Clay Minerals (1998) **33**, 103–107

Effect of particle size on the flocculation behaviour of ultra-fine clays in salt solutions

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(*Received 30 July 1996; revised 24 March 1997*)*

ABSTRACT: The Athabasca oil sands deposit in Alberta contains ~5 × 10^9 m^3 of bitumen accessible by surface mining. During bitumen separation from the mined ore, ultra-fine (<300 nm) aluminosilicate clays only a few layers thick (U/F) are mobilized and become dispersed in the process water. In this water containing dissolved salts from natural deposits, U/F are capable of forming thixotropic gels. The consequence of this is the production of large volumes of mature fine tailings (MFT) with a high water holding capacity. For mine planning purposes, the objective of predicting and possibly mitigating MFT formation requires an understanding of the colloidal behaviour of U/F particles in salt solutions. In this work, photon correlation spectroscopy and the deuterium NMR method are used to provide an insight into the U/F floc formation process. These results are correlated with conventional analysis of settling data.

Currently, two commercial plants are operating to produce ~20% of Canada's petroleum requirements from the Athabasca oil sands deposit in Alberta. The hot water extraction process is used to extract the bitumen from this resource. During processing, mechanical dispersion forces cause mobilization of ultra-fine clays into the process water (Kotlyar *et al.*, 1992a, 1993). The resulting slurry is transported to sedimentation ponds where the U/F interact with naturally occurring salts present in the water to form thixotropic gels that ultimately produce mature fine tailings (MFT) with a high water holding capacity.

In previous communications (Kotlyar *et al.*, 1995, 1996) we reported on aggregation of U/F particle mixtures having a broad range of sizes. The work presented here comprises a fundamental study of the colloidal characteristics of narrow particle size fractions.

EXPERIMENTAL

Materials

The bulk MFT sample was supplied by Suncor Inc. All chemicals used in the tests were of analytical grade.

Separation

The U/F separation, de-flocculation and purification protocols are described elsewhere (Kotlyar *et al.*, 1992a,b, 1994). Size-fractions identified as: # 1 (500 *g* for 1 h), # 2 (1500 *g* for 1h), # 3 (4000 *g* for 1 h), # 4 (10000 *g* for 30 min), # 5 (91000 *g* for 30 min) were obtained. The information in parenthesis denotes the centrifugation conditions used. Suspensions with volume concentration (ϕ) of 0.04 of each particle size-fraction were prepared. Dilutions of these stock suspensions were used in all subsequent experiments.

*Issued as NRC Publication Number: 37623

Photon correlation spectroscopy (PCS)

Dynamic light scattering, experiments on dilute suspensions, ϕ = 0.0005, were performed using a Malvern 4700 PCS system with a 15 mW 633 nm He-Ne laser. Measurements were made at a scattering angle of 90° using a 64 channel autocorrelator. In each test the value of the mean hydrodynamic radius, R, was determined 2 min after adding salt solution to the stock suspension of particles.

Morphology and particle size

Samples of clay particles were examined with a Philips CM20 transmission electron microscope (TEM) operated at 200 kV equipped with an Oxford Instruments Link EDX detector and a charge-coupled device (CCD) camera.

Sedimentation experiments

For sedimentation studies, suspensions containing ϕ = 0.0005 clays were allowed to settle in 100 ml cylinders (2.6 cm internal diameter and 19 cm long).

Gelation measurements

The samples for ^2H NMR gelation studies were prepared by replacing the distilled water in the stock suspension with model pond water. The ^2H NMR spectra were recorded with a Bruker MSL 300 spectrometer in a magnetic field of 7.1 Tesla at a frequency of 46.07 Mhz. About 7 wt% ^2H_2O was added to each of the suspensions.

RESULTS

Morphology

The TEM results, Table 1, show that median particle diameters (D) range from 60 to 270 nm. Platelet thickness increased with the planar dimension. Based on the TEM results the corresponding particle number concentrations for each fraction (N), expressed per unit volume of a 1% wt/vol suspension, were calculated. These results are shown in Table 1; as expected, N decreased as particle size increased.

Flocculation in diluted suspensions

The PCS was used to measure the flocculation value (FV) (van Olphen, 1991). The data are presented as a semilogarithmic plot in Fig. 1a. For each size-fraction there is a noticeable increase in the mean hydrodynamic floc radius (R) at a specific salt concentration. This transition point represents the flocculation value (FV). The salt concentrations at the FV increase from 30 mM to 90 mM NaCl for particles of 60 to 270 nm.

The settling behaviour in 100 mM NaCl solution of the ultra-fines fractions with sizes <200 nm (sample ## 3–5) is shown on Fig. 1b. Settling rates increased and the induction time, the period before settling started, decreased with increase in particle size. The results for suspensions containing particles >190 nm (##1,2) are not included because the sediment-supernatant boundary was obscured by haze formation.

Settling tests can be used to evaluate the physical properties of aggregates or flocs. Properties such as size, density and settling rate can be determined

TABLE 1. Particle morphology and properties for nano particle suspensions.

Sample #	Particle diameter (D), nm	Particle thickness nm	$N \times 10^{12}$ per 1 ml of 1% wt/vol	C_{hin}[a]	D^3N	Floc diameter (d), μm	C_{ak}[b]	V_{SA}[c], cm/h	ϕ_{sed}[d]
1	270	8	8.2	0.0012	0.16	n.a	n.a	n.a	n.a.
2	230	6	15.1	0.001	0.18	77.6	112	18.7	0.014
3	190	4	33.3	0.0005	0.23	103.1	206	18.0	0.009
4	160	3	62.5	0.0004	0.26	139.3	392	17.6	0.006
5	60	1	1330	0.0002	0.29	160.0[e]	566[e]	15.2[e]	0.004

[a] the onset of hindered settling concentration, [b] volume of aggregate/volume of clay, [c] settling velocity for single aggregate, [d] concentration of solids in the sediment, [e] reproducibility ± 5% (based on three repetitions). n.a. not available.

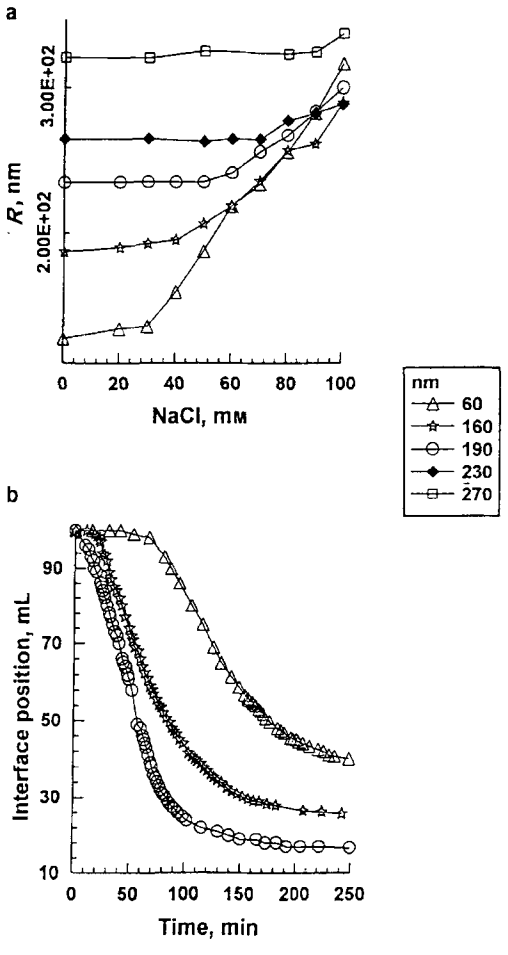

FIG. 1. (a) Mean hydrodynamic radius (R) of flocculated ultra-fine clay as a function of NaCl concentration; (b) settling behaviour of ultra-fine particles in 100 mM NaCl solution.

