Chemical Engineering Journal 162 (2010) 457–465

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

The pivotal role of polymer adsorption and flocculation conditions on dewaterability of talcaceous dispersions

Kai Ying Yeap, Jonas Addai-Mensah*, David A. Beattie

Ian Wark Research Institute, Australian Research Council Special Research Centre, University of South Australia, Mawson Lakes Campus, Mawson Lakes, Adelaide, SA 5095, Australia

ARTICLE INFO

Article history:
Received 11 December 2009
Received in revised form 11 April 2010
Accepted 12 April 2010

Keywords:
Fine talc particles
Polyethylene oxide adsorption
Flocculation
Dewatering
Sediment consolidation

ABSTRACT

In this study, the links between interfacial chemistry, polyethylene oxide (PEO) flocculant adsorption behaviour, orthokinetic flocculation and dewatering behaviour of talc mineral dispersion have been investigated. The effect of Mg(II) ions, suspension conditioning time, solid loading, PEO dosage and shear was probed. Unflocculated dispersion of weakly charged, polydispersed talc particles at pH 7.5 displayed very poor settling rate but good sediment consolidation (∼47 wt.% solid). PEO polymer adsorption rate and density were greater at higher than lower Mg(II) ion concentration. The adsorption propensity also decreased with increasing suspension conditioning time. An inverse correlation was observed between PEO adsorption rate/affinity and settling rate where slower adsorption kinetics led to larger and faster settling flocs. At equivalent PEO dosages (e.g., 200 g polymer t^{-1} solid), 8 wt.% solid dispersion solid produced both superior supernatant clarity and greater sediment consolidation than the markedly faster settling, dilute (2 and 4 wt.% solid) suspensions. The influence of Mg(II) ions and conditioning time on settling rate was PEO dosage dependent, however, these factors had no noticeable effect on sediment consolidation. Dramatic enhancement of flocculated sediment compaction (from 38 to 52 ± 2 wt.% solid) was achieved in secondary dewatering under moderate shear. The results provide useful fundamental knowledge of polymer adsorption rate, adsorption affinity and interparticle bridging behaviour which underpin the flocculation and dewatering of talcaceous clay suspensions for significant improvement.

1. Introduction

Water is critically essential for the existence and survival of the mining and minerals industry with approximately 20% of global water used by the sector. Currently, several Australian and overseas companies in the sector are limiting their operations due to acute water shortages, and this curtailed production leads to concomitant loss of several millions of dollars annually [1]. Nevertheless, substantial amount of recyclable water is trapped in voluminous clay mineral waste tailings generated at low to moderate solid loading by the mining and minerals industry. Needless to say, frugal water use and effective waste tailings management are important issues for sustainable development of the sector.

In hydrometallurgical operations, fine clay gangue (i.e., talc, kaolinite, smectite, muscovite chlorite, etc.), occurring with valuable minerals (e.g., gold, copper, nickel, etc.), invariably accumulate in the plant circuit as waste tailings. Such clay tailings are periodically delivered alone or with other minerals at dilute concentrations (e.g., <8 wt.% solid) to the thickeners for flocculation and dewatering. Thereafter, the resulting sediments are impounded in dams over long time for further consolidation and release of process water [2]. Of interest to the present work is the dewaterability of dilute dispersions containing fine talc particles. A 2:1 layered phyllosilicate mineral with $Mg_3(Si_4O_{10}(OH)_2)$ ideal chemical structure, the unit cell of talc comprises an octahedral brucite (Mg–OH) sheet sandwiched between two tetrahedral siloxane (Si–O–Si) sheets. The elementary particles which tend to be platy in morphology are bounded by hydrophobic Si–O–Si basal faces (>90% of the total surface area) and edge faces comprising pH-sensitive, hydrophilic SiOH and MgOH groups [3]. Despite its predominantly hydrophobic character (contact angle > 80°), fine (e.g., <10 μm) talc particles may display strong colloidal stability in aqueous dispersions at low to moderate ionic strength and pH > 5, reflecting poor dewatering (settling rate, supernatant clarity and consolidation) behaviour.

Whilst clay mineral particles' anisotropic crystal face charging character and cognate card house and banding formation are readily amenable to rapid flocculation and fast settling behaviour, the low compaction rate of the resulting flocculated sediments continue to pose intractable challenges [4]. For instance, dewatering of dilute kaolinite and smectite clay suspensions using conventional flocculants (e.g., polyacrylamide, PAM) at dosages in the range 50–500 g t^{-1} solid typically leads to good settling rates

---

* Corresponding author. Tel.: +61 8 83023673; fax: +61 8 83023683.
E-mail address: Jonas.addai-mensah@unisa.edu.au (J. Addai-Mensah).

1385-8947/$ – see front matter. Crown Copyright © 2010 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.04.021

(>10 m h^{-1}) but low solid sediment content (e.g., 20–35 wt.%) [5]. The incompressible flocs which are formed through hydrophilic PAM polymer flocculation mechanisms are generally not conducive to rapid release and drainage of trapped intra-floccule pore water under thickener raking and picket actions, and at atmospheric and tailings dam hydrostatic pressure loadings. Consolidation of the flocculated clay sediments can be perennially slow, taking up to 20 years for pulp solid loading increase from, say, 30–60 wt.%. This poor secondary dewatering behaviour causes significant long-term dam impoundment problems (e.g., voluminous space requirement and process water loss by evaporation). Thus, to date, the greatest challenge facing step change enhancement of clay tailings dewatering resides in the rapid consolidation rather than the settling behaviour.

Recent studies involving non-conventional, shear-sensitive polyethylene oxide (PEO) flocculant-assisted dewatering of smectite and kaolinite showed that for clay mineral dispersions, it is possible to produce fast settling behaviour and more compact (low moisture) sediment beds [4]. The PEO-flocculated clay sediments densified dramatically under moderate shear rates (10–40 s^{-1}) during secondary dewatering to form ‘spadeable’ pulps with solid loadings up to 48 wt.%. Similar use of PEO to facilitate markedly enhanced secondary dewatering of talcaceous dispersions is of interest. In addition, magnesium ions which may leach from talc particles if not already present in recycled process water, can impact on pulp particle interfacial chemistry and particle interactions, either exerting a positive or negative influence on dewaterability [6,7].

Other studies showed that the rates of polymeric flocculant adsorption and reconformation onto clay particles may be prudently controlled to produce a more effective particle bridging flocculation mechanism for better dewatering performance [8,9]. For instance, studies by McFarlane et al. [10] demonstrated that flocculant chemistry and structures which lead to relatively slower rate of polymer adsorption onto kaolinite and smectite clay particles, resulted in larger and faster settling flocs. Rapid polymer adsorption, on the other hand, leads to ineffective polymer distribution, flatter interfacial conformation and non-homogeneous bridging of particles, and hence, smaller and slower settling flocs resulted. Despite the persistence of challenges faced to dramatically improve the consolidation behaviour of talcaceous mineral dispersions, only a very limited number of studies dedicated to the subject has been reported [3,6]. Judicious extrapolation of the above findings from other clay mineral (e.g., kaolinite and Na-exchanged smectite) dispersions is yet to produce meaningful outcomes, warranting further studies [4,11,12].

Polymeric flocculant adsorption at mineral particle–solution interface may be driven by several factors which relate to Gibbs free energy of adsorption ($\Delta G^{\circ}_{\text{ads}}$). For instance $\Delta G^{\circ}_{\text{ads}}$ may be considered as the sum of the standard free energies of chemical, electrostatic, hydrogen bonding, hydrophobic and van der Waals interactions involved in the adsorption process [13,14].

More than one of the five terms may be operative under a given set of conditions. The dominant mechanism(s) will be determined, invariably, by the polymer structure and functionality, solution speciation and mineral surface specific chemistry. It is pertinent to note that due to isomorphous lattice substitution, specific adsorption of impurities and other crystal defects, talc particles from different sources or different faces of same or similar particles may display subtle to significant differences in surface chemistry, with a striking impact on their polymer adsorption behaviour. A non-face specific average adsorption free energy, however, may be estimated via polymeric flocculant adsorption isotherms studies [8,15]:

$$\Delta G^{\circ}_{\text{ads}} = -RT \ln K \qquad (1)$$

where R is the general gas constant, T is the absolute temperature and K is the adsorption equilibrium constant. Estimation of $\Delta G^{\circ}_{\text{ads}}$ from all of the adsorption isotherms was made in this work.

The main aim of the present work was to investigate the influential role of PEO adsorption behaviour and flocculation conditions on orthokinetic flocculation and dewaterability of talc clay suspension. Conducive conditions for orthokinetic flocculation and floc restructuring were explored and linked to dewatering performance for improved settling and consolidation behaviour under industrially relevant conditions. As an important outcome, process water recovery from talcaceous mineral waste tails for recycle will be greatly enhanced.

2. Experimental methods

2.1. Materials

Pure, polydispersed, crystalline talc particles (>99% purity, Merck, Australia) were used in the present work. The particle size distribution determined using laser diffraction was in the range of 0.5–100 μm, with 10th, 50th and 90th percentile sizes of 5, 15 and 52 μm, respectively. X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Energy Dispersive X-ray (EDX) analysis confirmed the high particle surface and bulk purity and crystallinity of the sample with trace (<1%) Fe, Al and C impurities. Non-ionic PEO polymer with molecular weight of 8×10^6 Da were used as a flocculant whilst $Mg(NO_3)_2$ salt was employed as a coagulant. Fresh 0.025 wt.% polymeric flocculant working solution was prepared by diluting a previously prepared 0.325 wt.% stock solution stored at room temperature and used within 3 days. Both the polymer solution and talc suspension pH were adjusted with small additions of 1.0 M KOH and 1.0 M HNO_3 solutions. Analytical grade reagents and high purity Milli-Q water (surface tension of 72.8 mN m^{-1} at 22 °C and a specific conductivity <0.5 μS cm^{-1} at pH 5.6) were used. All aqueous solutions used were maintained at pH 7.5 and 22 °C, with a 10^{-3} M KNO_3 background electrolyte, unless otherwise stated. Where the effect of Mg(II) ions used as a coagulant was investigated, a known mass of high purity (>99.9%) $Mg(NO_3)_2$ was dissolved in the 10^{-3} M KNO_3 background electrolyte. Particle zeta potential, PEO adsorption and settling rates measurements were carried out on 8 wt.% agitated suspensions of talc particles dispersed in 10^{-3} M KNO_3 with 0, 10^{-3}, and 10^{-2} M $Mg(NO_3)_2$ concentration at 22 °C.

2.2. Particle zeta potential

Talc particle–aqueous phase interfacial chemistry was characterized by electrokinetic zeta potential measurements. Particle zeta potential (ζ) as a function of pH was determined from dynamic mobility measurement using an Acoustosizer (Colloidal Dynamics, Australia). Background correction was applied to the measurement of zeta potential at different electrolyte concentrations.

2.3. Adsorption experiments

Polyethylene oxide adsorption as a function of time and equilibrium concentration was determined by batch depletion techniques [16]. In all cases, the actual concentration of PEO was analytically determined by using tannic acid complexation method [16], facilitated by presciently constructed calibration curves. For kinetic experiments performed in the manner of McFarlane et al. [10], flocculant dosage of 500 g polymer t^{-1} solid was added to 500 cm^3 agitated talc dispersions and 5 cm^3 aliquots were removed at recorded time intervals within 120 s. The liquor was filtered thorough syringe filter (0.45 μm) and the residual polymer concentration was determined. To determine the equilibrium polymer concentration following adsorption, a known concentration of the flocculant was added to 10 cm^3 of talc dispersion of 2.4 wt.% solid in 20 cm^3 vials and mixed for 2 h by rotary mixer. After centrifugation at 11000 rpm for 10 min to remove the residual solid, supernatant was removed for the determination of solution equilibrium polymer concentration.

To elucidate the adsorption mechanism, the adsorbed polymer density and the equilibrium conditions, the isotherms were fitted to the commonly employed monolayer or simple adsorption models. In the present work, the models used included those of Langmuir and Freundlich [9,14]. The Langmuir model which may account for molecular adsorption at homogeneous surfaces is expressed as:

$$\theta = \frac{\Gamma_{\mathrm{ads}}}{\Gamma^{m}_{\mathrm{ads}}} = \frac{KC_{\mathrm{eq}}}{55.5 + KC_{\mathrm{eq}}} = \frac{bC_{\mathrm{eq}}}{1 + bC_{\mathrm{eq}}} \tag{2}$$

where Γ_{ads} is the adsorbed amount (mg m^{-2}), $\Gamma^{\mathrm{m}}_{\mathrm{ads}}$ is the plateau adsorbed amount (mg m^{-2}), C_{eq} is the polymer equilibrium solution concentration (mol dm^{-3}), K is the adsorption equilibrium constant and b is the Langmuir affinity constant (dm^3 mol^{-1}). $\Gamma^{\mathrm{m}}_{\mathrm{ads}}$ and b are determined by linearized model (Eq. (3)) fitting to the adsorption data, where K is estimated as $b = K/55.5$, with 55.5 mol dm^{-3} being the concentration of the solvent (water), for dilute solutions. The Langmuir equilibrium constant is, thus, an indication of the affinity of a polymer for surface with homogeneous adsorption sites.

The Freundlich isotherm which better suits molecular adsorption onto heterogeneous surfaces may be quantified by the following equation:

$$\Gamma_{\mathrm{abs}} = k_{\mathrm{F}} C_{\mathrm{eq}}^{1/n_{\mathrm{F}}} \tag{3}$$

where k_{F} and n_{F} are empirical constants, with k_{F} as the absorbent capacity, and n_{F} the adsorption affinity constant [14,17]. The larger the value of n_{F}, the greater the adsorption affinity.

2.4. Suspension preparation

Talc dispersion of 8 wt.% solid was prepared by thoroughly mixing a known mass of dry solid talc powder and a known volume of 10^{-3} M KNO_3 solution with an overhead stirrer at an agitation rate of 500 rpm for 1 or 18 h. Talc dispersion of 2 and 4 wt.% solid were prepared by carefully diluting known masses of 8 wt.% talc dispersion (conditioned for 1 h) with known amount of 10^{-3} M KNO_3 solution.

2.5. Dewatering tests

For isothermal, batch flocculation and settling behaviour investigation, known volumes of 0.025 wt.% PEO-flocculant solution was added to 500 cm^3 of talc suspension within 5 s using a syringe. The suspension was then well mixed for 10 s at an agitation rate of 300 rpm. Thereafter, the initial settling rate of the flocculated suspension (and also that of the pristine slurry with no polymer) was determined by recording the time taken for the "mud line" (solid–liquid interface) in the 500 cm^3 graduated glass cylinder to fall between 450 and 350 cm^3 marks. The sediment was then allowed to stand quiescently for a period of 24 h after which the consolidated bed volume was recorded. The final sediment bed solid content of a representative sample was gravimetrically measured using infrared moisture balance. To examine the effect of shear on sediment consolidation, the supernatant was then decanted and further agitation at 100 rpm was applied to the sediment pulp for 10 min, using a four-blade impeller. After further 24 h quiescence, the final consolidated bed volume was recorded and solid content was measured. All tests were done at 22.0 ± 0.1 °C and were replicated at least 3 times. The error bars reported in this work were estimated from pure errors at 95% confidence interval (CI).

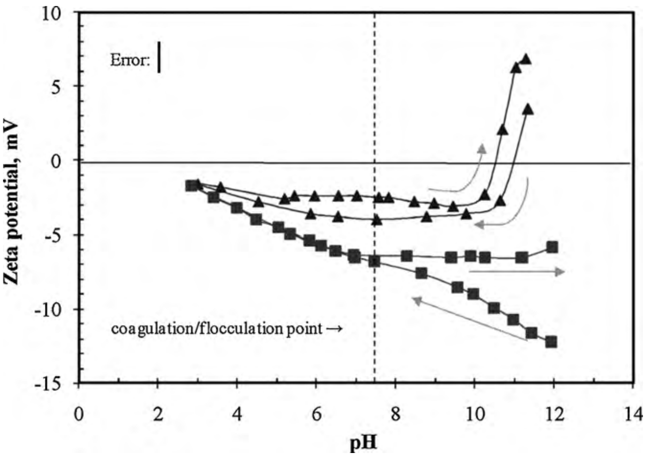

Fig. 1. Zeta potential of unflocculated 8 wt.% solid talc particles dispersion in 10^{-3} M KNO_3 solution as a function of pH and Mg(II) ion concentration. (▲ = 10^{-2} M and ■ = 0 M Mg(II)). pH was first altered from 11.5 to 3 and returned to 11.5 (as indicated by the arrows).

2.6. Supernatant clarity measurement

To determine the supernatant clarity of flocculated suspension, 20 cm^3 of supernatant was withdrawn using a syringe at a fixed distance above the sediment mudline 20 min after sedimentation and evaporated to dryness in an oven operating at 105 °C. The suspension turbidity is calculated as bone dry mass of talc in unit volume of suspension removed.

3. Results

3.1. Zeta potential of unflocculated talc particles

Particle zeta potential as a function of pH of 8 wt.% solid agitated dispersion determined from dynamic mobility in the background of 10^{-3} M KNO_3 and under different Mg(II) ions concentration is shown in Fig. 1. The decrease of zeta potential with decreasing pH from 12 to 2.5, resulting from talc particle surface protonation, indicated an isoelectric point (iep) around pH 2, consistent with previously reported iep values [3,18]. The zeta potential measured from pH 2.5 to 12, however, followed a different bifurcation path.

The presence of 10^{-2} M Mg(II) ions led to a marked reduction in the magnitude of the zeta potential, particularly at higher pH (>7). The zeta potentials for 10^{-3} M Mg(II) (not shown to avoid congestion of data) also laid mid way between those of 10^{-2} and 0 M Mg(II) ions. At pH ∼ 10 where Mg(II) ions begin to hydrolyse into specifically adsorbing $Mg(OH)^+$ complex, complete particle charge reversal, reflecting negative to positive zeta potential charge was observed at 10^{-2} M Mg(II). This irreversible, pH-history dependent behaviour displayed for no added Mg(II) ion dispersion is due to inherent leaching of Mg^{2+} ions from the talc particles at low pH (<5), accompanied by subsequent specific adsorption of Mg(II) hydrolysis products formed at high pH [3,19]. For the dispersion containing pre-added 10^{-2} M Mg(II) ions, the leached Mg(II) ions effect on the electrokinetic potential was quite subtle compared with the case of no Mg(II) ions pre-addition.

3.2. Particle specific area and supernatant quality

The BET surface area measurement of talc particles in aging, agitated dispersion indicated that the particle surface area increased

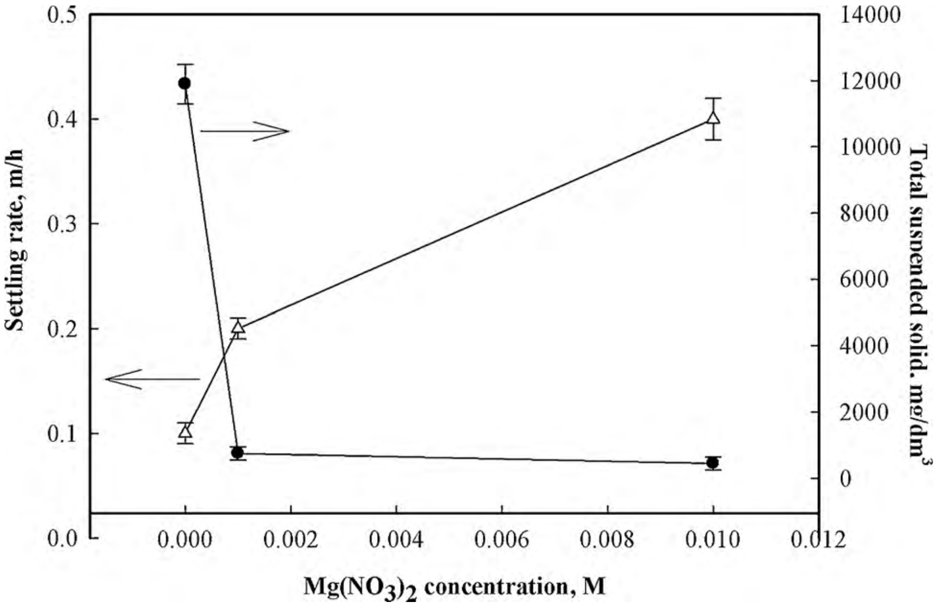

Fig. 2. Settling rate and supernatant clarity of unflocculated 8 wt.% solid talc dispersions as a function of Mg(II) ion concentrations at pH 7.5 and 10^{-3} M KNO_3.

from 3.0 to $3.4 \pm 0.1\ m^2\ g^{-1}$ after 18 h conditioning. The small but noticeable increase (≈10%) in surface area is consistent with shear-induced delamination of the sheet-like talc particles. Inductively coupled plasma mass spectroscopy (ICP-MS) analysis showed that leached Mg(II) ion concentrations in the supernatant were 10^{-5} and 2×10^{-4} M after 1 and 18 h suspension homogenization (conditioning), respectively, consistent with previous studies [3,19,20]. The concentrations of Si, Fe and Ca ions leached into solution were negligibly small (<10^{-6} M).

3.3. