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 Matis, K. A. , Zouboulis, A. I. , Mandjiny, S. and Zamboulis, D.(1997) 'Removal of Cadmium from Dilute Solutions by Hydroxyapatite. III. Flocculation Studies', Separation Science and Technology, 32: 13, 2127 — 2148
To link to this Article: DOI: 10.1080/01496399708000760
URL: http://dx.doi.org/10.1080/01496399708000760

SEPARATION SCIENCE AND TECHNOLOGY, **32**(13), pp. 2127–2148, 1997

Removal of Cadmium from Dilute Solutions by Hydroxyapatite. III. Flocculation Studies

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ABSTRACT

Synthetic hydroxyapatite in a fine particulate dispersion has been used previously for the removal of Cd^{2+} cations from dilute aqueous solutions. In the present work the flocculation of these hydroxyapatite particulates was examined with and without the presence of Cd^{2+} ions by applying the conventional inorganic flocculents ferric chloride and aluminum sulfate. An optical technique was applied in order to monitor the flocculation dynamics of the dispersed particles, complemented by electrophoretic and turbidity measurements. The relative size of aggregates formed during flocculation, expressed as a "flocculation index," could be continuously measured by this technique. Results indicated that the flocculation index provided important information about flocculation mechanisms. The main parameters examined included flocculent dose, solution pH, and mixing intensity. The optimum conditions for efficient flocculation were determined.

Key Words. Hydroxyapatite sorbent; Cadmium; Flocculation; Zeta potential

INTRODUCTION

Most physical and physicochemical unit operations (such as gravity, magnetic, and electrostatic separations, filtration, flotation, etc.) are usu-

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ally insufficient for the processing or separation of fine particles and ultrafine particulates. Flocculation, often applied to enhance subsequent solid/liquid (S/L) separation, shows considerable promise in many cases. In order to optimize the performance of S/L separation processes by flocculation, it is imperative that aggregates (flocs) of a certain size, strength, and density should be formed.

The basic principles of colloid stability, destabilization, and flocculation of fine particles have been examined in a number of articles—see, for example, Ref. 1. Although several methods are available for measuring the degree of flocculation of particle dispersions and for selecting the optimal dosage of flocculants (2) in general the fundamental understanding of flocculent reagent action under dynamic conditions is quite limited and few papers have reported such studies. Hydrolyzed metal salts are widely used in practice as primary flocculants to promote the formation of aggregates and, hence, to facilitate the separation of colloids (1).

A simple but sensitive optical technique to monitor the state of aggregation of fines dispersion, was recently reported (3). This technique, used in the present work, is based on measuring transmitted light fluctuations in flowing dispersions. The relative size of aggregates formed during flocculation can be determined continuously with a flow-through cell. It has been successfully applied to study the mechanism of flocculation of either dilute or concentrated dispersions by adding polymeric (4) or hydrolyzing metal salt flocculants (5, 6).

Literature on the flocculation for separation of fine mineral particles originates mainly from the investigation of apatite minerals behavior. For example, the flocculation behavior of single and mixed minerals of apatite and dolomite was previously reported (7). The selective flocculation of mineral hydroxyapatite from quartz and/or calcite was also published (8), and the flocculation or dispersion phenomena affecting the dewatering of phosphate slimes were discussed (9). The beneficiation of a low-grade phosphate ore slimes, employing a combined flocculation–flotation treatment process, was also reported (10).

In a similar application, the flocculation behavior of fine bentonite particles by adding a cationic surfactant and polyacrylamide (12) was used for the removal and separation of Cd^{2+}, Fe^{2+}, and Cu^{2+} ions by flotation. Precipitate flotation of cadmium as a hydroxide, but in the absence of an inorganic sorbent, has also been examined elsewhere (13).

The present paper investigates the possibility of flocculation of cadmium-loaded, ultrafine hydroxyapatite particulates (denoted hereafter as HAP); such particles are in the 10 to 1 μm range. Cadmium is generally considered to be a priority toxic pollutant. The first part of this work (11) covered studies of cadmium sorption from dilute aqueous solutions (e.g., wastewaters) onto dispersed synthetic HAP. Electrokinetic measurements of the system (expressed as zeta potential) were also conducted in an attempt to elucidate the possible mechanisms. A third part of this work will examine the application of flotation for the solid/liquid separation of Cd-loaded HAP fines.

EXPERIMENTAL MATERIALS AND METHODS

Stock solutions of common inorganic flocculent agents, namely ferric chloride ($FeCl_3 \cdot 6H_2O$) and alum [aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$], were prepared by dissolving the respective analytical grade reagents (supplied from Merck) in deionized water to a concentration of 1 M. Fresh solutions of 0.01 M were prepared from the stock solutions before every experimental set and were used in order to improve the flocculation of HAP fine particles.

HAP is a well-known inorganic sorbent, widely used in chromatography columns. The structure and chemistry of apatites have been extensively described recently (14). The material used in the present study was supplied by Merck. It had been previously characterized by particle size distribution analysis (average 2.5 μm), its density (2.96 g/cm^3), as well as by SEM microphotographs and microprobe analysis (11). The need for a preliminary flocculation stage of the metal-loaded particulates in order to achieve subsequent efficient S/L separation was found to be of great importance. HAP was used at a dispersion density of 0.500 g/L. The initial concentration of Cd^{2+} usually applied in the laboratory experiments was 20 mg/L, unless otherwise stated.

The Photometric Dispersion Analyzer PDA 2000 (Rank Brothers, UK), a light-scattering instrument with a flow-through cell connected to a chart recorder, was used to monitor the flocculation dynamics. The light source was a high intensity light-emitting diode (820 nm). Figure 1 gives a schematic diagram of the experimental apparatus, operated mostly in the nonrecycling mode, i.e., the examined dispersion flowing through the cell was not returned to the flocculation tank.

The dispersion to be examined (3 L) was prepared using either deionized or tap water (of 550–650 μmho conductivity) in a plastic beaker. It was mixed by using a 6 cm in diameter mechanical propeller-type stirrer, kept at $\frac{1}{3}$ of the height of the dispersion in the beaker, and driven by an adjustable speed motor. The dispersion was passed through the measuring cell with a peristaltic pump (Watson-Marlow) located downstream of the cell. The flow-through cell consisted of 3 mm i.d. special plastic tube provided by the manufacturer. The sampling inlet was located at half height of the dispersion level and about 2 cm from the tank walls. The applied flow

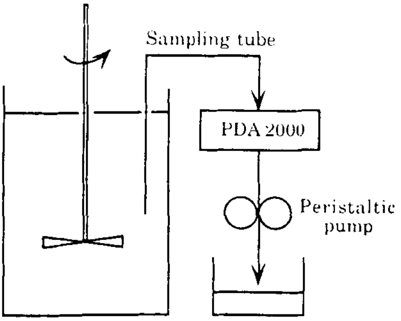

FIG. 1 Batchwise laboratory setup for monitoring the flocculation dynamics of HAP particles (without recycling).

rate was 34 mL/min unless otherwise mentioned. The time required for the dispersion to reach the flow-through cell was approximately 11 seconds. All experiments were conducted at room temperature (20 ± 2°C).

The flow through the cell and the location of the sampling tube were strictly maintained throughout the experiments so that the flocculation index dynamics behavior under various chemical and physical conditions could be compared to each other. The flow pattern in the tube under the applied conditions was laminar.

The initial mixing speed during the sorption of metal on HAP was 500 rpm for 15 minutes. The inorganic flocculent was subsequently added (one dose corresponds to 0.05 g/L, i.e., 10% w/w of the added sorbent = 0.5 g/L), during which a rapid mixing period (715 rpm) was applied for 30 seconds. At the end of rapid mixing a small sample was taken for electrophoretic mobility measurements. The measurements during the flocculation stage lasted 20 minutes, and during this stage the mixing speed was set to 200 rpm and the measurement (flocculation index *R*) was monitored every 1 minute. Under these conditions, which had been optimized experimentally in preliminary experiments, the mixing intensity in terms of velocity gradient was about 11 s^{-1}. The dispersion was allowed to settle for 15 minutes after the slow mixing period. Samples for residual turbidity measurements were then taken.

Turbidity measurements were conducted using a Hach Ratio XR turbidimeter, while zeta-potential measurements were obtained by the microelectrophoretic apparatus Mark II by Rank Brothers.

Flocculation Behavior and Study of Dynamics

The root-mean-square (rms) value of the fluctuating signal of the transmitted light has been found to be related with the average concentration and the size of dispersed particles (3). However, it is more convenient to divide the rms value by the steady direct current value of the transmitted light to obtain the dimensionless term R = rms/dc, often referred to as the *flocculation index*. As flocculation proceeds, the value of R increases. (More information regarding the applied method can be found in the Appendix.) Although this ratio does not provide quantitative information on aggregate size, the relative increase in the R value is a useful indicator of the degree of flocculation. For a given dispersion, it can be assumed that larger R values imply larger aggregate sizes (15).

The flocculation curves obtained by the instrument can be arbitrarily divided into four regions (4). In the first region there was generally little change in the flocculation index with time, and particle collisions did not result in aggregate formation. The extent of this region depended on the mixing conditions—the more rapid the stirring, the shorter the "lag phase." This phase disappeared because flocculation began immediately after adding flocculent agents. In the second region the value of R showed a distinct rise as flocculation started. The rise in R did not continue indefinitely because the aggregates (flocs) eventually reached a limiting size which depends on the stirring state and on the floc strength. This led to a maximum in the observed R values (third region). In the fourth region, R values may remain constant (unchanged) or decrease depending on whether equilibrium was attained between the formation and breakage of flocs.

The adsorption of trivalent metal hydrolyzing ions [Fe(III) and Al(III)] onto particle surfaces can affect both the speciation of metal ions in solution and the surface properties of the particles (5). Adsorption onto HAP can occur by formation of surface complexes between HAP and the surface hydroxyl groups of the sorbent. At any pH value, the maximum dissolved concentration of aluminum or ferric ions in equilibrium with the hydroxide solid is determined by the solubility of the solid phase and by the extent of formation of monomeric and polymeric hydrolysis species in solution. On the other hand, the adsorption of cations, such as cadmium, can involve both ion exchange (particularly at low pH) and surface complex formation (11).

In the surface complexation model, the surface charge of the sorbent is attributed to the presence of charged surface species (5). Therefore, the formation of ferric or aluminum surface complexes and adsorption of polymeric ionic species, especially highly charged species, can dramatically affect the surface charge. In practice, however, the adsorption of polymeric species may be separated from precipitation of am-$Fe(OH)_{3(s)}$ or am-$Al(OH)_{3(s)}$ at the surface. With increasing adsorption of ferric or aluminum ions and surface coverage, the acid–base properties of the surface will be increasingly characteristic of the amorphous hydroxides.

According to the surface precipitation model (5), a surface phase may be formed with a composition that varies continuously between that of the original solid and that of a pure precipitate of the adsorbing cation. Therefore, am-$Fe(OH)_{3(s)}$ or am-$Al(OH)_{3(s)}$ may be formed at the surface of particles and affect their surface properties, even when the solubility product for the formation of these hydroxides was not exceeded in the bulk solution. A continuum between surface complexation (adsorption) and precipitation is described by the surface precipitation model (6).

There is relatively little information available on the kinetics of flocculent adsorption/interaction on dispersed particles, but it seems reasonable to consider the process as transport-limited, at least in the early stages of the process, where surface coverage was still quite low. Under these conditions, the adsorption rate depends on the rate of arrival of flocculent ions at a particle surface. It has also been suggested (4) that the adsorption rate under turbulent conditions passes through a maximum at a certain value of the energy input rate, although there was little experimental evidence to support the premise.

RESULTS AND DISCUSSION

Flocculation of HAP by Adding Aluminum Sulfate as Flocculent

Preliminary Experiments

When a particle dispersion passes through a narrow tube under laminar flow conditions, a shear (velocity gradient) is developed (5). The average shear rate in the tube (G) is given by $G = 3Q/3\pi r_i^3$, where Q is the volumetric flow rate and r_i is the inner radius of the tube. The velocity in this investigation (5–16 cm/min) is within the laminar flow regime. For the flow conditions used in this work (Q = 22 mL/min, r_i = 1.5 mm), the average shear rate calculated from the previous equation is 140 s^{-1}, although it should be noted that the duration of the application of this shear rate is only 11 seconds compared to 20 minutes detention time in the flocculation vessel. Therefore, the average Gt value ["Camp number" (5)] in the tube during the experiment is small compared to that in the stirred vessel. Under these conditions it is not considered likely that some aggregates would be disrupted on passage through the tube before reaching the optical flow-through cell. Hence, the extent of flocculation in the tube is regarded as negligible.

Aluminum sulfate, a conventional inorganic flocculent agent used mainly in drinking water treatment, was examined first. During preliminary flocculation experiments in deionized water the effect of dispersion flow rate through the cell was evaluated (Fig. 2a). The maximum floccula-

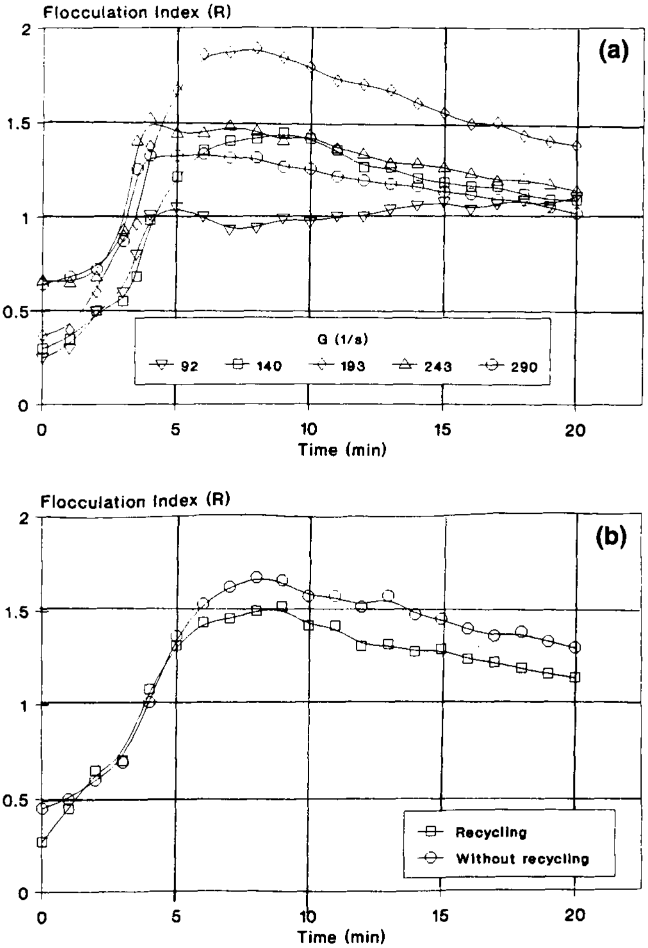

FIG. 2 Flocculation of HAP particles by aluminum sulfate without cadmium (rapid mixing 120 s, pH 5.5–6.5): flocculation index against contact time. (a) Influence of different flow rates of the dispersion through the flow cell, applying recycling; (b) effect of recycling under the same conditions (46 mL/min flow rate).

tion index, implying larger aggregates, was obtained after 7 minutes at natural pH values (6–6.5), employing a flow rate of 46 mL/min, which corresponded to a G value of 193 s^{-1}. The duration of the initial flash mixing was 120 seconds in this case. It is likely that a given particle would undergo several collisions with other particles in sheared dispersions before it had acquired enough flocculent ions to allow aggregates to form. This effect can be seen experimentally as a "lag time" between the addition of flocculent agent and the onset of flocculation.

On the other hand, under conditions of high shear, and especially in turbulent flow, there is a possibility of flocs breakage/destruction as a result of shear forces at the particle surface. In certain experiments the flocculation indices did not change significantly over time, indicating that the rates of aggregation and floc breakage were comparable.

When the effect of recycling was examined under the same conditions of flow rate, rapid mixing time, and pH value, higher R values were obtained without the application of recycling (Fig. 2b).

Initial (rapid) Mixing Duration and Flocculation Mixing Intensity

The effect of the duration of preliminary rapid mixing during flocculation of HAP particles was studied using a flow rate of 34 mL/min at natural pH values (5.5–6.5), and the results are presented in Fig. 3. Maximum values for R ratios were observed (i.e., where the flocs reached the greatest size) when 30 seconds of flash mixing time was applied (Fig. 3a). An interesting point of the flocculation index curves was the "lag phase" before the flocculation index curves started to increase. In the early stages of flocculation, aluminum precipitates formed slowly and the flocs had a very small size, hence they had little effect on the flocculation rate of HAP particles. Once the precipitates reached a critical size and number density, a rapid rise in the flocculation index indicated that the aggregate size increased rapidly. The duration of the lag phase was reduced and the slope of the curves increased as the duration of mixing increased, implying higher flocculation rates.

The intensity of mixing (expressed in terms of velocity gradient) on HAP flocculation by alum is shown in Fig. 3(b). Over the range of mixing intensities studied, the flocculation rate increased with G up to 11 s^{-1}. This was due to an increase in the collision rate of the flocculent precipitates and the HAP particles, after which it passed through a maximum, followed by a continuous decrease. This phenomenon suggested that the aggregate size decreased after the time corresponding to the peak in the curve. For the following experiments, 200 rpm was selected as the mixing speed, corresponding to $G = 20.1$ s^{-1}.

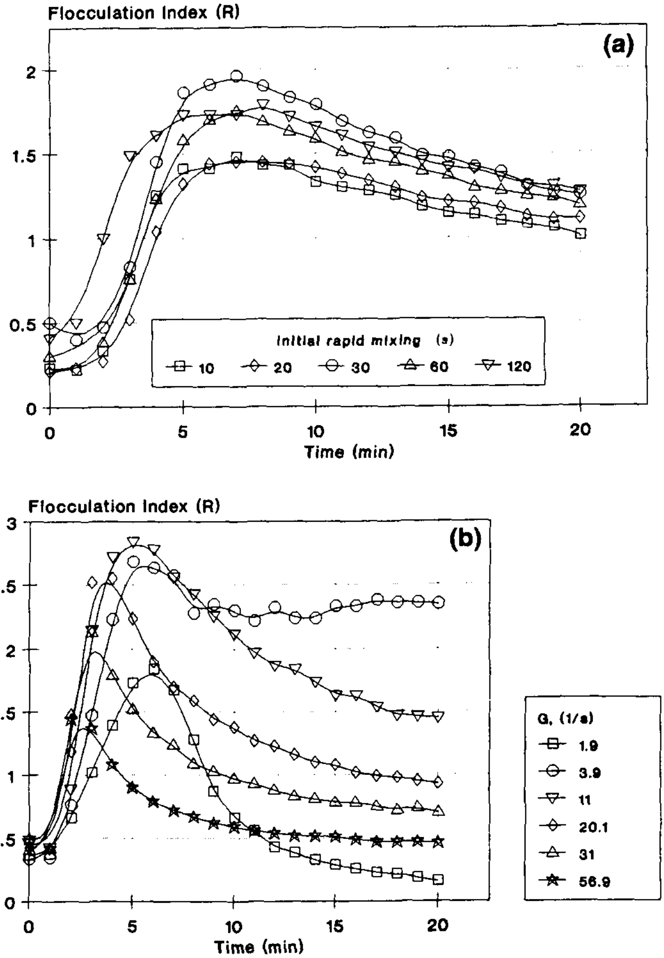

FIG. 3 Flocculation of HAP particles by aluminum sulfate (flow rate 34 mL/min, $G = 140$ s^{-1}, without cadmium or recycling, pH natural). (a) Influence of preliminary rapid mixing duration, using 200 rpm mixing intensity during flocculation ($G = 11$ s^{-1}); (b) effect of shear rate, applying preliminary rapid mixing for 30 seconds.

At low mixing velocities ($G = 1.9$–3.9 s^{-1}) the decrease in the value of the flocculation index resulted from large aggregates of flocs settling during the flocculation process because it was difficult to keep these large flocs dispersed in water. Therefore, the number of particles sampled by the inserted plastic tube leading to the photodispersion analyzer decreased. Since the flocculation index is proportional to the particle size and to the square root of the particle concentration [3], the flocculation index decreased because fewer particles enter the sampling tube. At higher mixing velocities (20.1–56.9 s^{-1}) the flocculation indices attained their maximum values at an earlier stage (3 minutes instead of 5 minutes); i.e., the more rapid the stirring, the shorter the lag phase. The initial slope of the flocculation index curve increased with increasing mixing intensity, indicating higher aggregation rates. This was caused by an increased particle collision rate. In addition, the maximum R values increased up to a certain mixing intensity and then decreased. The flocs reached a limiting size, and although they did not settle at higher mixing intensities (over $G = 20\ s^{-1}$), breakage by fluid shear forces was more dominant than aggregate growth after the initial flocculation period, hence their size and the respective R values decreased.

Zeta-Potential Measurements

The precipitated (amorphous) aluminum hydroxide has an isoelectric point at a pH around 8 (16) and is least soluble near neutral pH (17). The aluminum concentration mostly used (50 mg/L) corresponded to a supersaturated solution between pH values of 5.5 to 10, which meant it was most likely that aluminum precipitates were formed in the solution, which in turn increased the particle collision rate. At these relatively high aluminum concentrations, large precipitates enmeshed the smaller particles and removed them from the dispersion by settling. Good agreement has been reported between experimental data of alum solubility and theoretical predictions (17); the soluble species included, among many others, Al^{3+}, $Al(OH)_2^+$, and $Al(OH)_4^-$. Above a pH value of 8, most of the aluminum was present as soluble species.

The charge density of the ionic species present is important in determining the optimum dosage for flocculation (4). The interactions between the sparingly soluble calcium minerals (such as apatite) during flotation were reviewed, and the problem of minerals solubility was stressed (18). Equilibria between an aqueous solution and minerals (including apatites) was studied thermodynamically (19), although it has to be pointed out that the concept of solubility alone could not explain the flocculation caused by alum, as the whole process is also influenced by such other parameters as ionic strength, the existence of other (possibly interfering) complexing agents, etc.

The respective electrophoretic measurements of metal-loaded HAP were conducted against the solution pH and are presented in Fig. 4. The HAP particles were found to be negatively charged at all pH values examined (from 5 to 12). Increased (less negative) zeta-potential values (of

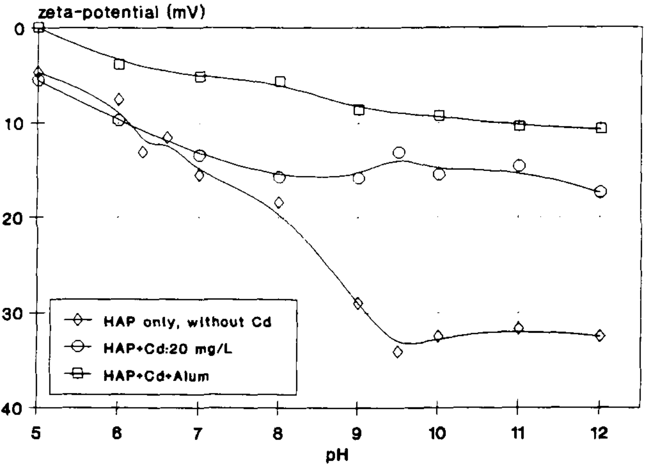

FIG. 4 Zeta-potential measurements before and after flocculation of HAP particles by alum (0.05 g/L) with and without the presence of alum and of cadmium ([Cd^{2+}]: 20 mg/L, pH natural 5.5–6.5).

the order of 5–10 mV) were measured with the flocculated particles and compared with the values obtained before flocculation or without the addition of flocculants, which may be partly due to the result of adsorption of highly charged polymeric species at this pH range, although no charge reversal was noticed. However, it has been suggested that the electrokinetic behavior of sparingly soluble minerals is very sensitive to many parameters. Therefore, this behavior is not considered as specific enough in order to be used either for characterizing them or to elucidate the interactions between them and the aqueous medium (1).

Influence of Presence of Cadmium under Different Conditions

The role of metal ion hydrolysis for the selective flocculation and flotation of oxide and silicate minerals has been previously presented (20). The examination of the presence of cadmium cations on HAP flocculation by alum for natural pH values (5–6) is presented in Fig. 5. It was observed that an increase of cadmium concentration led to decreased flocculation ratios, i.e., the presence and sorption of cadmium cations onto HAP were found to interfere with the flocculation of HAP, possibly due to insufficient interparticle contacts. For a 20 mg/L initial Cd^{2+} concentration, the floc-

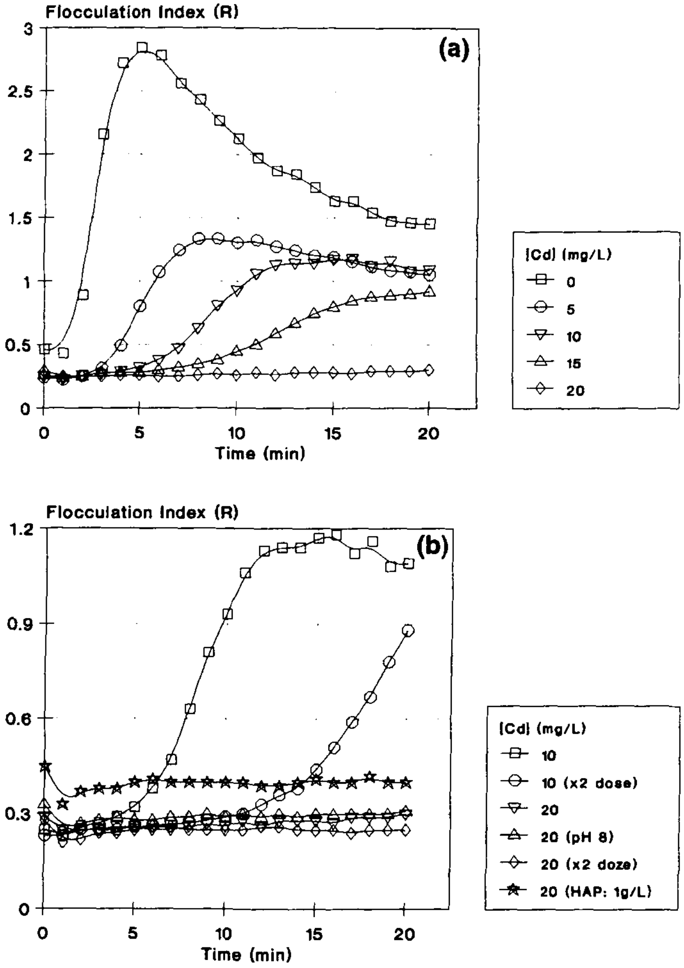

FIG. 5 Influence of different initial cadmium concentrations on flocculation of HAP particles by aluminum sulfate under several conditions (1 dose corresponded to 50 mg/L, pH natural 5–6.2).

culation index remained unchanged during the entire period of slow mixing, indicating that the particles were relatively stable.

Doubling the flocculent dose when the cadmium concentration was 10 or 20 mg/L i.e, applying an overdose, also led to lower flocculation indices. In the case of a 10 mg/L cadmium concentration, the *R* values continued to increase with time after a retardation (''lag'') time of 10 minutes implying that the aggregates did not reach equilibrium size. An increase of the initial HAP concentration to 1 g/L and an increase of the initial (natural) pH to 8 (from a natural pH value of around 6) for a 20 mg/L initial cadmium concentration, again led to negligible *R* values. The flocculation indices remained mostly unchanged, showing that there was no change in the size of the particles in dispersion, i.e., that the aggregates attained equilibrium size. As the precipitation of nonsorbed cadmium (as the respective hydroxide) was expected only over a pH value of approximately 9.5, the negative influence of cadmium should be due to the presence or interaction of ionic Cd forms.

Flocculation of HAP by Adding Ferric Chloride as Flocculent

pH Influence Using Either Deionized or Tap Water

The change of the flocculation index of HAP particles at different pH values when ferric chloride was used as a flocculent agent is shown in Fig. 6(a). The shapes of the curves are similar, and the flocculation indices approached comparable values within around 2–3 minutes with the exception of pH 5, where the dissolution of HAP starts and the values obtained for the flocculation index are significantly lower. The flocculation indices attained a maximum value around 5, i.e., greater than that presented in the previous experiments (lower than 3 for the case of alum), indicating that the aggregates were larger. Although visible aggregates were formed during these experiments, the flocs did not reach equilibrium size, i.e., the rates of aggregation and floc breakage were never comparable. For the concentration of ferric ions used in these experiments (50 mg/L), the formation of large hydroxide precipitates was more favorable in the 6–8 pH range. These precipitates increased the solids concentration in dispersion, and as a result the flocculation rate increased.

The same result can be also drawn from the respective turbidity measurements (for the pH values examined) of around 10 NTU (Fig. 6b). A plausible explanation can be drawn from the zeta-potential measurements (Fig. 6b) which showed in this case that the sign of values obtained was different (positive) in comparison with the previously studied case of alum (Fig. 4). Without the presence of Fe(III) ions in solution, HAP particles were negatively charged at all pH values. When Fe(III) was present, HAP particles adsorbed ferric hydroxide precipitates, which then dominated the surface acid–base properties, surface charge, and electrophoretic mobilities of the HAP particles. The particles reverse their charge (from negative to positive) at all pH values studied (from 5 to 12). This was

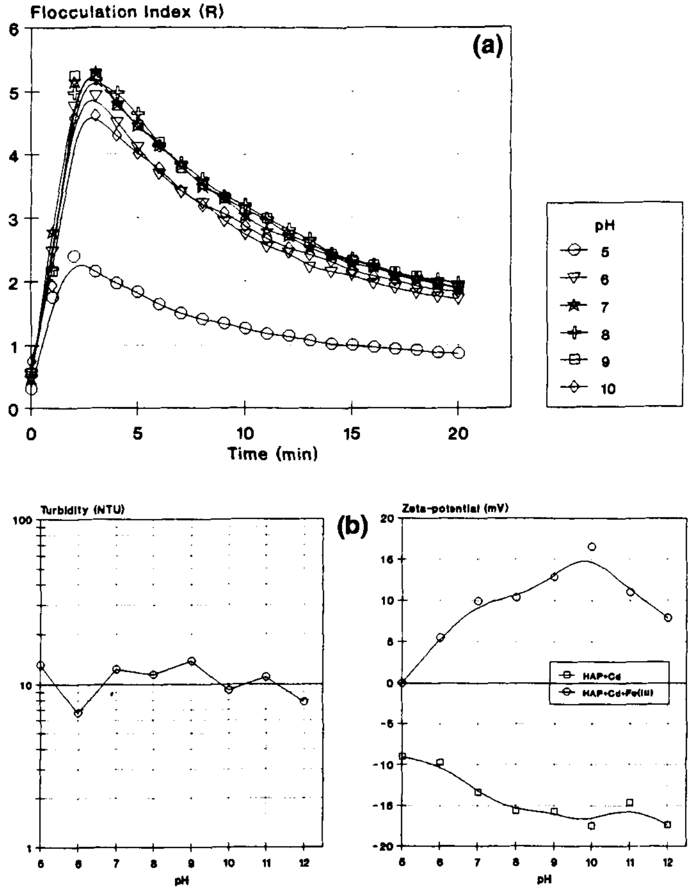

FIG. 6 Influence of different pH values of the dispersion on HAP flocculation by ferric chloride (50 mg/L), using deionized water and 20 mg/L [Cd]. (a) Flocculation index; (b) the respective turbidity and zeta-potential measurements before and after flocculation.

attributed to adsorption of positively charged ferric species and ferric hydroxide precipitates onto the surface of HAP particles.

Ferric ions at pH values above 3 produce ferric monomeric or polymeric hydroxo-complexes (due to hydrolysis) in equilibrium with the hydroxide solid (17). These are positively charged at pH values lower than approximately 8, depending on the specific conditions of the aqueous solution. The chemistry of Fe(III) salts was recently extensively reviewed, and based on solubility diagrams, amorphous ferric hydroxide is least soluble at a pH value close to 8 (5). Adsorption of ferric ions onto HAP particle surfaces could affect both the speciation of ferric ions in solution and the surface properties of the particles, and could occur by formation of surface complexes between ferric and surface hydroxyl groups of the mineral particles. Adsorption of cations onto HAP could also involve ion exchange, particularly at low pH. The formation of a surface phase on HAP particles could result in a composition that varies continuously between that of the original solid and that of a pure precipitate of the adsorbing cation.

When the aforementioned experiments (using ferric chloride) were repeated using tap instead of deionized water, in general, lower flocculation ratios were obtained, showing some interference caused by the change of the aqueous medium composition, due mainly to the presence of alkalinity-generating ions (Fig. 7a). In this case the influence of different dispersion pH values was found to be more critical in comparison with the previously presented experiments of deionized water (Fig. 6). The measured turbidities (Fig. 7b) were also found to be slightly higher than before, possibly showing that at the Fe(III) ions concentration used for these experiments (50 mg/L), the formation of large hydroxide precipitates (easier settled) was more favorable in the pH range between 6 to 8, consistent with the shape of the domain of am-$Fe(OH)_{3(s)}$ stability (6).

The results indicated that the flocculation index was a much more sensitive indicator for flocculation than simple residual turbidity measurements, such as those reported in Fig. 7(b). Positive values were also measured after flocculation for zeta potential and compared with the previously studied case of alum. However, in this case, without the presence of flocculent, zeta-potential measurements were observed to be positive up to a pH between 10 to 11. In the respective results of deionized water (Fig. 6b), charge reversal was observed at this pH value.

Comparisons between tap and demineralized water using ferric ions as flocculent agents (50 mg/L) for a 20 mg/L initial cadmium concentration and for natural pH values (5.8–7.3) can also be observed in Fig. 8. The presence of tap water was found to interfere to a certain extent with the flocculation of HAP fines, even when the flocculent dose was decreased to half or the initial HAP concentration was doubled (1 g/L). The demineralized water was not found to interfere with the flocculation of HAP particles in the presence of 20 mg/L Cd^{2+} (different behavior from alum—see Fig. 5a).

Influence of Flocculent Concentration

A systematic examination of the presence of flocculent concentration showed that above and below certain concentration limits, the flocculation

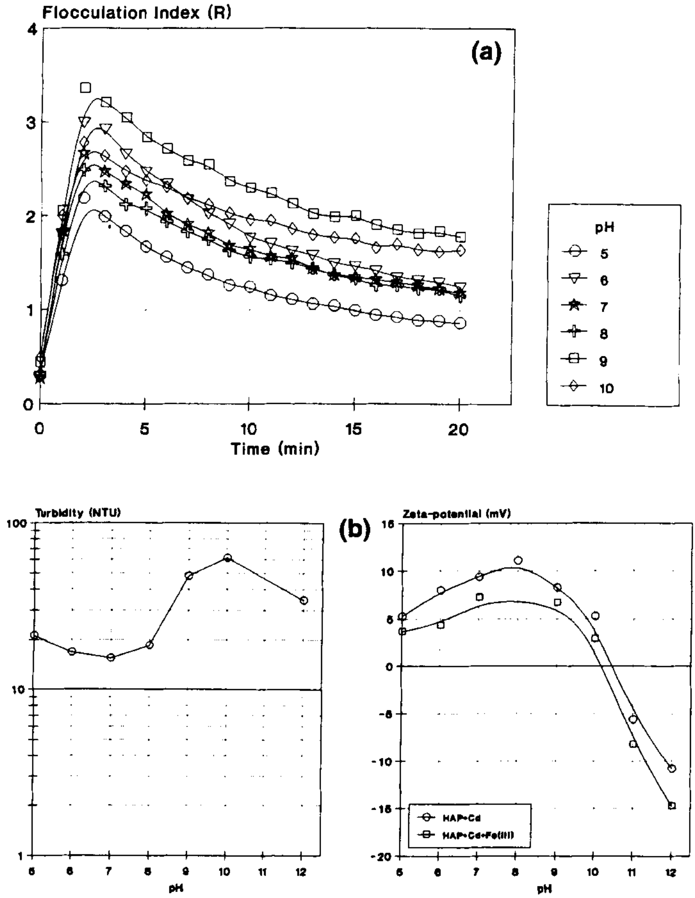

FIG. 7 Effect of different pH values (same conditions were applied as in Fig. 6 but tap water was used).

ratio is decreased (Fig. 9a), noting that in this case the pH was regulated constantly to 6. With increasing dosages, two distinct effects were apparent. There was a reduced "lag phase" before flocculation began, and the slope of the curves became steeper, indicating more rapid flocculation rates caused by the increased concentrations of ferric hydroxide precipitates, resulting in an increased collision rate of the particles. The curves pass through a maximum, followed by a gradual decrease of the flocculation index. Under these conditions, the presence of 50 mg/L Fe(III), corresponding to 10% w/w of the initial HAP concentration (0.500 g/L), was

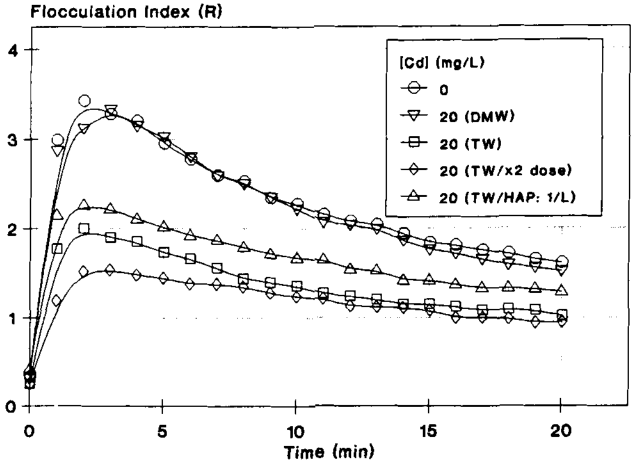

FIG. 8 Flocculation of HAP particles by ferric ions in the presence of 20 mg/L [Cd]; comparison between tap (TW) and deionized water (DMW) under different initial conditions at natural pH values (5.5–7.0).

found to be the optimum concentration to obtain the highest flocculation ratios.

At ferric ions concentrations lower than 50 mg/L, flocculation was induced by the formation of ferric precipitates in solution, i.e., increasing particle collision rate, and by adsorption of the positively charged ferric precipitates and dissolved species on the HAP particles. At larger than 50 mg/L ferric dosages the formation of large hydroxide precipitates was very fast and the sweep-floc mechanism dominated. These precipitates were quite large and they were capable of enmeshing dispersed particles, effectively removing them by settling. The maximum and subsequent decrease of the flocculation index at high ferric dosages was partly attributed to the settling of large aggregates. The amount of added flocculent could not be much in excess of the amount required to adsorb, otherwise there would be at best a wastage of flocculent and often an eventual restabilization of the particles because excess flocculent was present (1).

The residual turbidity curve decreased as the Fe(III) concentration increased, and it reached a constant value for concentrations higher than about 50 mg/L (Fig. 9b). Although lower flocculation indices maxima were observed for the higher Fe(III) dosages, this did not affect the following settling, and hence the residual turbidities.

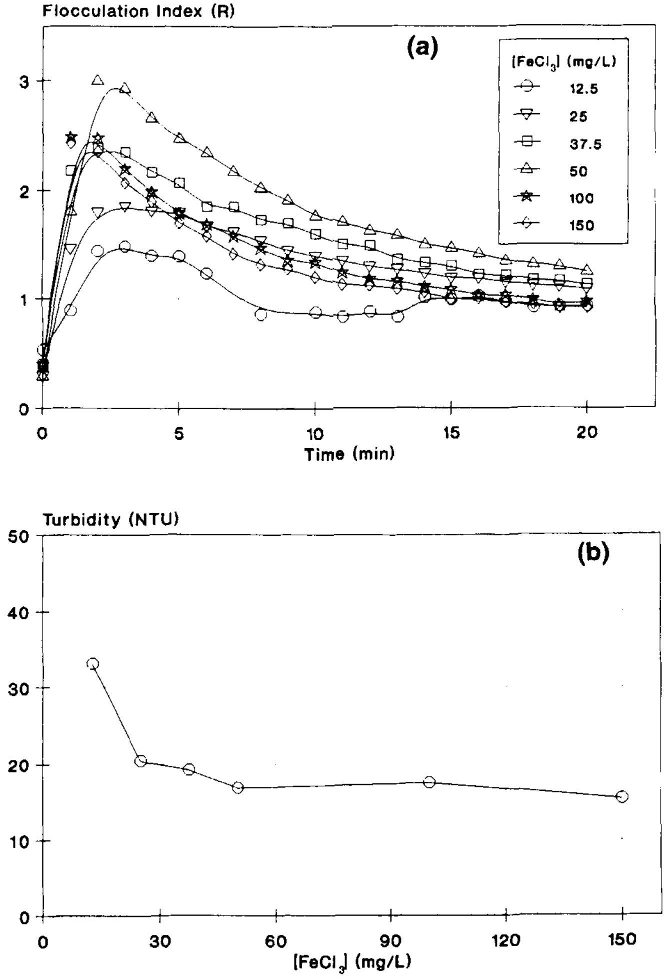

FIG. 9 Effect of different flocculent concentrations of ferric chloride at constant pH value 6 using tap water. (a) Flocculation index; (b) the respective turbidity measurements after flocculation.

Influence of NaCl Concentration (different ionic strengths)

Increased ionic strength caused by various salt additions was also investigated for its possible influence on flocculation of HAP particles. Sodium chloride added in various concentrations (0–0.1 M) was found to cause the same, more or less, values of the flocculation index *R*, except for the case when the highest NaCl concentration (0.1 M) was examined (Fig. 10a). Therefore, NaCl concentrations up to 0.01 M were not found to influence the flocculation behavior of HAP particles.

The respective turbidities were also found to be slightly increased (around 20 NTU), while zeta-potential measurements remained positive for all cases (Fig. 10b). In a related study of flocculation of negatively charged silica particles by cationic polymers (4), it was noted that as the ionic strength was increased, also caused by NaCl addition, flocculation was found to be favored and occurred over a broader range of flocculent

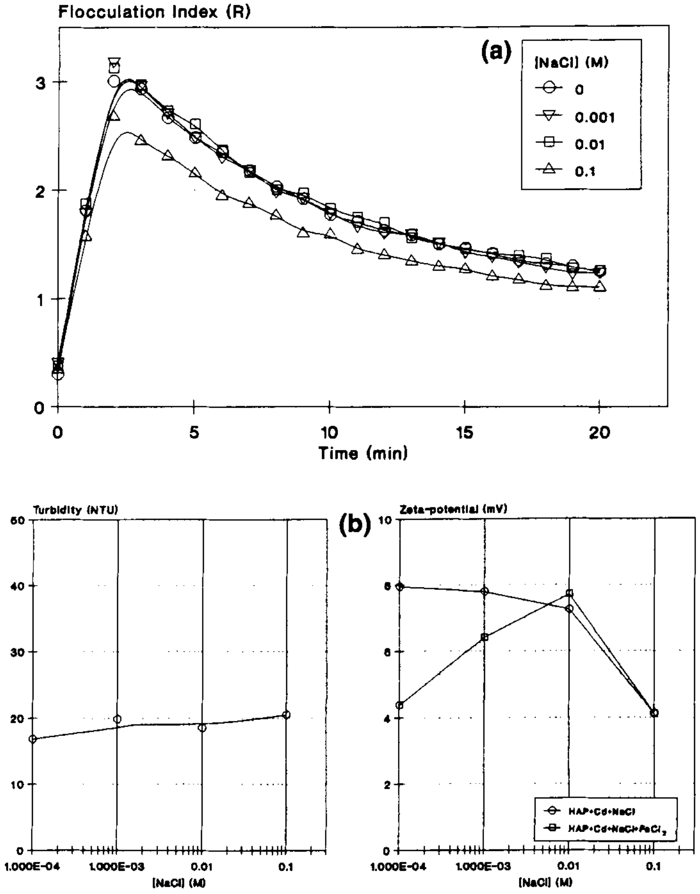

FIG. 10 Influence of different ionic strengths on HAP flocculation by ferric chloride, using tap water at pH 6.0 and in the presence of 20 mg/L [Cd]. (a) Flocculation index; (b) the respective turbidity and zeta-potential measurements after flocculation.

dosage. Since the flocculent and HAP particles were of opposite charge sign, the destabilization was at least partly caused by charge neutralization, and the salt effect could be explained simply in terms of the effect caused on double-layer interaction.

CONCLUSIONS

The results presented show that useful insight into the behavior of inorganic flocculants in stirred dispersions can be gained by a relatively simple but sensitive optical monitoring technique. This method gives information on the dynamics and the state of aggregation of aqueous dispersions of ultrafine HAP particles after the addition of commonly used flocculent agents. HAP was used as a suitable sorbent material for the abstraction of dissolved cadmium, a priority toxic pollutant. Flocculation is expected to help the subsequently required solid/liquid separation process by settling or flotation (21).

The size of the flocs was determined by two competing processes: (a) growth of aggregates, induced by particle collisions, and (b) breakage of aggregates by shear forces. It has been shown that as the time required for the action of flocculents could be several minutes, an appreciable lag time was found between the addition of flocculent and the onset of flocculation. Measurements of flocculation index dynamics complemented the data obtained from residual turbidity and electrophoretic mobility measurements, and thus helped in selecting the optimal flocculent dose. The operational optimum dosage also depended on the mixing conditions and on the specific requirements of the process.

APPENDIX: PRINCIPLES OF TURBIDITY FLUCTUATIONS

When a flowing dispersion is illuminated by a narrow light beam, the transmitted light intensity, monitored by a photo-cell, fluctuates randomly about some mean value (4). The output from the flow-through photo-cell consists of steady (dc) and a fluctuating (ac) components/signals. The dc value is a measure of the average transmitted light intensity and depends on the turbidity of the dispersion. The fluctuating component is a result of random variation in the number of particles in the illuminated volume, because of the fundamental nonuniformity of dispersions and the fact that the sample is continuously being renewed by flow. It can be shown that the fluctuations follow the Poisson distribution, so that the root-mean-square (rms) value of the fluctuating signal varies as the square root of the particle concentration. For a given solids concentration, the fluctuating signal increases markedly as particle aggregation occurs and provides a very sensitive measure of the extent of flocculation. In practice, it is more convenient to divide the rms value by the steady dc value to obtain the dimensionless term R. With the use of this ratio, the effects of optical surface fouling and electronic drift can be avoided.

It can be also shown that for heterodisperse dispersion, the ratio R can be expressed as (4)

$$R = \left(\frac{L}{A}\right)^{1/2} (\Sigma N_i C_i^2)^{1/2} \tag{1}$$

where L is the optical path length, A is the effective cross-sectional area of the light beam, and N_i and C_i are the number concentration and scattering cross-section of particles of size i, respectively. This equation demonstrates that the fluctuating signal depends on the square root of particle concentration and on the first power of the scattering cross-section. The latter is highly dependent on the size of dispersed particles. An analysis of the term $(\Sigma N_i C_i^2)^{1/2}$ in Eq. (1) reveals that smaller particles have a negligible effect on R, and that in a flocculating dispersion the larger aggregates have a significant influence on R. This means that as flocculation progresses, the value of R increases. The rate of increase of R may be taken as an empirical measure of the rate of flocculation.

ACKNOWLEDGMENTS

This work has been partially supported by a European Union Human Capital and Mobility Program (Contract CHRX-CT03-0272). Thanks are due to Dr. Ch. Loos-Neskovic (Centre d'Etudes de Saclay, CNRS, Paris), coordinator of the program.

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Received by editor April 22, 1996
Revision received December 1996