(Michaels & Bolger, 1962). The method is based on values for the interface subsidence rate (Q, cm/h), calculated from the linear portion of the settling curve. The relationship between Q and the clay volume concentration (ϕ) is used to obtain the Stokes velocity for a single aggregate (V_{SA}) (Richardson & Zaki, 1954):

$$Q = V_{SA}\,\varepsilon^{4.65} \qquad (1)$$

where ε is the liquid volume concentration. If the aggregates have the same density and the aggregate structure is independent of solids concentration in the dilute range eqn. (1) can be rewritten in the form:

$$Q_0^{1/4.65} = V_{SA}^{1/4.65}(1 - C_{AK}\phi) \qquad (2)$$

where C_{AK} is the ratio of the aggregate volume concentration (ϕ_A) to (ϕ).

Experimental determination of the structural parameters of flocs involved the following steps: (a) each particle size-fraction was suspended in NaCl solutions covering a range of clay concentrations in the 'dilute' region. It was noticed that the lowest concentration of clays at which a well-defined interface occurs, i.e. the onset of hindered settling (C_{hin}), increased with increase in particle size, Table 1. (b) The interface positions are plotted *vs.* time; typically these plots are linear. (c) Plots of $Q^{1/4.65}$ against the corresponding values of ϕ for each size-fraction are also linear. From the ordinate and the abscissa intercepts of these lines, V_{SA} and C_{AK} may be determined. The average value of the equivalent floc diameter, d (μm), is calculated from the equation:

$$V_{SA} = 0.349(d)^2/C_{AK} \qquad (3)$$

The results of these calculations are summarized in Table 1. Comparison of fractions 2 to 5, shows floc diameter increasing as the primary particle size decreases. The water to clay ratio (C_{AK}) increases with decrease in particle size. The V_{SA} values range from 15.2 cm/h (# 5) to 18.7 cm/h (# 2).

Observation of settling behaviour shows that change in interface position eventually becomes extremely slow. Equivalent final volumes, expressed as volume concentration of solids in the sediment (ϕ_{sed}), ranged from 0.014 to 0.004 for the coarsest to the finest size-fractions, see Table 1.

Concentrated suspensions

A ^2H NMR method (Ripmeester *et al.*, 1993) was used to monitor the sol-gel transition in concentrated (ϕ = 0.012) suspensions. This method relies on measurement of deuterium peak splitting as a function of time. A gelation index (I, %), calculated from the normalized change in splitting, reflects a change in particle mobility caused by cluster formation. Values of I range between 0%, for a sol to 100% for a stiff gel.

For the fraction containing particles <200 nm, suspended in 100 mM NaCl solution, gelation was instantaneous and the results are not shown. The dependence of gelation index on time for the

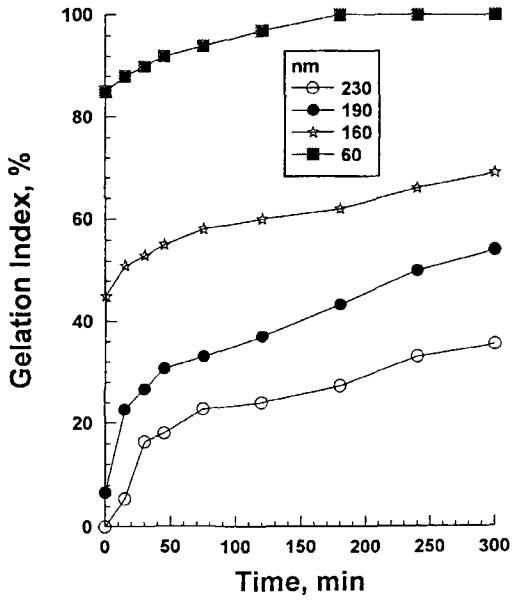

FIG. 2. Gelation behaviour of flocculated ultra-fine clay in 20 mM NaCl solution.

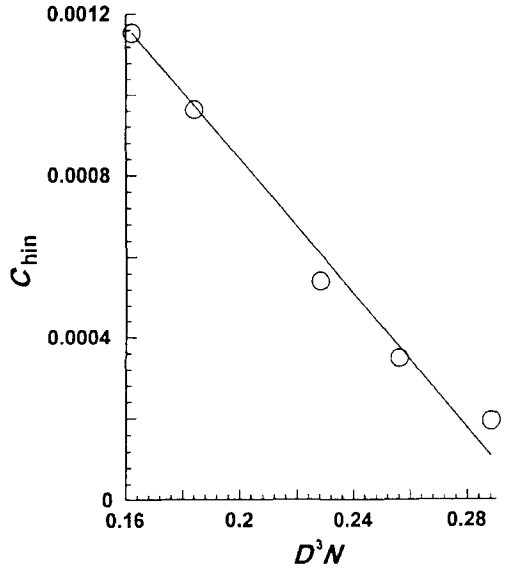

FIG. 3. The onset of hindered settling concentration (C_{hin}) *vs.* the product D^3N.

different size-fractions in 20 mM NaCl solution is given on Fig. 2. At the end of the observation period the coarsest fraction showed some thickening, (I = 37%), whereas the finest fraction formed a stiff gel (I = 100%) after only 4 h. In the latter case, more than 80% of the mobility was lost before the tubes were inserted into the magnet.

DISCUSSION

Evaluation of the relative stability of a sol to flocculation is typically achieved through electrolyte addition to determine the flocculation value (van Olphen, 1991). Our results show that for particles in the range 60 to 270 nm, the propensity to flocculate decreases with increase in particle size, that is small particles flocculate more rapidly (Fig. 1a). This behaviour may result from the low absolute values of the repulsive potential for small particles (van Olphen, 1991).

Flocs are characterized by a loose porous structure (Mandelbrot, 1982). During the initial stage of flocculation primary particles form microflocs, such as doublets, triplets, etc. As the process continues these microflocs group into larger aggregates or macroflocs. Within the flocs, part of the liquid is immobilized, effectively controlling their density and porosity.

It is well known that floc structure is dependent on salt concentration (Weitz *et al.*, 1991). In the presence of high salt levels more voluminous flocs are formed by diffusion limited aggregation. Our results show that floc structure may also be dependent on particle size or particle number concentration.

The results in Table 1 demonstrate that smaller particles form larger flocs than the coarser sizes. For a given volume concentration the particle number concentration increases with decrease in particle size. If the average number of microflocs is related to the primary particle number concentration and size by means of the product D^3N (Tambo, 1991) then the number of microflocs must increase with decrease in particle size (Table 1). As the number of microflocs per unit volume increases the probability that they will collide and adhere to each other is greater.

Larger flocs are more voluminous, i.e. they have higher C_{AK} values. Such flocs display an appreciable delay in sedimentation as denoted by the long

induction periods for the finer size-fractions on Fig. 1b. As floc structure becomes more voluminous the concentration of particles required for hindered settling is less (Table 1). In other words, for hindered settling to occur, a 'critical concentration' of solids (C_{hin}) is needed to provide an adequate number of microflocs. It is noteworthy that the concentration at which suspensions start to exhibit hindered settling correlates nearly linearly with the product D^3N, see Fig. 3. This suggests that C_{hin} may be a useful relative parameter for characterization of flocculated systems.

For all particle sizes the flocs settle until a space-filling gel forms. The voluminous flocs, formed by the smallest particles, produce the largest final sediment volume, lowest ϕ_{sed}, see Table I.

For concentrated suspensions, the original particle concentration is of the same order of magnitude as the final concentrations in the sediments produced from dilute suspensions by flocculation with electrolyte. In these circumstances, close approaches between particles occur almost immediately. The effect of instantaneous thickening decreases with increase in particle size but increases with salt concentration.

CONCLUSIONS

In dilute suspensions, smaller U/F particles lose their colloidal stability faster than coarser fractions. Aggregation of coarser particles produces smaller, more compact flocs compared to the voluminous flocs formed from finer particles. The corollary to this observation is that finer solids flocculated from diluted suspensions produce a greater final sediment volume. There is a correlation between the physical properties of flocs such as size, density, settling rate and final volume and the onset of hindered settling for each fraction. Flocculation behaviour of concentrated dispersions is found to be salt and particle size dependent.

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