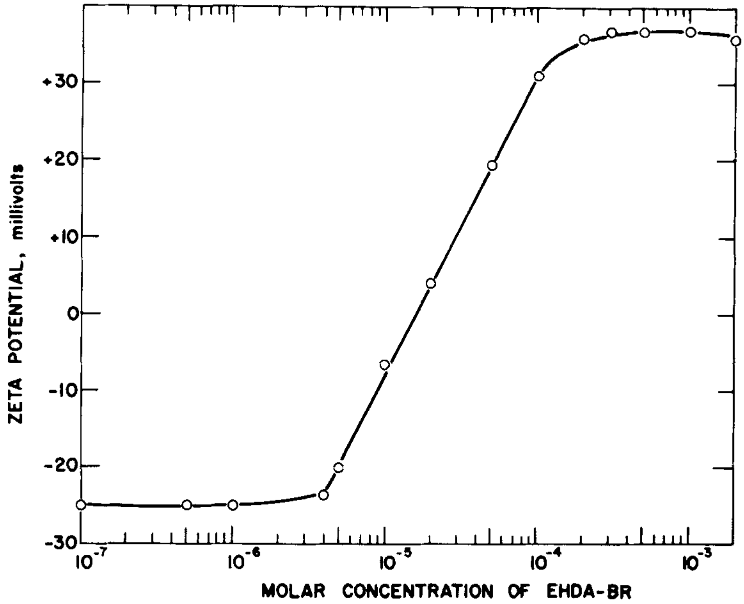

FIG. 3. Zeta potential of kaolin related to molar concentration of EHDA-Br. Kaolin concentration of 100 mg/l.

et al. (*26*) and Jaycock and Ottewill (*10*). The former authors pointed out that froth flotation of minerals with ionic surfactants involves the attachment of the polar group of the surfactant molecule to the mineral surface; thus, flotation behavior depends on the orientation of the surfactant molecule with respect to the mineral surface after attachment. Jaycock and Ottewill examined the interaction of ionic surfactants with colloidal silver iodide. The authors observed that although silver iodide particulates initially had a negative electrophoretic mobility, the mobility decreased to zero and then increased to a high positive value as the concentration of cationic surfactant was increased. The same effect has been observed in this study for kaolin in the presence of EHDA-Br. Figure 3 shows a plot of zeta potential vs EHDA-Br concentration. Initially, the particulates have a zeta potential of —25 mV. As the concentration of EHDA-Br is increased, the zeta potential decreases to 0 and then increases to approximately +37 mV.

Jaycock and Ottewill have presented a model to explain the charge reversal phenomenon. When the hydrophobic colloid was contacted with an oppositely charged surfactant, the polar groups were attracted to the charged surfaces of the particulates owing to electrostatic forces. A monolayer was built up as the surfactant concentration was increased. This electrostatically attracted monolayer neutralized the original surface charge and caused the zeta potential to drop to zero. Following the completion of the monolayer, a second layer of surfactant molecules was formed by van der Waals' forces of attraction between the hydrocarbon chains of the surfactant molecules (*10*). During the formation of this second layer, the charge increased from zero to a positive value. At the completion of the second layer, the charge was opposite to the original charge and likewise, the zeta potential sign was the reverse of the original.

The magnitude of the resultant opposite charge on the colloidal particulates is dependent not only upon the type and concentration of the surfactant present, but also upon the type and concentration of electrolytes and the amount of particulates present in a given mass of sol (*27*). These same factors which affect the magnitude of the charge of the surfactant-particulate species are also of prime importance in the flotation process (*21, 23, 28*). The intimate relationship between the magnitude of the charge of particulates in a sol and the degree of aggregation is well known (*29*). Aggregation of colloidal particulates increases as the charge and therefore the electrostatic repulsion between particulates is decreased. Since aggregation increases the particle size in the sol, it is not surprising that the flotation process is affected by this factor and is thus dependent upon those parameters which affect the degree of aggregation in a sol. Consequently, the magnitude of the charge of the particulate-surfactant species should be relatable to flotation behavior. The zeta potential or electrophoretic mobility is intimately related to the surface charge and can be used as a convenient quantification of the surface charge (*27*). Consequently, zeta potential is a measure of the stability of the sol toward formation of aggregates (coagulation) and may thus be used to evaluate the affect of aggregation on the flotation process.

In this work, clay particulates adsorb cationic surfactant and have their charge reversed from negative to positive. The magnitude of this positive charge affects the degree of aggregation and flotation. The zeta potential of the charge-reversed sol can be lowered by decreasing the amount of surfactant present or by adding electrolytes, such as sodium sulfate. The lowering of the zeta potential of this sol increases the degree of aggregation present in the sol. This behavior has been observed in our laboratory for kaolin and montmorillonite sols containing EHDA-Br. In addition to electrical effects, the rate of aggregation and therefore the size of the aggregates present in a sol at a specific time after sparging at a constant rate is dependent upon the quantity of particulates present according to the Smoluchowski coagulation law (*30*).

In assessing the affect of aggregation upon the flotation of colloidal particulates using oppositely charged surfactants, it is of value to discuss the empirical results in terms of a mathematical model or rate equation. This allows a quantitative evaluation in addition to a qualitative discussion of the results. A quantitative empirical evaluation of the relation of aggregation, through zeta potential measurements, and particulate quantity to the flotation process can be made by fitting kinetic data for the flotation of a hydrophobic colloid, such as a clay, with an oppositely charged surfactant to a mathematical model or rate equation. This approach allows the assessment of the relative significance of the parameters chosen for investigation and their relationship to the flotation process.

It was decided to examine the correlation of the zeta potential of the surfactant-particulate species and the quantity of particulates present with the flotation rate of kaolin and montmorillonite particulates using EHDA-Br. While any industrial scale flotation unit would be operated in a continuous mode, a batch process can be used in the laboratory to evaluate various parameters affecting the flotation rates. The results obtained can then be used to design or to optimize a continuous system. The batch operations used in this work were described in the experimental section.

The rate of removal of particulates from the bulk sol can be expressed as:

$$\frac{d(Z_F V_F)}{d\theta} = \frac{-d(Z_R V_R)}{d\theta}$$

where $Z_F V_F$ = quantity of particulates in the foam (mg), $Z_R V_R$ = quantity of particulates in the residual sol (mg), θ = time of sparging (min). Thus, $d(Z_F V_F)/d\theta = -d(Z_R V_R)/d\theta$ = instantaneous rate at time θ (mg/min) for a variable volume, batch process (*23*).

The fit of experimental rates, obtained from smoothed curves through the original data, to a rate equation of the form:

$$\frac{-d(Z_R V_R)}{d\theta} = k\left(\frac{Z_R V_R}{Z_i V_i}\right)^{\alpha}\left(\frac{ZP_\theta}{ZP_i}\right)^{\beta} \tag{1}$$

[where k = rate constant (mg/min), Z_iV_i = initial amount of particulates present, ZP_θ = zeta potential of surfactant-particulate species at time θ (mV), ZP_i = initial zeta potential of surfactant-particulate species (mV), and α and β = constants] can be accomplished by a least squares analysis using a digital computer. It may be noted that the use of ratios on the RHS of the rate expression eliminates a major problem in the determination of zeta potential, arising from the indirect calculation of zeta potential from the electrophoretic mobility using the Helmholtz-Smoluchowski equation (*27*). The equation is only approximate and was derived from a rather simple physical model, which is seldom realized in experimental systems. By using a relative parameter such as ZP_θ/ZP_i, the above errors are minimized. It should be noted that it is only necessary to divide the zeta potential by a factor of 13 to convert to electrophoretic mobility, and thus zeta potential and electrophoretic mobility are interchangeable in Eq. (1).

Grieves and Bhattacharyya have used an approach similar to that reported in this paper to study the flotation of positively and negatively charged surfactants (*23*). The rate equations developed by these authors were functions of the initial and residual quantities of surfactant and particulates.

RESULTS AND DISCUSSION

Data obtained for the batch flotation of kaolin and montmorillonite clays with EHDA-Br were used to evaluate several solution parameters affecting the colloid flotation process. The results for typical batch flotations of kaolin and montmorillonite in the apparatus shown in Fig. 1, utilizing bubbles of approximately 1–2 mm diameter, are shown in Fig. 4. The results are expressed in terms of total residual amount of particulates as a function of sparge time. Rates of removal for kaolin and montmorillonite approach zero after 10–14 min of sparging at 2000 ml/min for kaolin and 14–16 min of sparging at 1000 ml/min for montmorillonite. During these time periods, approximately 95% of the kaolin particulates and 94% of the montmorillonite particulates were removed when EHDA-Br was used as the surfactant.

Several experiments were performed to evaluate the relation between flotation rate and two parameters; the zeta potential of the surfactant-particulate species and the quantity of particulates remaining in the residual sol at any time, θ, for both kaolin and montmorillonite. The experiments involved varying the initial zeta potential of the sur-

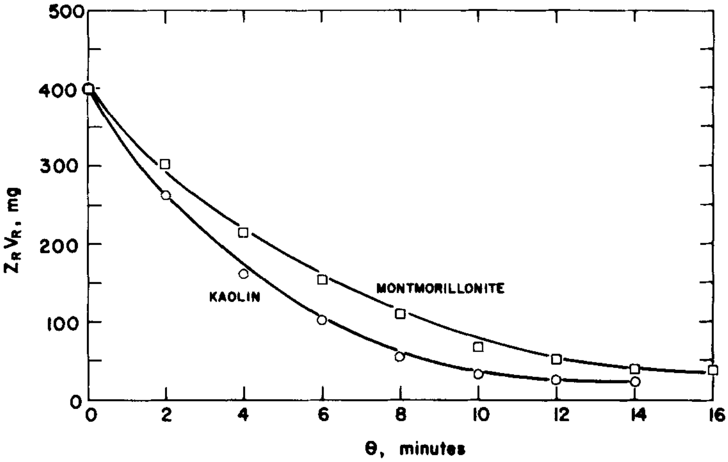

FIG. 4. Residual amounts of kaolin and montmorillonite particulates related to time for initial conditions of 100 mg/l particulates and 37.8 mg/l EHDA-Br. Plexiglas flotation column (50–60 μ frit).

factant-particulate species in the bulk sol from +37 to 0 mV in the kaolin study and from +17 to 0 mV in the montmorillonite. The zeta potentials of the surfactant-particulate species for 100 mg/l particulates and 37.8 mg/l EHDA-Br were +37 and +17 mV for kaolin and montmorillonite, respectively. The variation of the initial zeta potentials through the above ranges was achieved by adding different amounts of sodium sulfate to the bulk sol except for the zero value of zeta potential (fully coagulated). Coagulation was achieved by addition of a small amount of the surfactant which corresponded to the quantity required to produce the zero electric point and then allowing coagulation to take place before adding the balance of the surfactant to give a total of 37.8 mg/l. It should be noted that the total amount of surfactant used in all the experiments (37.8 mg/l) was chosen on the basis of the quantity needed to produce a suitable foam in terms of stability and reproducibility of measurements. A typical plot of zeta potential vs concentration of sodium sulfate for kaolin-EHDA-Br is shown in Fig. 5. During the flotation experiments, the amount of particulates and surfactant present and the zeta potential were determined simultaneously at periodic time intervals.

The initial zeta potential, and therefore the extent of aggregation in the sol, affected the flotation rate and maximum removal of both kaolin and montmorillonite. Figures 6 and 7 show the effect of initial

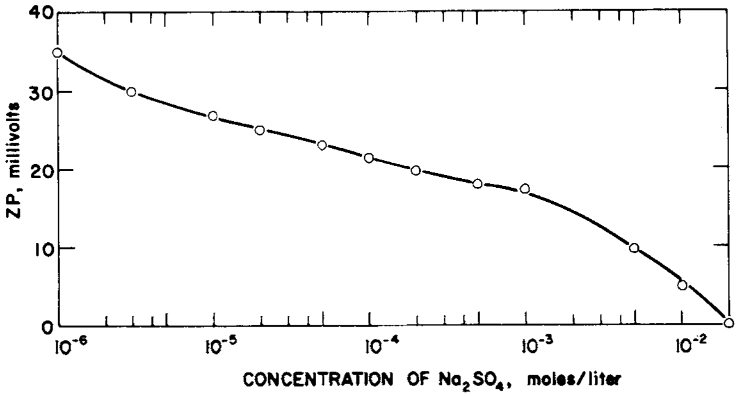

FIG. 5. Zeta potential related to concentration of Na_2SO_4 for a kaolin sol of initial concentrations of 100 mg/l kaolin and 37.8 mg/l EHDA-Br. Plexiglas flotation column (50–60 μ frit).

zeta potential, ZP_i, on the percent removal of kaolin and montmorillonite as a function of sparge time, θ. For a given set of initial conditions, the percent removal of both kaolin and montmorillonite for each value of θ decreased as ZP_i was decreased. The poorest flotation

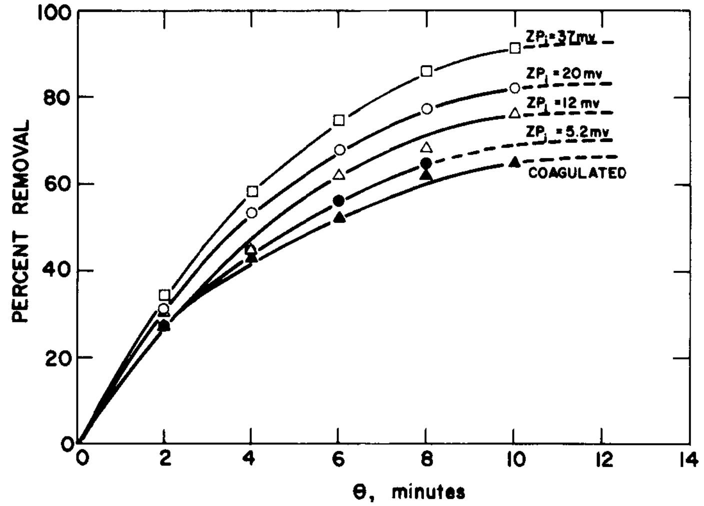

FIG. 6. Percent removal of kaolin particulates related to time for different values of ZP_i and initial concentrations of 100 mg/l kaolin and 37.8 mg/l EHDA-Br. Plexiglas flotation column (50–60 μ frit).

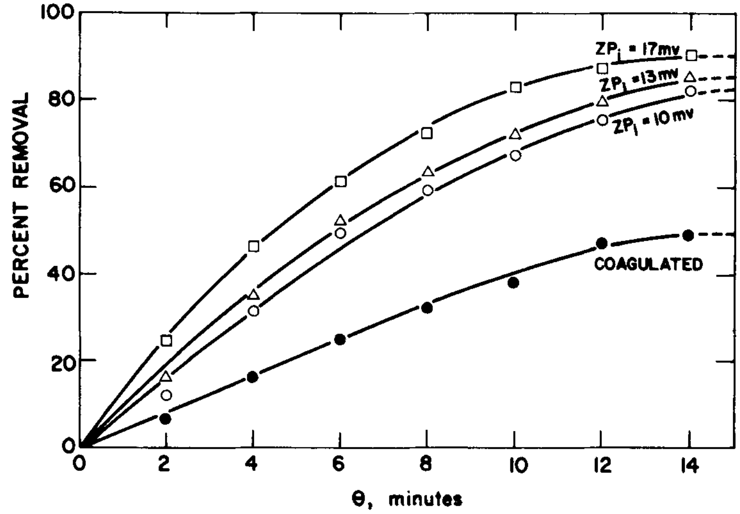

FIG. 7. Percent removal of montmorillonite particulates related to time for different values of ZP_i and initial concentrations of 100 mg/l montmorillonite and 37.8 mg/l EHDA-Br. Plexiglas flotation column (50–60 μ frit).

in our system was observed when the initial sol was coagulated ($ZP_i = 0$).

The trends shown in Figs. 6 and 7 indicate that the flotation of clay particulates using the system of Fig. 1 is adversely affected by aggregation of the particulates. As discussed in the theory section, the degree of aggregation existing in a sol, for example a kaolin or montmorillonite sol, is dependent on the magnitude of the surface charge on the particulates. Thus, the flotation trends observed reveal an inverse relationship between the flotation and the size of the particulate species. This argument is strengthened by the fact that montmorillonite particulates are floated much faster than are the kaolin particulates, montmorillonite particulates being much smaller than kaolin particulates according to turbidimetric measurements.

A discrepancy exists between the results in Figs. 6 and 7 and those of other investigators who have studied the affects of aggregation on the flotation of certain colloidal bacterial organisms. Rubin and Lackey (*31*) found that aggregation of *Bacillus cereus* with alum considerably improved the flotation of the organisms. In their experiments, Rubin and Lackey used a flotation cell which utilized much smaller bubbles and much slower sparge rates to affect the flotation of the organisms. We decided to examine the affect of aggregation on the flotation of kaolin and montmorillonite using a cell similar to that employed by Rubin and Lackey, as seen in Fig. 2. The results for the colloid flotation of the two clay species using the above cell are shown in Fig. 8. An examination of the flotation data in Fig. 8 shows that the coagulated form of both clays floats considerably better than does the dispersed form. This behavior is contrary to the trend observed for the same species when the larger column apparatus was used with its concomitant larger bubbles, much higher flow rates, and larger convection currents.

The explanation of the disparity between the flotation behavior observed in the two different systems appears to involve bubble size and the transport of the particle attached to the bubble across the interface between the bulk liquid and the foam. The large column unit employs a 50–60-μ porosity frit to generate bubbles while the small cell utilizes a fine porosity, 5–10 μ frit. On the basis of Spargo's work on bubble diameters (*32*), it is reasonable to assume that a difference of an order of magnitude exists between the average bubble diameters in the two apparatuses. This is indeed supported by observations of a qualitative nature. Bubble size should affect the buoyancy imparted to the surfactant-particulate species by attachment to the bubble at

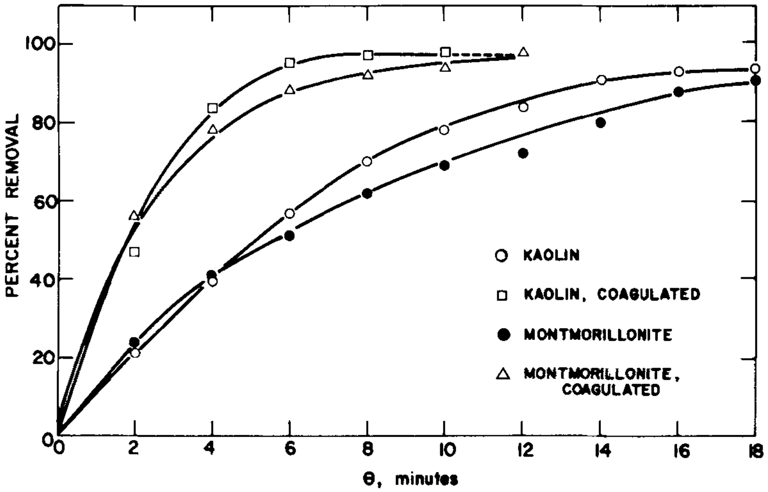

FIG. 8. Percent removal of kaolin and montmorillonite particulates related to time for dispersed and coagulated sols. Pyrex flotation cell (5–10 μ frit).

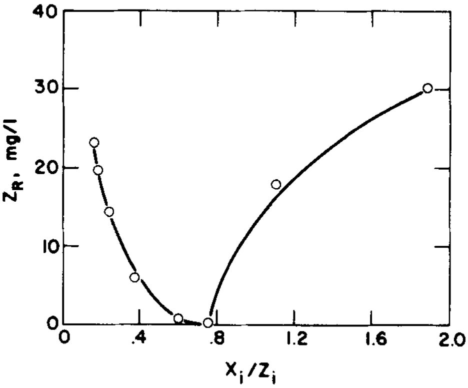

FIG. 9. Residual concentration of kaolin after 14 min of sparging related to the initial ratio of surfactant concentration to particulate concentration. Plexiglas flotation column (50–60 μ frit).

the gas–liquid interface. In the 50–60-μ frit system, the bubbles are approximately the same size or larger than the aggregates in the sol (i.e., 1–2 mm). The large size of the bubbles makes the attachment of more than one bubble to a single aggregate unlikely, while the attachment of several aggregates to a single bubble is probable. Buoyancy of the aggregates is therefore poor and the flotation of large aggregates proceeds at a slower rate than dispersed particulates. In the case of the fine-fritted cell with bubbles of average diameter of approximately 0.2 mm or less (*32*), the possibility of multiple bubble attachment to single aggregates is reasonable. The larger the aggregates, the larger the number of bubbles which can become attached to the aggregates, with improved buoyancy. Flotation is therefore enhanced by aggregation in the small bubble system contrary to the behavior in the large bubble system.

The above behavior implies many advantages of a small bubble system employing low flow rates over a large bubble, high flow rate system for the removal of colloidal particulates. Not only does the small bubble system require less sparge gas, but the amount of surfactant actually needed to effect a good removal should be considerably less. The surfactant concentration need only be that which causes coagulation of the particulates. In the large bubble system, enough surfactant must be used to effect charge reversal and thus keep the particulates in a fairly dispersed state.

In addition, the stability of the foam is somewhat dependent on the bubble size (*33*). The dependency is indirect and therefore foams formed from fairly large bubbles are unstable unless enough surfactant is present to stabilize the foam. The results of a study in the large bubble cell using the 50–60-μ frit of residual particulate concentration vs the initial ratio of surfactant to particulate ratio (X_i/Z_i) are shown in Fig. 9. Examination of the data reveals that optimum removal of particulates occurred at X_i/Z_i equal to 0.76. It is to be noted that this value is higher than the minimum quantity of surfactant needed (Fig. 3) to obtain the maximum charge reversal. Based on studies by Rubin and Lackey (*31*), the surfactant requirements for a small bubble system are much less than the amount needed in the large bubble system described in this paper. In addition, frothers can be used to lower the amount of surfactant needed in the small bubble system (*31*). The amount of surfactant needed to effect good flotation is extremely important since it is the limiting factor in the economic evaluation of flotation for commercial application. While the capital expenditure for flotation equipment is low, the cost of surfactant is high compared to the cost of reagents used in conventional processes.

A least squares analysis of the batch flotation data obtained with the large bubble system shown in Fig. 1 for the flotation experiments involving the affect of zeta potential was performed on a CDC-3300 computer using a Fortran program written for this application. A copy of the program is available from the authors upon request. For kaolin floated with EHDA-Br, a total of 22 data points was used to obtain the following equation for the best fit of the data:

$$\frac{-d(Z_R V_R)}{d\theta} = 78 \left(\frac{Z_R V_R}{Z_i V_i}\right)^{0.15} \left(\frac{ZP_\theta}{ZP_i}\right)^{1.4} \tag{2}$$

The values of θ included in this equation were 10 min and less; at longer times, $-d(Z_R V_R) d\theta$ was very close to zero. The average of the percentage deviations calculated with Eq. (2) from the experimental values for 20 out of 22 data points (two points were disregarded owing to disproportionately high error) was approximately 10%. An identical treatment was applied to data for the batch flotation of montmorillonite. The best fit for 24 data points is shown in Eq. (3):

$$\frac{-d(Z_R V_R)}{d\theta} = 42 \left(\frac{Z_R V_R}{Z_i V_i}\right)^{0.34} \left(\frac{ZP_\theta}{ZP_i}\right)^{0.97} \tag{3}$$

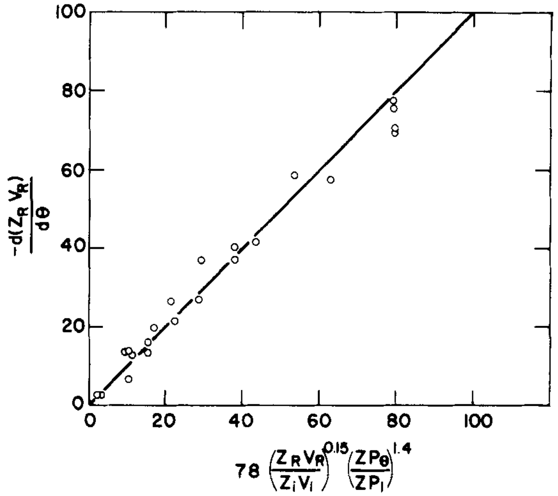

FIG. 10. Rate data for kaolin particulates for initial concentrations of 100 mg/l kaolin and 37.8 mg/l EHDA-Br. Plexiglas flotation column (50–60 μ frit).

The values of θ used to get Eq. (3) were 14 min and less. Equation (3) showed an average percentage deviation of approximately 11%. The fits between experimental data and Eqs. (2) and (3) are shown in Figs. 10 and 11, respectively. Comparison of experimental and calculated rates was chosen as an evaluation of Eqs. (2) and (3) in preference to using the integrated form of the equations. This method of comparison obviated long graphical integrations and proved satisfactory for our purpose.

Equations (2) and (3) show the dependency of the flotation rate of kaolin and montmorillonite on the amount of particulates present and on the zeta potential ratio of the surfactant-particulate species. Mathematical relationships such as the above equations are useful in analyzing a specific flotation process. The results can be used to help in the optimization process or in the design of a continuous process from batch process data. There are several weaknesses, as well as the above advantages. For instance, an examination of Eqs. (2) and (3) shows that the degrees of significance of the two terms on the RHS of the two equations differ considerably. In Eq. (2) the significance ratio (β/α) is almost ten, while in Eq. (3) the ratio is less than three. While the differences in the chemical properties of kaolin and montmorillonite, such as exchange capacity and wettability, could account for the disparity, it is also likely that other variables or factors in the flotation system, in addition to particulate concentration and charge effects, must be considered. With the exception of the initial values of variables chosen, none of the solution variables available for consideration in the flotation process are independent of one another. Once the flotation process has begun, variables such as electrokinetic potentials, surfactant concentration, and particulate concentration all become interrelated in a very complicated manner. This is especially true for the electrokinetic properties. In our work, we found that ZP_θ/ZP_i at a particular θ value depended not only on ZP_i as expected, but was obviously affected in an irregular way by some other parameters in the flotation process. The reproducibility of the ZP_θ/ZP_i measurements was good (~10%), though, for all but the lowest ZP_θ values where the precision decreased considerably owing to experimental difficulties in measuring very low mobilities. Another problem is the variation, though small, of the average bubble diameter during the foaming process. This variation results from changes in the surfactant concentration during the foaming period. The fact that the zeta potential term on the RHS of Eqs. (2) and (3) is more significant than the particulate amount term is in agreement with the hypothesis

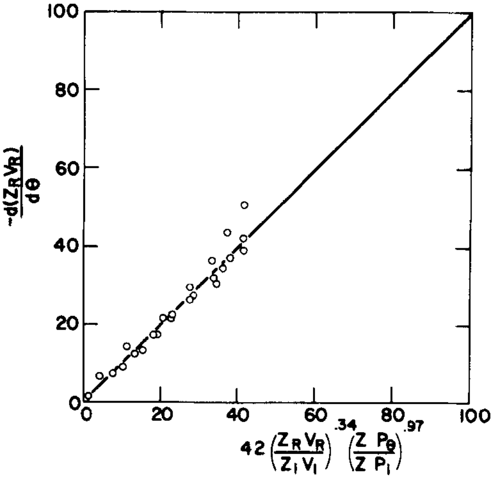

FIG. 11. Rate data for montmorillonite particulates for initial concentrations of 100 mg/l montmorillonite and 37.8 mg/l EHDA-Br.

that aggregation plays a very important role in the flotation of colloidal particulates. As mentioned earlier, aggregation effects should be reflected in the zeta potential term.

The quantitative approach using kinetic models could not be made when the fine frit apparatus was used because the kinetics of the removal process were too fast. In addition, any equations obtained would have been useless owing to their inapplicability at the optimum removal conditions when the zeta potential was equal to zero (fully aggregated).

Flotation Interference by Inorganic Cations

Experiments reported in this section were conducted to establish the influence of several inorganic cations, commonly found in natural waters, on the flotation of colloidal kaolin in the large bubble apparatus shown in Fig. 1. The cations chosen were Na^+, Ca^{2+}, and Fe^{3+} added as NaCl, $CaCl_2$, and $FeCl_3$, respectively. Turbidimetric measurements were unsatisfactory for analyses of suspended solids in sols containing Fe^{3+}. Samples containing ferric ion were thus assayed gravimetrically. Figure 12 shows the data for experiments in which the concentrations of the above ions were varied prior to addition of the

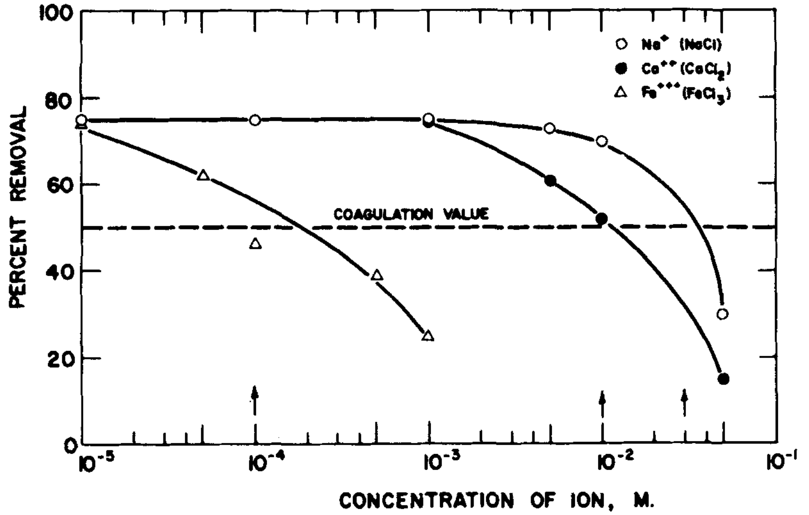

FIG. 12. Percent removal of kaolin after 6 min of sparging related to ion concentration for Na^+, Ca^{2+}, and Fe^{3+}. Plexiglas flotation column (50–60 μ frit).

surfactant. The results are expressed in terms of percent removal after 6 min of sparging as a function of initial cation concentration. The presence of mono- and divalent cations in the bulk sol created no difficulties at concentrations below approximately 10^{-2} and 10^{-3} M, respectively. A pronounced interference was provided by trivalent iron at initial concentrations greater than 10^{-5} M. An examination of Fig. 12 shows that the interference of these ions is not wholly an aggregation effect. If interference was due only to aggregation effects, the percent removal after 6 min of sparging should not have differed greatly from 50%, which was the value obtained for the removal of fully aggregated kaolin particulates in the large bubble apparatus after 6 min of sparging. The decrease in removal up to the 50% value (shown as a dotted line on Fig. 12) appeared to be due to increasing aggregation while the decrease beyond 50% suggests a different mode of interference. A plausible explanation of this behavior is based on the interference of the ions with the adsorption of the cationic surfactant by the negatively charged particulates. Reduction of the negative charge on the particulates by electrostatic interactions not only promotes aggregation, but above certain concentrations of ions the surfactant adsorption step becomes more difficult and, therefore, the flotation process is less efficient. The concentrations at which this secondary interference occurs depends on the charge on the cation and are indicated by arrows in Fig. 12.

Effect of pH on Flotation of Kaolin

The effect of pH on the flotation of kaolin was studied in the large bubble apparatus and the results are shown in Table 1 for the residual concentration of particulates, Z_R, as a function of initial pH. Results are shown for Z_R after 6 and 8 min of sparging had elapsed. The pH values are for the initial bulk sol. A statistical examination of the data showed that for 95% confidence limits, pH variation from 2.6 to 11.2 produced no interference in the flotation of kaolin. Any pH value outside this range would be of no interest and the extremes of the pH range were thus eliminated from consideration. The initial concentrations of particulates and EHDA-Br were 100 and 37.8 mg/l, respectively. The results obtained are in agreement with those found by Grieves for the flotation of a sol containing illite clay, Fuller's earth, and natural dirt and sand (*34*). Since pH has little or no effect on the flotation of clay particulates, an extra degree of freedom is

TABLE 1

Results for Variable pH

$\theta = 6$ min		$\theta = 8$ min	
pH	Z_R (mg/l)	pH	Z_R (mg/l)
2.6	24	2.7	13
4.1	30	4.3	17
6.2	29	6.1	17
6.5	26	6.5	14
8.0	24	8.1	13
9.2	27	9.0	16
10.0	30	10.0	16
11.1	23	11.2	17

$2\sigma = \pm 4.8$ mg/l

allowed in the flotation process. This is especially desirable in water treatment where one wishes to avoid the addition of any unnecessary reagents.

CONCLUSION

An experimental investigation has been carried out on the flotation of colloidal kaolin and montmorillonite with ethylhexadecyldimethylammonium bromide. Zeta potential measurements of the surfactant-particulate species have proved useful in assessing the effect of aggregation on the flotation of clays.

The optimum flotation in a system employing bubbles of 1–2 mm average diameter is obtained for the dispersed particulates as opposed to the aggregated ones. A comparison study has been made between the system employing 1–2 mm bubbles and a system using bubbles of average diameter of approximately 0.2 mm to effect the flotation of the two clay species. This study indicated that bubble size plays an important role in the flotation process. In the two systems compared, the affect of coagulation on flotation was directly opposite.

The superior flotation of coagulated clay sols in the fine bubbles (0.2 mm) system has important economic implications. A much smaller quantity of surfactant is required in this system owing to the increased stability of a fine structured foam and lack of the need for charge reversal, which is required in the large bubble (1–2 mm) system. Only a surfactant concentration at or below that needed to achieve the zero electric point must be considered. Inexpensive reagents, such as alum, may be used to promote coagulation, thus aiding flotation in the fine bubble system (*31*). The proper combination of coagulant and surfactant would minimize the surfactant needed and, therefore, keep the operating cost of a commercial flotation process competitive with other methods of water clarification. While a detailed economic study has not been made of such a flotation process, the cost might be minimized to allow flotation to compete successfully with conventional clarification methods.

In addition, it should be pointed out that while flotation systems utilizing large bubbles of the order of 1–2 mm do not appear to operate as efficiently as a fine bubble system, such systems may find use in specific situations in which the colloids present cannot be coagulated by alum or polyelectrolytes. An example of such a situation is the clarification of waters in asphalted catchment basins used in the arid southwestern United States. These waters contain colloids which are so highly peptized that they cannot be coagulated. While large-scale electrophoresis has been proposed for clarification of these waters (*35*), flotation should be tried. Such an application could be optimized using a quantitative approach such as discussed in this paper. Optimization of a large bubble system can be achieved by maintaining the colloid in the dispersed form. This can be done by adding sufficient surfactant to effect charge reversal or, perhaps, by use of dispersants such as polyphosphates.

Acknowledgments

The support of the Federal Water Pollution Control Administration under Grant Number WP-01129 is gratefully acknowledged. We also thank Dr. Thomas A. Pinfold, University of Witwatersrand, Johannesburg, South Africa, for his many stimulating discussions and helpful suggestions while Visiting Assistant Professor at Northeastern University.

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Received by editor December 20, 1969