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CHAPTER IV
AQUEOUS DISPERSION BEHAVIOR OF BARIUM CHROMATE CRYSTALS: EFFECT OF CATIONIC POLYELECTROLYTE

ABSTRACT

In polyelectrolyte-enhanced ultrafiltration (PEUF), a cationic polyelectrolyte binds to chromate and is ultrafiltered from solution. The permeate passing through the membrane can contain a very low chromate concentration; the retentate solution not passing through the membrane must be treated to recover a large fraction of the polymer for reuse for economical operation. In the regeneration step, barium chloride can be added to the retentate to precipitate chromate anion as a compact barium chromate solid waste. The solution containing the polymer can be directly recycled after the solid barium chromate is separated from the solution. Gravity settling is much less expensive than filtration or centrifugation, so this investigation studies the ability to separate solid from solution in a settling unit. Unfortunately, the polyelectrolyte can act as a dispersing agent that stabilizes the dispersion of barium chromate particles, resulting in poor separation efficiency in the settler. The adsorption of cationic polyelectrolyte on barium chromate particles increases with increasing polymer concentration, increasing ionic strength, and decreasing barium to chromate ratio. In addition, adsorption of the polyelectrolyte onto the barium chromate particles inhibits the growth of crystals and affects the crystal morphology. The average particle size of barium chromate crystals formed in the presence of the polymer is less than in the absence of the polymer. As a consequence, slower settling of the smaller particles occurs in the presence of polymer. The sedimentation rate of barium chromate increases with decreasing polymer concentration, increasing temperature and increasing electrolyte concentration, and reaches a maximum when there is a stoichiometric ratio of barium to chromate present. At this stoichiometric ratio in the absence of polymer, the zeta potential is zero, confirming that the rapid settling is due to the absence of electrostatic repulsion between the particles. Even though the barium chromate settles rapidly in the absence of polymer, the polymer adsorbs on the crystals and acts like a dispersant as well as causing a solution viscosity increase, resulting in slow settling rates in the PEUF process where the polyelectrolyte must be present.

INTRODUCTION

Chromate removal using the polyelectrolyte-enhanced ultrafiltration process (PEUF) requires the addition of a soluble cationic polyelectrolyte to the feed chromate-laden wastewater to bind chromate anions electrostatically, followed by ultrafiltration to produce a filtrate (permeate) containing a very low concentration of the chromate anions and which can be discharged to the environment. From our previous work,[1,2] the removal of chromate, a carcinogenic heavy metal, by the PEUF process with rejections above 99% was demonstrated. High polymer concentrations in the retentate are possible, while maintaining high flux, which is desirable because it leads to high water recovery (permeate/feed) and a minimization of the volume of retentate effluent to be further treated. Other electrolytes present (e.g., NaCl) result in lower chromate rejection due to the competition of dissimilar anions with chromate for binding sites on the polymer.

Economical operation of PEUF requires that a substantial fraction of the separating agent (polymer) be recovered from the retentate for reuse. This can be achieved by adding a cation with a very low K_{sp} to precipitate the chromate. We have identified barium as an effective precipitating cation to form barium chromate precipitate. After the solid barium chromate is separated from the solution, the concentrated polyelectrolyte solution can be recycled to the feed to the ultrafiltration unit. The solid barium chromate can be removed from solution by centrifugation or filtering, but these methods tend to be expensive. So, we have focused on developing a gravity settling process to achieve solid/liquid separation. In a batch field test at the U.S. Coast Guard Support Base in Elizabeth City, North Carolina for treating industrial process wastewater and groundwater containing chromate and sulfate, this gravity settling was demonstrated to work effectively[3-5] (where overnight settling in a quiescent environment was used). We desire to develop a continuous, steady state separation process, which would be required to economically treat high flow rate streams. We have found that excellent separations are observed in a continuous crystallizer for barium chromate crystals in the absence of the polymer, but poor separations are observed in the presence of the polyelectrolyte since it acts as a dispersant.[6] Understanding the interaction between the polymer and barium chromate

crystals and effect on dispersion stability, particle size distribution produced during crystallization, and other properties is the purpose of this study to support the development of an effective separation process.

Dispersions of solid particles are important in many areas.[7-16] Examples include inhibition of calcium phosphate deposition in industrial water systems, the treatment of barium sulfate scale problem in oil industries, suspensions in pharmaceutical applications, and modification of solid surfaces by polyelectrolyte-based coatings and adhesives. Dispersions can be undesirable in some applications and additives can cause coagulation; e.g., removal of clay fines from drinking water.[17, 18]

Polyelectrolytes can have the tendency to adsorb at the surface of solid dispersed particles, the level of adsorption depending on factors such as the nature of the particle surface, the concentration and chemical structure of polymer, and the solvent quality of the dispersion medium.[19] The effect of additives; sodium tripolyphosphate (STP), ethylenediaminetetramethylenephosphonic acid (ENTMP), and 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), on the crystallization of barium chromate was studied conductometrically, where stoichiometric concentrations of barium and chromate were present at 298 K.[20, 21] Increasing the additive concentration decreases the growth rate due to the blocking of the active sites for crystallization on the crystal surface through adsorption, which could be interpreted in terms of a Langmuir type adsorption isotherm. It has been reported that the barium chromate crystallization occurs by a surface-controlled growth mechanism.[20] The study of adsorption behavior of polyelectrolytes in relation to the crystal growth kinetics of barium sulfate indicate that the adsorption of polyphosphinoacrylate, poly(acrylic acid), poly(styrenesulfonic acid), poly (vinylsulfonic acid), and a copolymer of maleic acid and vinylsulfonic acid disturb the growth rate of barium sulfate.[7, 8, 15, 16] Williams and Harrop[9] described the adsorption of an amphoteric polymer, a copolymer of diallyldimethylammonium chloride (QUAT) and acrylic acid, on barium sulfate crystals, and demonstrated its ability to greatly enhance the colloid stability of a barium sulfate dispersion. Moreover, the adsorption capacity for the polymer increases with increasing ionic strength. The influence of QUAT on the precipitation of amorphous calcium

phosphate exhibits no pronounced effect on the induction period preceding amorphous calcium phosphate precipitation, while the adsorption of polyacrylic acid and benzene hexacarboxylic acid on calcium phosphate is significant.[10] The study of the adsorption of QUAT and copolymers of N-methyl-N-vinyl-acetamide and QUAT on colloidal silica particles showed that the adsorbed levels as well as the hydrodynamic layer thickness of the adsorbed polyelectrolyte layer increases with the ionic strength and the pH of the suspension at high salt concentration. At low salt concentration, the adsorption increases with decreasing charge density of the polyelectrolyte [11, 13, 14] Terayama *et al.*[12] studied the effect of surfactant and polymer on dispersion stability of aqueous suspensions of 5-(3-ethoxy-4-pentyloxyphenyl)-2,4-thiazolidinedione (CT112), a drug particle, by measuring the adsorbed amount of surfactant and polymer, zeta potential, particle size, and sedimentation rate The addition of cellulose rather than sodium dodecyl sulfate (SDS) produces a highly stable suspension, while mixed systems of cellulose and SDS enhance CT112 dispersion stability even more effectively.

In this study, the effect of the barium/chromate concentration ratio, QUAT concentration, temperature, and added electrolyte on particle size distribution, sedimentation rate, viscosity, crystal morphology, and zeta potential of particles in the barium chromate crystallization process was measured in support of development of a crystallization/settling process for separation of chromate from QUAT in a PEUF retentate solution

EXPERIMENTAL

Materials

Poly(diallyldimethylammonium chloride) or QUAT having an average molecular weight of approximately 240,000 Dalton was supplied by Calgon Corporation (Pittsburgh, PA) and has the trade name MERQUAT® The empirical formula of the repeating unit of the polymer is $(H_2C{=}CHCH_2)_2N(CH_3)_2Cl$ The polyelectrolyte was purified using a 10,000 Dalton molecular weight cut-off, spiral wound membrane in order to remove the lower molecular weight components as had been done in studies of the ultrafiltration step in PEUF studies [1, 2] A stirred cell equipped with a 10,000 Dalton molecular weight cut-off Spectrum™ cellulose acetate (type C) ultrafiltration membrane from Spectrum Medical Company (Houston, TX) was used to concentrate the purified polymer solution up to the desired polymer concentration for preparing stock solutions. Sodium chromate and barium chloride dihydrate used in barium chromate solid preparation were analytical grade (purity of 99%) supplied by Reidel-DeHaen (Seelze, Germany) and Merck (Darmstadt, Germany), respectively. Sodium chloride (99 5%) was obtained from Carlo Erba (Milan, Italy). Silver nitrate (99 8%) supplied from Merck (Darmstadt, Germany) was used to prepare the titrant to double check polyelectrolyte concentration obtained from total organic carbon or TOC measurement All chemicals were used as received Deionized and distilled water was used to prepare solutions

Sedimentation rate measurement

The sedimentation rate of barium chromate particles at different conditions was measured in screw cap test tubes by observing the heights of suspended solutions and the interface between clear liquid and suspended solids as a function of time This was measured until this height was constant the experiment is known as the batch settling test.[22-24]

Polyelectrolyte adsorption measurement

Adsorption isotherms of QUAT on barium chromate particles were measured at 30°C using the solution depletion method [13, 14] The barium chromate precipitate was prepared by the rapid mixing of molar solutions of analytically pure barium chloride and sodium chromate, followed by washing with methanol/water mixtures and finally drying at 105°C [25] The barium chromate solids at [barium]/[chromate] ratios of 0.5 and 1.5 were prepared in the same manner. The equilibrium polymer concentrations were determined by mixing 1.0 g of barium chromate powders with varied QUAT concentrations, ranging from 0.5 to 100 mM. The suspended solutions were shaken by a Vortex-Genie2 vortex mixer (Scientific Industries, Inc., Bohemia, NY) for 1 minute and were subjected to an ultrasound treatment[9] by a Branson 2200 ultrasonic cleaner (Branson Ultrasonics Corporation, Danbury, CT) for 1 minute at 120 W and 47 kHz before equilibrating in a shaking bath at controlled temperature (30.0 ± 0.2°C) and 100 rpm shaking speed for 24 hours to allow adsorption equilibrium to be reached. After centrifugation at 2000 rpm for 10 minutes by a Centrifuge 4236 (A.L.C. International, Milan, Italy), barium chromate powder was then separated by filtering using a 0.2 μm pore size cellulose acetate membrane filter[10, 15] (Lida Manufacturing Corporation, Kenosha, WI), and the supernatant was sampled to determine the equilibrium polyelectrolyte concentration. The quantity of polyelectrolyte adsorbed was then calculated from the change in concentration of the polymer solution. A Shimadzu TOC-5000A total organic carbon (TOC) analyzer (Kyoto, Japan) was used to determine the QUAT concentration in supernatant solutions. The QUAT concentration reported in this work is based on the concentration of monomer or diallyldimethylammonium chloride molecules. So the molecular weight used to convert mass concentration to molar concentration was 96.08 Dalton, not 2.4×10^5 Dalton (molecular weight of polymer)

Particle size measurement

The particle sizes of barium chromate particles with and without adsorbed polymer were determined using a Coulter® LS 230 counter particle size analyzer with a small volume module (Coulter Corporation, Hialeah, FL). This LS 230 uses laser light at a wavelength of 750 nm to obtain the size of particles with diameter from 0.4 μm to 2000 μm by light diffraction (Fraunhofer diffraction). When particles are smaller than 0.4 μm in diameter, polarization intensity diffraction scattering (PIDS) is used, which provides polarized monochromatic light at 450 nm, 600 nm, and 900 nm. Measurements were carried out in both aqueous solution and electrolyte solution at different ionic strengths. The suspended solutions, containing synthesized barium chromate, were equilibrated in a water bath at the desired temperature for 24 hours. The suspensions were shaken homogeneously by the vortex mixer before loading into the Coulter counter particle size analyzer. The particle size distributions and mean diameter of particles were obtained graphically from the instrument.

Crystal morphology characterization

The morphologies of barium chromate crystals in aqueous solution and in polyelectrolyte solution were investigated using a JSM-6400 scanning electron microscope or SEM (Jeol Ltd., Tokyo, Japan).

Zeta potential measurement

The zeta potential measurements were made with a zeta meter 3.0+ unit (Zeta-Meter, Inc., Staunton, VA). The determination of surface charges of the barium chromate particles in water at different barium to chromate ratios was made in diluted suspensions to avoid a salting out effect. Even though the dilution is not recommended because the concentration of the dissolved ions significantly affects the charge of the colloid, the dilution can be a valuable tool for comparative study. In this study the dilution ratio used for all samples was 10 to 1.

Viscosity measurement

The viscosity of the polyelectrolyte solution at the studied condition was measured using a Brookfield digital rheometer DV-III (Brookfield Engineering Laboratories, Inc., Stoughton, MA). The polymer solutions were equilibrated in a water bath at controlled temperatures (10°C, 25°C, and 50°C) before transferring 500 mL of sample into a 600 mL low form beaker. Three rotational speeds of the spindle (RV-1) were used: 100, 125, and 200 rpm. The viscosity of the polyelectrolyte solution at zero shear rate was determined by a linear extrapolation of these measured values. The measuring time used was 10 minutes. The temperature was measured by a temperature probe during the viscosity determination

RESULTS

Sedimentation rate

The rate of barium chromate sedimentation, which is presented as the percentage of solid volume as a function of time, is shown in Figs. 1-7. An average of required settling time to obtain a solid volume below 20% is summarized in Table 1 for the conditions studied. The measurement of sedimentation rate of the particle were carried out 3 times with standard deviation ± 30 seconds for 0 to 0.1 M QUAT and up to ± 3 minutes for 0.2 to 0.4 M QUAT.

For a stoichiometric ratio of [barium]/[chromate]=1, Figs. 1 and 2 show the rate of sedimentation at 10°C, 25°C, and 50°C in the absence of QUAT and in the presence of 0.1 M QUAT. In either the presence or absence of QUAT, as the temperature increases, the rate of sedimentation increases. In the absence of QUAT, barium chromate particles were visibly flocculated, showing rapid settling. Conversely, in the presence of QUAT, flocculation was not observed, leading to a slower sedimentation. Particle size distribution is described quantitatively later. The sedimentation rate decreases substantially when [QUAT] is increased, as shown in Fig. 3. For example, at 50 °C in the absence of QUAT, the residence time required for suspended solids to settle to a solid volume below 20% is only 1 minute, while in the presence of [QUAT] of 0.1, 0.2, 0.3, and 0.4 M, settling times of 8, 23, 55, and 90 minutes were required, respectively (Table 1).

Figures 4 and 5 illustrate the rate of barium chromate sedimentation at [barium]/[chromate] ratios of 0.5, 1.0, 2.0, 5.0, and 10.0 in the absence and in the presence of QUAT. The results at [barium]/[chromate] ratios of 0.5, 1.0, and 2.0 in the absence of QUAT are similar, however, it should be noted that at a [barium]/[chromate] ratio of 1.0 (stoichiometric), the highest sedimentation rate is observed. The higher [barium]/[chromate] ratios (5.0 and 10.0) give a lower sedimentation rate than lower ratios. In the presence of 0.2 M QUAT at any [barium]/[chromate] ratio, sedimentation is slower than in the absence of QUAT. For example, at 50°C at [barium]/[chromate] ratios of 0.5, 1.0, 2.0, 5.0, and 10.0, in the absence of QUAT,

the respective residence time requires for suspended solid to settle to a solid volume below 20% are 2, 1, 2, 8, and 14 minutes. In the presence of 0.2 M QUAT, settling times of 23, 40, 55, and 75 minutes were required at analogous [barium]/[chromate] ratios of 1.0, 2.0, 5.0, and 10.0, respectively. In the presence of 0.2 M QUAT, the most rapid sedimentation occurs at the stoichiometric ratio of barium to chromate. Interestingly, at [barium]/[chromate] ratio of 0.5, no solid settling occurred within the time period studied.

For a stoichiometric [barium]/[chromate] ratio, rates of barium chromate sedimentation at various ionic strengths (added [NaCl] levels) in the absence of QUAT and in the presence of QUAT are shown in Figs. 6 and 7. In the absence of QUAT, the sedimentation rates do not change with ionic strength. In contrast, with 0 2 M QUAT, increasing electrolyte concentration leads to an increase in the barium chromate sedimentation rate.

Viscosity

The viscosity of the polymer solution at different polymer concentrations, salt concentrations, and temperatures, which is presented in term of relative viscosity (viscosity/viscosity of water) at zero shear rate, is shown in Table 2. The viscosity of the polyelectrolyte solution increases with increased polyelectrolyte concentration, decreased temperature, and decreased ionic strength

Actually, the viscosity of suspended solution can differ substantially from the particle-free solution since the viscosity of a dispersed system also depends on hydrodynamic interactions between particles and solvent, particle-particle interaction, and interparticle attractions that promote the formation of aggregates.[26] However, in order to measure the viscosity of the dispersed system, a vibrating viscometer and a specially designed device are needed to maintain the stability of the suspended solution during viscosity measurement.[27, 28] The viscosity reported in this work is the viscosity of the polymer solution in the absence of barium chromate particles, which are useful to qualitatively explain observed effects on dispersion stability.

Zeta potential

The average zeta potential of barium chromate particles in aqueous solution as a function of [barium]/[chromate] ratio is shown in Fig. 8 in the absence of QUAT. At the stoichiometric ratio, the zeta potential is zero, which represent no net charge on the surface of particles, whereas a negative charge is observed at a [barium]/[chromate] < 1, and a positive charge at a [barium]/[chromate] >1. The average zeta potential shown in this work was obtained from 30 measurements. Most of the sample has a high uniformity of charge (electrophoretic mobility), a standard deviation of the zeta potential values is around ± 0.5 to ± 2.0 mV. At a [barium]/[chromate] ratio of 1, the heterogeneity of the particles as indicated by their electrophoretic mobility was greater (some particles moved toward the anode and some to the cathode), but the average velocity (and hence zeta potential) is approximately zero. It can also be confirmed by an interpolation of the zeta potential at [barium]/[chromate] ratios of 0.8 and 1.2, which gives zero zeta potential at a [barium]/[chromate] ratio of 1. Due to high viscosity, the zeta potential of the solid could not be measured in the presence of the QUAT with our instrument. Moreover, in the presence of polyelectrolyte there was a non-horizontal particle movement along a tracking path between the two electrodes because of an excess cationic charge on the particles.

Particle size distribution

The barium chromate particle size distribution, which is presented as volume fraction as a function of the logarithm of particle diameter, is shown in Figs. 9-16. Average particle diameter, and range of particle diameters are summarized in Table 1 for the conditions studied. Each value of the average particle diameter represents the average from five particle size measurements with standard deviations reported in Table 1.

The effect of QUAT concentration on the barium chromate particle size at low concentration range from 1 to 100 mM and at high concentration range from 100

to 400 mM are shown in Figs. 9 and 10, respectively at 50°C. The average particle size is shown as a function of [QUAT]. There is clearly a critical [QUAT] range of 10 to 50 mM over which the particles sharply decrease in size and above which the average particle size levels off at around 0.9 μm (compared to 2.0 μm with no QUAT). Qualitatively similar results were observed in the study of the adsorption of SDS or cellulose on 5-(3-ethoxy-4-pentyloxyphenyl)-2,4-thiazolidinedione (CT112).[12] The particle diameter of CT112 was 47 μm without additives and decreased below 10 μm in the presence of 1 mM SDS or 0.2 g/L cellulose.

Figures 11 and 12 present the particle size distribution of barium chromate at different temperatures in the absence and in the presence of QUAT. Without QUAT, increased temperature generated a broader particle size distribution and a larger average particle diameter of barium chromate shown in Fig. 11 and Table 1; however, in the presence of 0.1 M QUAT, increased temperature does not cause a significant effect on barium chromate particle size distribution. The particle diameter observed here compares reasonably with the particle diameter of barium chromate reported by Packter and Alleem,[29] which was in between 1.5 μm and 7.0 μm at pH from 3 to 8 and initial overall metal concentration from 0.13 to 10 mM at 22°C.

The effect of [barium]/[chromate] ratio on particle size distribution of barium chromate is presented in Figs. 13 and 14 in the absence and the presence of QUAT, this [barium]/[chromate] ratio has an insignificant effect on the particle size distribution. It should be noted that the initial barium chloride concentration used in this experimental part (1.0 M) was higher than other experiments (0.2 M) in order to be able to prepare samples to give a [barium]/[chromate] ratio up to 10, where the initial sodium chromate concentration was 0.2 M throughout this work. This higher initial barium chloride concentration results in a larger average particle diameter both in the absence and in the presence of QUAT even at the same [barium]/[chromate] ratio. For example, at 50°C in the absence of QUAT, the average particle diameters are 2.0 μm for a 0.2 M barium chloride solution and 3.8 to 4.9 μm for a 1.0 M barium chloride solution. Similarly, in the presence of QUAT, the average particle diameters are 0.9 μm for a 0.2 M barium chloride and 1.1 to 1.2 μm for a 1.0 M barium chloride solution.

Figures 15 and 16 show the ionic strength effect on barium chromate particle size in the absence and in the presence of QUAT by varying added [NaCl]. From Fig. 15 and Table 1, in the absence of QUAT, the average particle diameters vary little with [NaCl], but the particle size distribution is broader at higher ionic strengths. At 0.2 M QUAT, there is little change in particle size distribution and average particle diameter with electrolyte concentration. Interestingly, in the absence of QUAT, the average particle diameter of barium chromate with added salt is slightly higher (2.2 to 2.6 μm) than without added salt (2.0 μm). Conversely, in the presence of 0.2 M QUAT, the average particle diameters are 0.9 μm for no added salt and 0.5 to 0.6 μm for the system with added salt.

Polymer adsorption

The adsorption isotherms of QUAT on barium chromate solid in water and in 0.1 M NaCl are shown in Fig. 17. The adsorption increases with increasing polyelectrolyte concentration in a Langmuirian fashion and reach a plateau with different adsorption densities at different equilibrium QUAT concentrations. For example, at a [barium]/[chromate] ratio of 0.5 and 1.0, the equilibrium concentrations are around 70 mM and 50 mM, respectively. However, at a [barium]/[chromate] ratio of 1.5, there is an insignificant amount of polyelectrolyte adsorbed on the barium chromate. It was found that the adsorption of polymer on solid decreases with increased [barium]/[chromate] ratio and increases with increased ionic strength.

Figure 18 shows the effect of QUAT concentration on sedimentation rate of barium chromate, barium chromate particle size, relative viscosity, and polymer adsorption to permit simultaneous comparison of several properties. QUAT concentration in the region of 0.001 to 0.1 M provides a significant influence on every parameters studied. For example, the sedimentation rate decreases dramatically with increasing QUAT concentration to 0.1 M and slowly declines when QUAT is increased from 0.1 M to 0.4 M, the average particle size of barium chromate decreases and reaches a certain value around 0.05 to 0.1 M, the adsorption of

polymer on barium chromate solid increases sharply with increasing QUAT concentration and remains constant at around 2 mg/g of $BaCrO_4$ at approximately 0.05 M of QUAT, and the relative viscosity increases sharply until 0.05 M QUAT is reached and continues to increase steadily at higher [QUAT].

Crystal morphology

The barium chromate crystal morphology is shown in scanning electron micrographs in Figs. 19 and 20 in the absence and in the presence of 0.2 M QUAT, respectively. A defective crystalline structure is observed in the presence of QUAT. It should be noted that in the presence of QUAT, there was a dried polymer layer coated on the top of the barium chromate particle, resulting in blurred SEM pictures in Fig. 20. At [barium]/[chromate] of 1 in the absence of QUAT, the result from EDX shows that the particles only consist of barium, chromium and oxygen.[30] Moreover, atomic absorption spectroscopy measurements have shown that the molar ratio of barium to chromate in the solid is always 1 to 1 at any QUAT concentration.[30]

DISCUSSION

Dispersion stability

Simultaneous consideration of rate of sedimentation, particle size distribution, zeta potential, polymer viscosity, polymer adsorption, and crystal morphology of barium chromate suspensions can provide insight into dispersion stabilization of the crystal particles in water and hints to strategies for more rapid settling in an industrial separation process.

In the absence of added polymer, particles are relatively large and settle rapidly. As expected, the most rapid settling occurs for the electrically neutral barium chromate crystals in a stoichiometric mix of barium and chromate, where the particles have no net electrical charge (zero zeta potential), where the average particle diameter is a maximum also. Heterocoagulation (coagulation of oppositely charged particles) may also contribute to flocculation at zero net zeta potential since the charge distribution of particles is not exactly homogeneous. A little surprising is the increased settling rate with increasing temperature as Brownian motion might be expected to keep particles in suspension longer. However, for dispersions of fine solids in liquid, instability is caused mainly by coagulation resulting from the Brownian motion (sticky collision). Collision between particles will lead to growth of the particle. Because of their close contact, clusters of aggregates and/or primary particles form.[31-33] This phenomenon was also found in removal of kaolinite clay dispersed particles from water in a settling tube experiment; the effective settling velocity is higher when temperatures increases.[34] As the [QUAT] increases, polymer adsorption on the crystals increases, average particle size decreases, particle size distribution narrows, viscosity increases, and sedimentation rates decrease dramatically. There is a range of [QUAT] over which polymer adsorption increases sharply and particle size decreases sharply. Above this concentration, polymer adsorption plateaus, particle sizes stabilize, but sedimentation rates continue to decline. This latter important effect is due to solution viscosity increase caused by increasing polymer concentration.[11] Further addition of the polymer to the full coveraged-particle system will cause an increase in the concentration of the free

polymer in the suspending fluid and hence increase the viscosity of the suspension. Therefore, the stability of colloidal dispersions in the presence of polymer is not only affected by the adsorption density of the polymer onto the surface of the particles, but also by the concentration of free polymer chains in the suspending fluid.[35] This is consistent with the increased sedimentation rate with increasing temperature inducing a viscosity reduction. The effect of viscosity on settling rate of ground silica particle has been study by other researchers[27] in hydrocyclone classifiers, they reported that the settling rate of particles decreases as slurry viscosity increases. Moreover, the viscosity of the slurry can be altered by factors other than temperature variation, such as changing solid fraction. The adsorption of polymer mainly inhibits the crystal growth of barium chromate, which can be shown by SEM and particle size measurements of bare and covered barium chromate particles, where at sufficiently high polyelectrolyte concentration, polyelectrolyte is able to retard or to block the crystallization process by adsorption at active growth sites of the crystal surface,[16] leading to smaller barium chromate particles in the presence of QUAT. Since the mechanism of the barium chromate crystallization is a surface-controlled growth mechanism,[20] the decrease in the particle size resulted from the inhibition of particle growth rather than the lack of aggregation of primary particles.

Polymer adsorption on barium chromate particles can enhance the dispersion stability through electrostatic and/or steric stabilization mechanisms, leading to a slower sedimentation rate due to repulsive forces. At low polymer concentration or at low ionic strength of the aqueous solution, the adsorbed polymers develop a train structure (flat conformation) on the surface because of mutual repulsion of charged segments, hence the adjacent charge on polymer segments adsorbed onto the surface cause electrostatic repulsion forces (large increase in zeta potential). In contrast, at high polyelectrolyte concentration or at high ionic strength, the QUAT adsorbed on the barium chromate surface take the conformation of mainly tails or loops, containing unadsorbed functional groups extending away from the surface, rather than a flat conformation. In this case the high dispersion stability occurs as a consequence of high steric hindrance between the adsorbed polymer layers accompany with high electrostatic repulsion between charges of polymer segments. These phenomena have been reported in other systems as well.[12, 16, 36, 37]

An increase in the sedimentation rate with increasing electrolyte concentration is observed in this work. Addition of electrolyte leads to an increase in the polymer adsorption on the solid particles[9, 11, 13, 14, 37] (see Fig. 17) and results in more steric repulsion between particles due to the coil conformation of polymers. Increasing adsorption due to added electrolyte leads to a smaller average barium chromate particle size. Added electrolyte leads to screening of polymer charges through compression of the electrical double layer next to the surface that can suppress the electrostatic repulsion between the polyelectrolyte segments. If the magnitude of the electrostatic repulsion is lower than the magnitude of the van der Waals attraction, the dispersion will be unstable and particles will form aggregates in the suspension.[35] Increase in the sedimentation rate with increasing [NaCl] in the presence of QUAT indicates that at least some of the dispersion stabilization induced by the polymer is electrostatic in nature. Additionally, the electrolyte added can reduce the dispersed solution viscosity, resulting in poorer dispersion stabilization. This result was also observed in clay system, where the turbidity of the solution decreases with increasing NaCl concentration.[31]

As [barium]/[chromate] ratio increases well above stoichiometric ratios (up to 10), the sedimentation rates of 0.2 M [QUAT] compared to no-polymer systems decreases. For example, the ratio of residence times from Table 1 for no QUAT system to the 0.2 M QUAT system varies from 1/23 to 14/75 as [barium]/[chromate] ratio varies from 1 to 10. At a [barium]/[chromate] ratio of 10 in the presence of QUAT, there is no significant polymer adsorption, so the decrease in the sedimentation rate is mainly due to the increase in viscosity of the polymer solution. The dispersion stability also depends on the solid/solution ratio. For example, the absolute value of the zeta potential of barium chromate at a [barium]/[chromate] ratio of 10 (ZP=+35 mV) is higher than at a ratio of 0.5 (ZP=-15 mV), however, the residence time required for the suspended solid to settle to a solid volume below 20% at a [barium]/[chromate] ratio of 10 (75 minutes) is lower than that at a [barium]/[chromate] ratio of 0.5 (more than 120 minutes). This is expected since the fraction of barium chromate precipitated at a [barium]/[chromate] ratio of 0.5 is 41.7%, while that at a [barium]/[chromate] ratio of 10 is nearly 100.0%.[30] Therefore, less

agglomeration occurs due to the lower solid/solution ratio at the lower [barium]/ [chromate] ratio.

From Fig. 18, polymer adsorption leading to a decreased particle size, as well as increased solution viscosity, causes sedimentation rate to decrease with increasing QUAT concentration up to about 0.05 M QUAT. Above that concentration, polymer adsorption and particle size level off, so further reductions in sedimentation rate are primarily due to continuing viscosity increase with QUAT concentration.

Implications for process design

In the PEUF process, the higher the [QUAT] in the retentate stream from the ultrafiltration step (feed stream to the crystallizer/settler), the higher the water recovery (permeate/feed in ultrafiltration) and the smaller the retentate volume to be treated. The maximum retentate [QUAT] is often limited by low flux[2] through the membrane at high [QUAT], which often limits practical [QUAT] to 0.2 to 0.4 M. This work has shown that [QUAT] needs to be about two orders of magnitude lower than that to see poor dispersion stabilities and high settling rates (as observed in a crystallization unit for barium chromate with no added polymer).[6] Operating at stoichiometric ratios of barium and chromate, increasing temperature or increasing added electrolyte concentration decreases dispersion stability. At the [QUAT] necessary for the PEUF process to operate economically (high recovery of QUAT for reuse), dispersion stabilities are always much higher than in the no-polymer case. Therefore, although a continuous, steady-state crystallizer is effective for separation of polymer-free barium chromate crystals from solution, PEUF retentate solutions will probably require semi-batch quiescent settling tanks with long residence times for effective separation of particles from solution.

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สำนักงานวิทยทรัพยากร
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REFERENCES

(1) Sriratana, S.; Scamehorn, J. F.; Chavadej, S.; Saiwan, C.; Haller, K. J.; Christian, S. D.; Tucker, E. E. *Sep. Sci. Technol.* **1996**, *31*, 2493.

(2) Tangvijitsri, S.; Saiwan, C.; Soponvuttikul, C.; Scamehorn, J. F. *Sep. Sci. Technol.* **2002**, *37*, 993.

(3) Christian, S. D.; Tucker, E. E.; Scamehorn, J. F. *Spec. Chem.* **1995**, *13*, 148.

(4) Sabatini, D. A.; Knox, R. C.; Tucker, E. E.; Puls, R. W. *Innovative Measures for Subsurface Chromium Remediation: Source Zone, Concentrated Plume, and Diluted Plume (EPA 600/S-97/005)*, U.S. Government Printing Office: Washington, D.C., 1997.

(5) Tucker, E. E.; Christian, S. D.; Scamehorn, J. F.; Uchiyama, H.; Guo, W. In *Transport and Remediation of Subsurface Contaminants*, Sabatini, D. A.; Knox, R. C.; Eds.; American Chemical Society: Washington, D.C., 1992; Chapter 7.

(6) Soponvuttikul, C.; Saiwan, C.; Scamehorn, J. F. *222nd ACS National Meeting*, Chicago, 2001.

(7) Balastre, M.; Persello, J.; Foissy, A.; Argillier, J.-F. *J. Colloid Interface Sci.* **1999**, *219*, 155.

(8) van der Leeden, M. C.; van Rosmalen, G. M. *J. Colloid Interface Sci.* **1995**, *171*, 142.

(9) Williams, P. A.; Harrop, R.; Robb, I. D. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 403.

(10) Amjad, Z. *Colloids Surf.* **1990**, *48*, 95.

(11) Bauer, D.; Killmann, E.; Jaeger, W. *Colloid Polym. Sci.* **1998**, *276*, 698.

(12) Terayama, H.; Okumura, K.; Sakai, K.; Torigoe, K.; Esumi, K. *Colloids Surf., B* **2001**, *20*, 73.

(13) Bauer, D.; Killmann, E.; Jaeger, W. *Prog. Colloid Polym. Sci.* **1998**, *109*, 161.

(14) Killmann, E.; Bauer, D.; Fuchs, A.; Portenlanger, O.; Rehmet, R.; Rustemeier, O. *Prog. Colloid Polym. Sci.* **1998**, *111*, 135.

(15) van der Leeden, M. C.; van Rosmalen, G. M. In *Mineral Scale Formation Inhibition*, Amjad, Z.; Ed.; Plenum Press: New York, 1995, Chapter 9.

(16) Thompson, R. G. In *Colloid-Polymer Interactions: Particulate, Amphiphilic,*

and Biological Surfaces; Dubin, P. L., Tong, P., Eds.; American Chemical Society: Washington, D.C., 1993; Chapter 15.

(17) Kretzschmar, R.; Robarge, W. P.; Weed, S. B. *Soil Sci. Soc. Am. J.* **1993**, *57*, 1277.

(18) Lagaly, G. In *Coagulation and Flocculation: Theory and Application*, Dobias, B., Ed.; Marcel Dekker, Inc.: New York, 1993; Chapter 10.

(19) Dickinson, E.; Eriksson, L. *Adv. Colloid Interface Sci.* **1991**, *34*, 1.

(20) Antonious, M. S.; Ramsis, M. N.; Youssef, A. O. *Monatsh. Chem.* **1996**, *127*, 15.

(21) Ramsis, M. N.; Antonious, M. S.; Rizkalla, E. N.; Youssef, A. O. *Monatsh. Chem.* **1996**, *127*, 1099.

(22) Foust, A. S.; Wenzel, L. A.; Clump, C. W.; Maus, L.; Andersen, L. B. *Principles of Unit Operations*; 2nd ed.; John Wiley & Sons: Singapore, 1980; Chapter 22.

(23) McCabe, A. S.; Smith, J. C.; Harriott, P. *Unit Operations of Chemical Engineering*; 5th ed.; McGraw-Hill Book Company: Singapore, 1985; Chapter 30.

(24) Rushton, A.; Ward, A. S.; Holdich, R. G. *Solid-Liquid Filtration and Separation Technology*; 2nd ed.; WILEY-VCH: Darmstadt, 2000; Chapter 3.

(25) Wright, J. A.; Harrop, R.; Williams, P. A.; Pass, G.; Robb, I. D. *Colloids Surf.* **1984**, *24*, 249.

(26) Wilkes, G. L. In *Concise Encyclopedia of Polymer Science and Engineering*, Kroschwitz, J. I., Ed.; John Wiley & Sons: New York, 1990, p 994.

(27) Kawatra, S. K.; Bakshi, A. K.; Rusesky, M. T. *Miner. Eng.* **1996**, *9*, 881.

(28) Bakshi, A. K.; Kawatra, S. K. *Miner. Metall. Process.* **1996**, *13*, 165.

(29) Packter, A.; Alleem, A. *Cryst. Res. Technol.* **1981**, *16*, 33.

(30) Soponvuttikul, C. Ph.D. Dissertation, The Petroleum and Petrochemical College, Thailand, 2003.

(31) Sonntag, H. In *Coagulation and Flocculation: Theory and Application*, Dobias, B., Ed.; Marcel Dekker, Inc.: New York, 1993; Chapter 3.

(32) Everett, D. H. *Basic Principles of Colloid Science*, Royal Society of Chemistry: London, 1992, Chapter 9.

(33) Hunter, R. J. *Foundations of Colloid Science I*; The Universities Press (Belfast)

Ltd.: Belfast, 1991; Chapter 8.

(34) Yl, L. *J. Hydraul. Res* **1994**, *32*, 41.

(35) Zaman, A. A. In *Polymers in Particulate Systems: Properties and Application*; Hackley, V. A., Somasundaran, P., Lewis, J. A., Eds.; Marcel Dekker, Inc.: New York, 2001; Chapter 7.

(36) Sato, T.; Ruch, R. *Stabilization of Colloidal Dispersions by Polymer Adsorption*, Marcel Dekker, Inc.: New York, 1980; Chapter 2.

(37) Fleer, G. J.; Scheutjens, J. M. H. M. In *Coagulation and Flocculation: Theory and Application*, Dobias, B., Ed.; Marcel Dekker, Inc.: New York, 1993; Chapter 5.

Table 1. Summary of dispersion stability results.

Temperature (°C)	[QUAT] (M)	$\frac{[Ba^{2+}]}{[CrO_4^{2-}]}$ (M/M)	[NaCl] (M)	Residence time [c] (min)	Average particle diameter (μm)	Particle diameter range (μm)
10	0	1.0 [a]	0	7	1.52 ± 0.04	0.38-4.66
25	0	1.0 [a]	0	3	1.89 ± 0.01	0.08-6.16
50	0	1.0 [a]	0	1	2.06 ± 0.03	0.04-6.16
10	0.1	1.0 [a]	0	38	1.00 ± 0.05	0.05-3.21
25	0.1	1.0 [a]	0	16	0.95 ± 0.09	0.05-3.21
50	0.1	1.0 [a]	0	8	1.00 ± 0.05	0.04-3.91
50	0.001	1.0 [a]	0	1	2.05 ± 0.03	0.05-6.97
50	0.005	1.0 [a]	0	1	1.93 ± 0.08	0.05-6.78
50	0.01	1.0 [a]	0	2	1.67 ± 0.06	0.04-5.52
50	0.05	1.0 [a]	0	4	0.82 ± 0.08	0.04-3.21
50	0.2	1.0 [a]	0	23	0.86 ± 0.02	0.04-3.96
50	0.3	1.0 [a]	0	55	0.91 ± 0.06	0.06-3.96
50	0.4	1.0 [a]	0	90	0.91 ± 0.04	0.07-3.96
50	0	0.5 [b]	0	2	3.82 ± 0.04	0.12-12.99
50	0	1.0 [b]	0	1	4.86 ± 0.03	0.04-18.30
50	0	2.0 [b]	0	2	4.44 ± 0.05	0.07-16.67
50	0	5.0 [b]	0	8	4.05 ± 0.08	0.10-14.86
50	0	10.0 [b]	0	14	4.01 ± 0.07	0.04-12.99
50	0.2	0.5 [b]	0	no settling	1.24 ± 0.04	0.10-3.21
50	0.2	2.0 [b]	0	40	1.23 ± 0.07	0.05-3.21
50	0.2	5.0 [b]	0	55	1.24 ± 0.01	0.12-3.57
50	0.2	10.0 [b]	0	75	1.14 ± 0.03	0.06-3.21
50	0	1.0 [a]	0.01	1	2.24 ± 0.09	0.04-8.94
50	0	1.0 [a]	0.05	1	2.34 ± 0.05	0.04-8.94
50	0	1.0 [a]	0.10	1	2.65 ± 0.09	0.08-8.94
50	0.2	1.0 [a]	0.01	24	0.47 ± 0.05	0.06-4.66
50	0.2	1.0 [a]	0.05	20	0.65 ± 0.02	0.09-4.66
50	0.2	1.0 [a]	0.10	15	0.53 ± 0.08	0.06-4.66

a Initial barium chloride concentration = 0.2 M, initial sodium chromate concentration = 0.2 M

b Initial barium chloride concentration = 1.0 M, initial sodium chromate concentration = 0.2 M

c Required settling time to obtain a solid volume below 20% (± 30 seconds for 0 to 0.1 M QUAT and ± 3 minutes for 0.2 to 0.4 M QUAT). Since this is an interpolated value, more precise standard deviations are not available.

Table 2. Zero-shear relative viscosity of particulate-free QUAT solutions.

Temperature (°C)	[QUAT] (M)	[NaCl] (M)	Relative viscosity
25	0	0	1.0
25	0.001	0	1.3
25	0.005	0	1.6
25	0.010	0	1.8
25	0.020	0	2.0
25	0.030	0	2.2
25	0.040	0	2.4
25	0.050	0	2.5
25	0.100	0	2.9
25	0.200	0	3.9
25	0.300	0	4.8
25	0.400	0	5.6
10	0.100	0	3.5
50	0.100	0	2.2
25	0.200	0.01	3.9
25	0.200	0.05	3.4
25	0.200	0.10	3.2

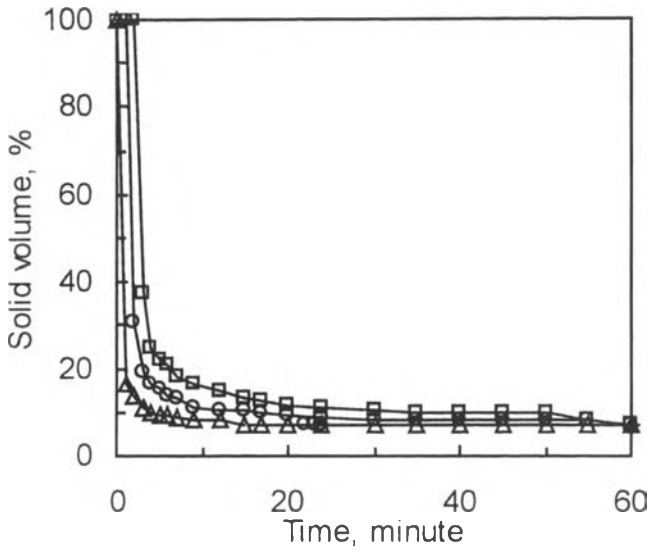

Figure 1. Rate of barium chromate sedimentation in the absence of QUAT at various temperatures (□) 10°C, (○) 25°C, (△) 50°C

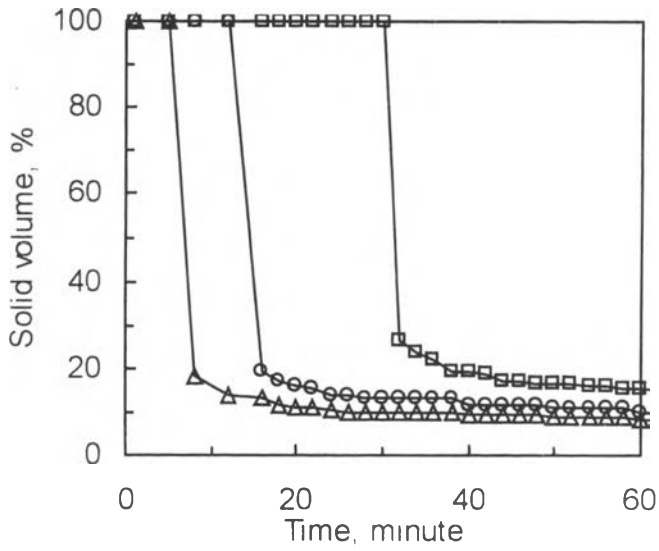

Figure 2. Rate of barium chromate sedimentation in the presence of 0.1 M QUAT at various temperatures (□) 10°C, (○) 25°C, (△) 50°C

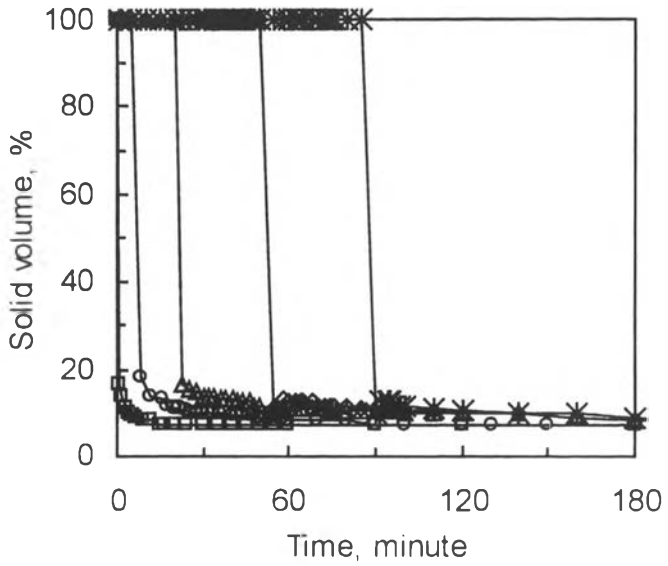

Figure 3. Rate of barium chromate sedimentation at 50°C at various QUAT concentrations. (□) 0 M, (○) 0.1 M, (△) 0.2 M, (◇) 0.3 M, (✳) 0.4 M.

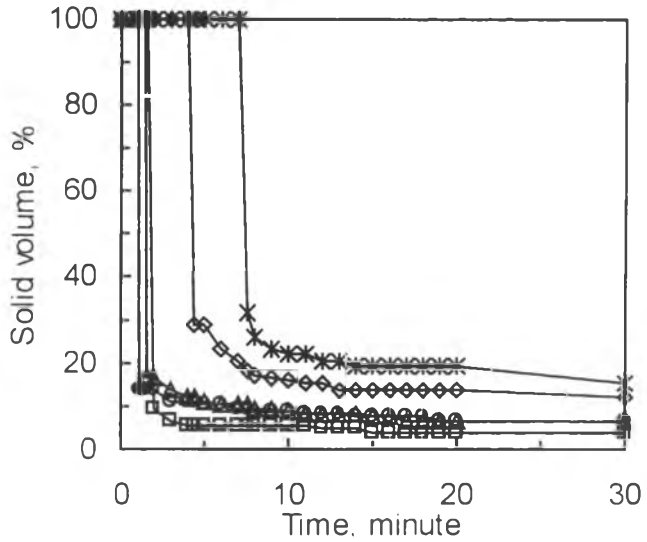

Figure 4. Rate of barium chromate sedimentation in the absence of QUAT at 50°C at various [barium] to [chromate] ratios. (□) 0.5, (○) 1.0, (△) 2.0, (◇) 5.0, (✳) 10.0.

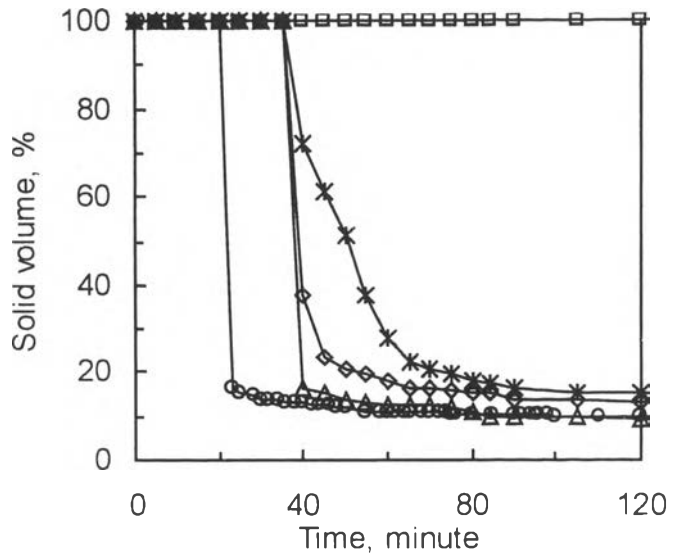

Figure 5. Rate of barium chromate sedimentation in the presence of 0.2 M QUAT at 50°C at various [barium] to [chromate] ratios. (□) 0.5, (○) 1.0, (△) 2.0, (◇) 5.0, (✳) 10.0.

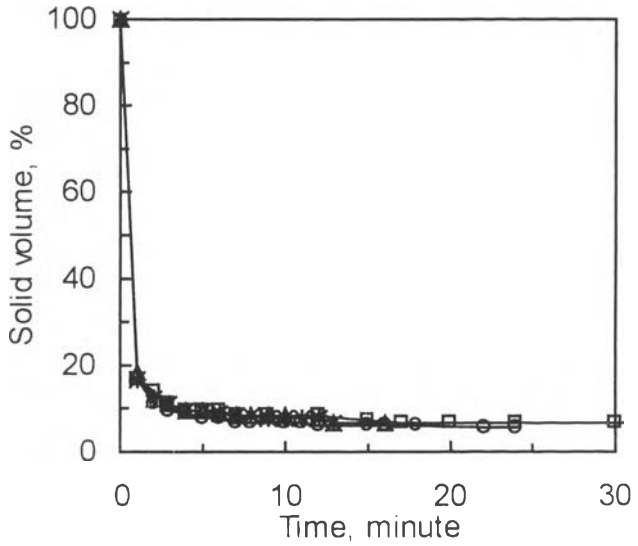

Figure 6. Rate of barium chromate sedimentation in the absence of QUAT at 50°C at various NaCl concentrations. (□) 0 M, (○) 0.01 M, (△) 0.05 M, (✳) 0.10 M NaCl.

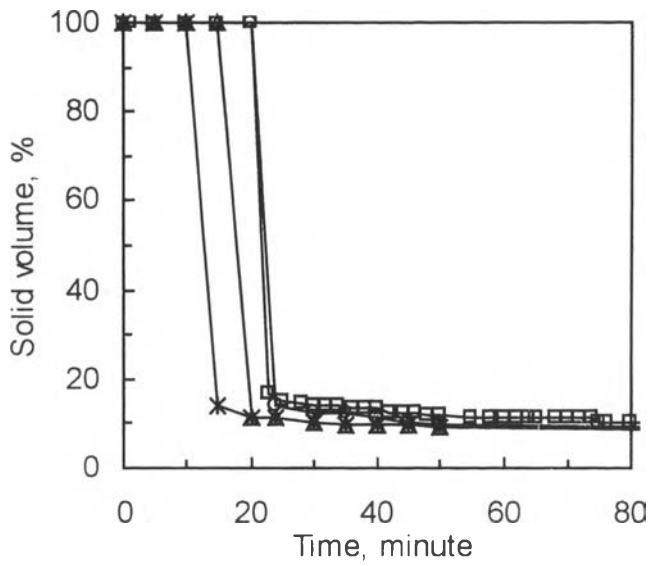

Figure 7. Rate of barium chromate sedimentation in the presence of 0.2 M QUAT at 50°C at various NaCl concentrations. (□) 0 M, (○) 0.01 M, (△) 0.05 M, (✳) 0.10 M NaCl.

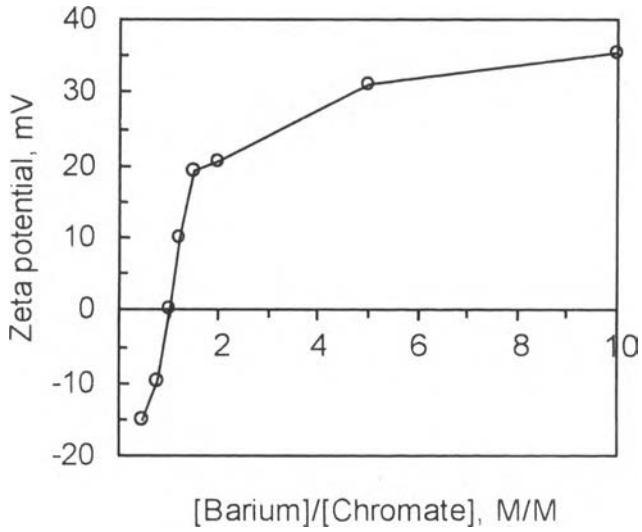

Figure 8. Effect of [barium] to [chromate] ratio on zeta potential of barium chromate particles.

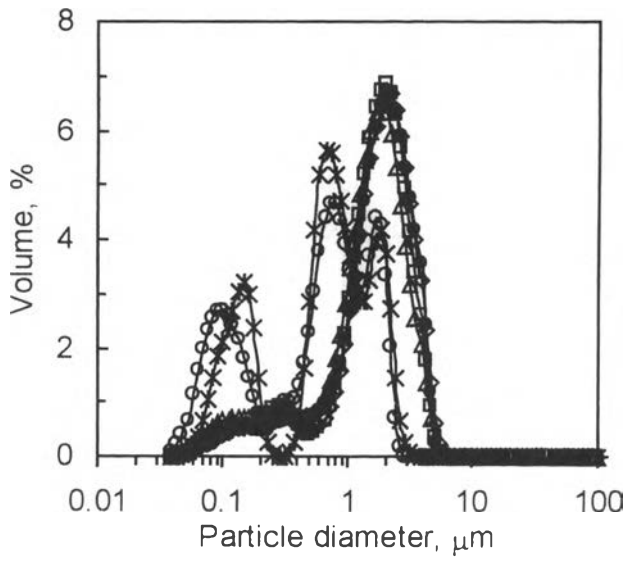

Figure 9. Barium chromate particle size distribution at 50°C at a low QUAT concentration range. (●) 0 mM, (◇) 1 mM, (□) 5mM, (△) 10 mM, (○) 50 mM, (✳) 100 mM.

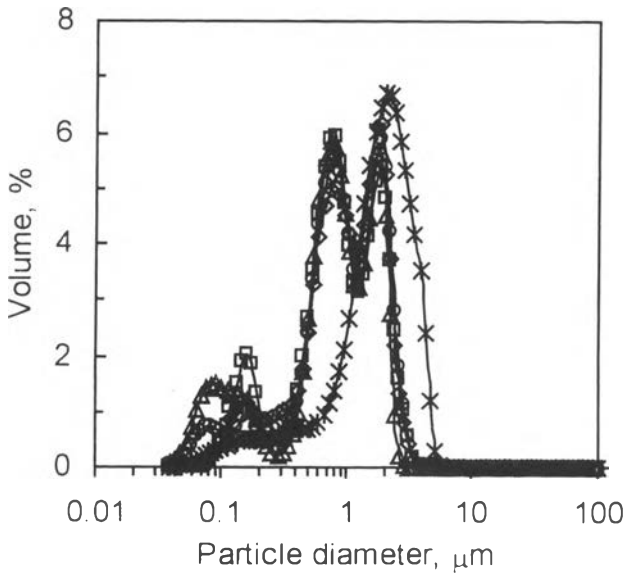

Figure 10. Barium chromate particle size distribution at 50°C at a high QUAT concentration range. (✳) 0 M, (◇) 0.1 M, (□) 0.2 M, (△) 0.3 M, (○) 0.4 M.

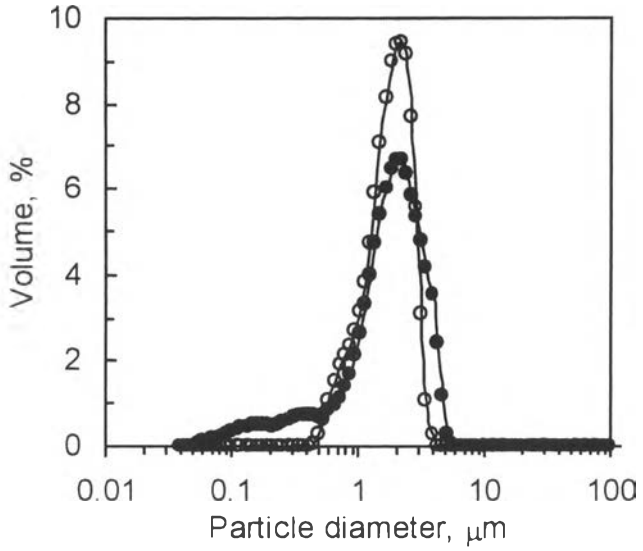

Figure 11. Barium chromate particle size distribution in the absence of QUAT at various temperatures. (○) 10°C, (●) 50°C.

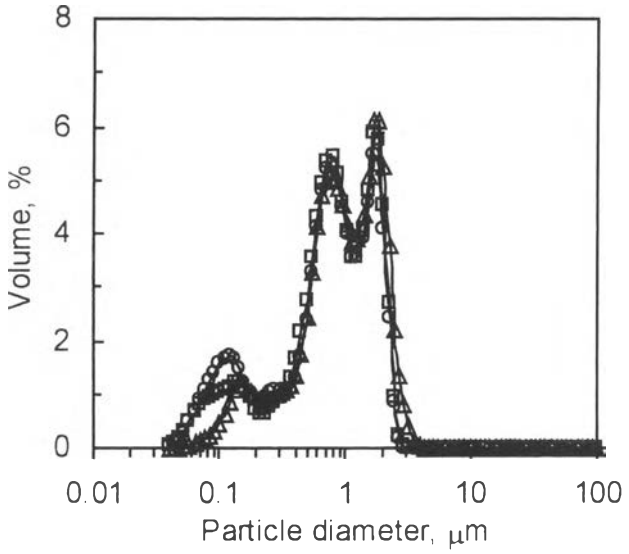

Figure 12 Barium chromate particle size distribution in the presence of 0.1 M QUAT at various temperatures. (□) 10°C, (○) 25°C, (△) 50°C.

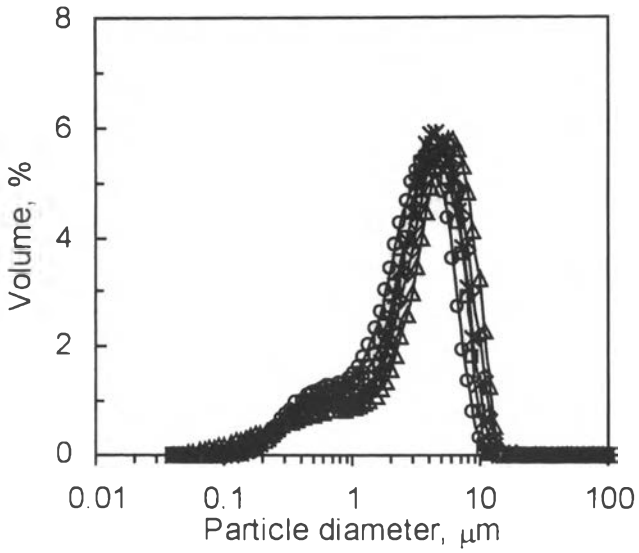

Figure 13. Barium chromate particle size distribution in the absence of QUAT at 50°C at various [barium] to [chromate] ratios. (○) 0.5, (△) 1.0, (◇) 2.0, (✱) 5.0, (□) 10.0.

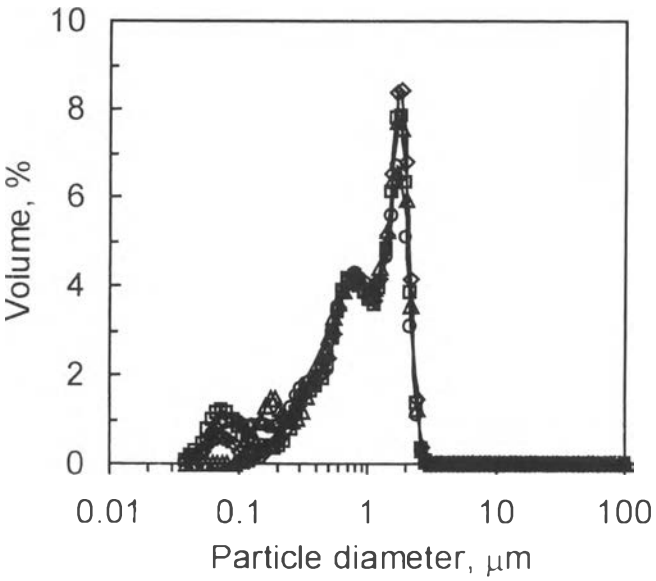

Figure 14. Barium chromate particle size distribution in the presence of 0.2 M QUAT at 50°C at various [barium] to [chromate] ratios. (◇) 0.5, (□) 2.0, (△) 5.0, (○) 10.0.

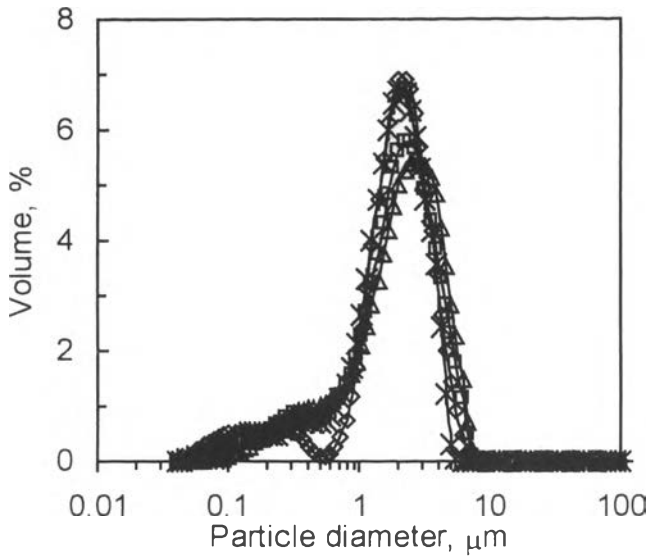

Figure 15. Barium chromate particle size distribution in the absence of QUAT at 50°C at various NaCl concentrations. (✳) 0 M, (◇) 0.01 M, (□) 0.05 M, (△) 0.10 M NaCl.

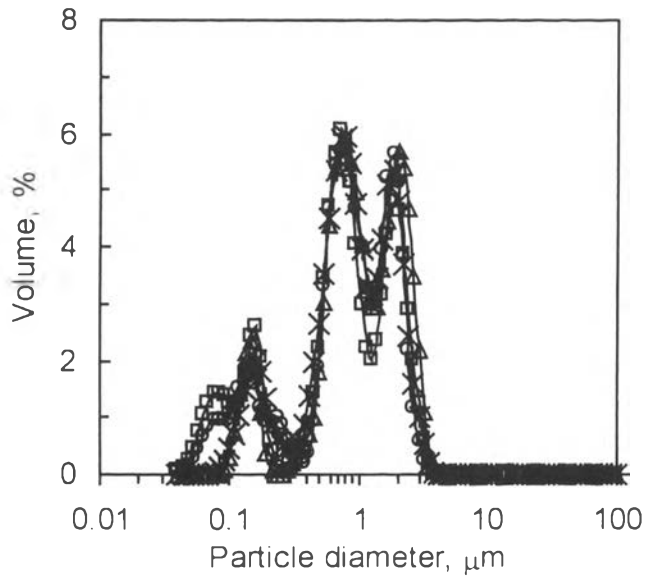

Figure 16. Barium chromate particle size distribution in the presence of 0.2 M QUAT at 50°C at various NaCl concentrations. (✳) 0 M, (□) 0.01 M, (△) 0.05 M, (○) 0.10 M NaCl

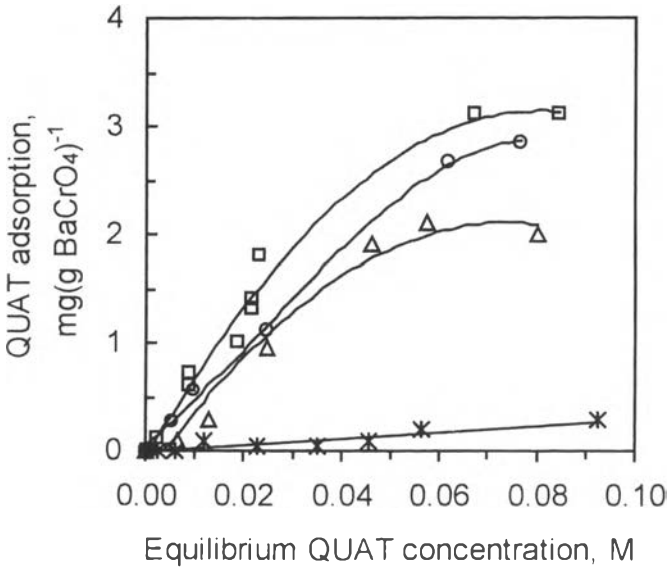

Figure 17. Adsorption isotherm of QUAT on barium chromate in water and in 0.1 M NaCl at various [barium] to [chromate] ratios. (□) 0.5 in water, (△) 1.0 in water, (✳) 1.5 in water, (○) 1.0 in 0.1 M NaCl.

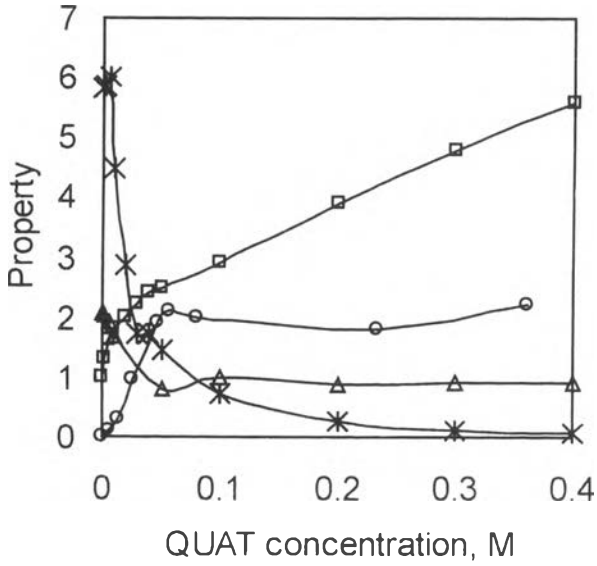

Figure 18. Effect of QUAT concentration on barium chromate sedimentation, barium chromate particle size, polymer adsorption, and relative viscosity of polymer solution. (✳) sedimentation rate (cm/min), (△) average particle diameter (μm), (○) QUAT adsorption ($mg(gBaCrO_4)^{-1}$), (□) relative viscosity

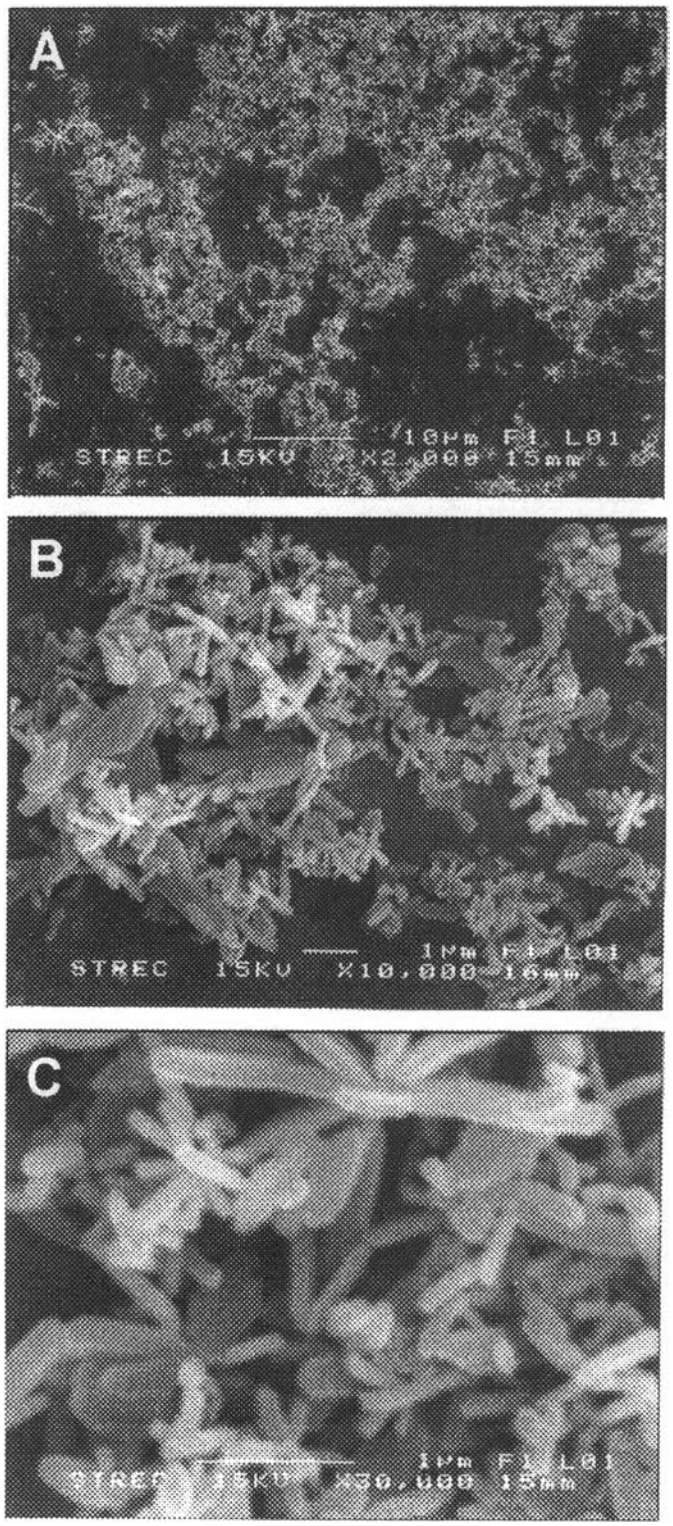

Figure 19. SEM views of barium chromate crystals in the absence of QUAT. Magnification (A) 2000X, (B) 10000X, (C) 30000X.

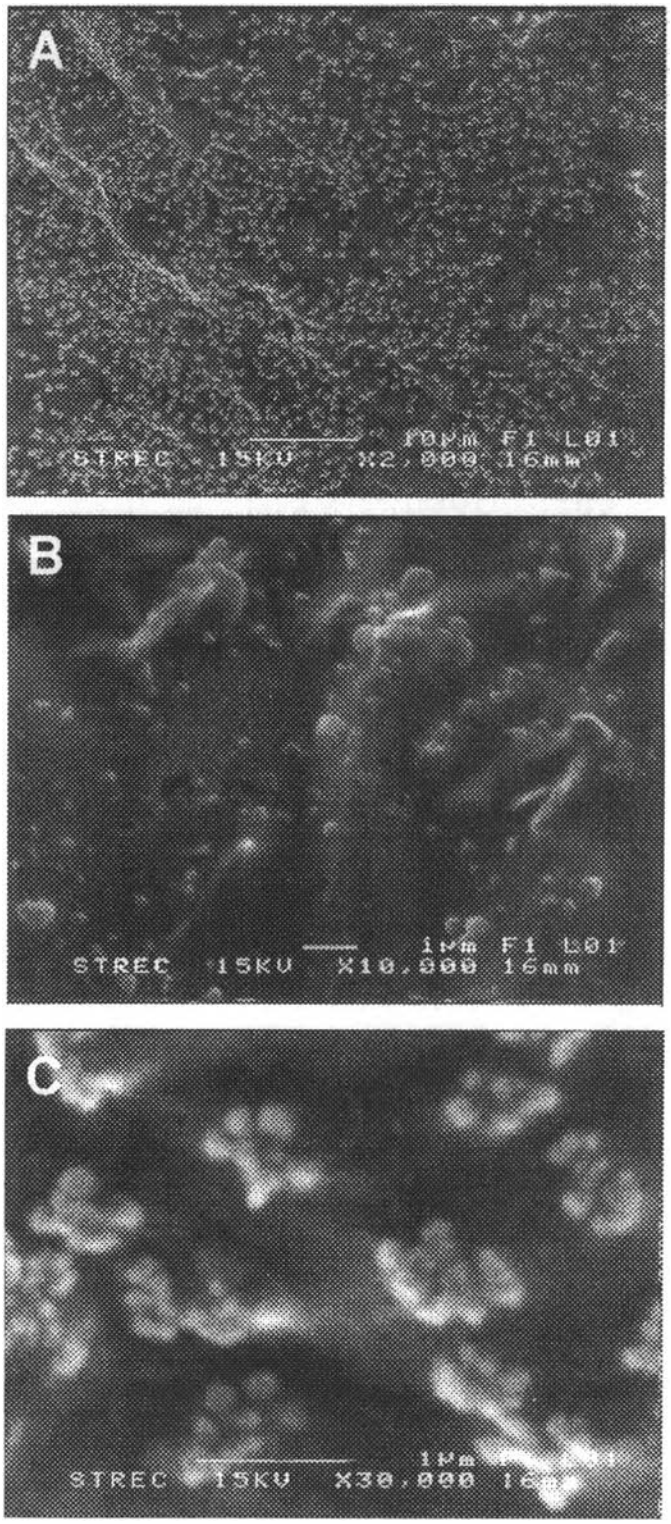

Figure 20. SEM views of barium chromate crystals in the presence of 0.2 M QUAT. Magnification (A) 2000X, (B) 10000X, (C) 30000X.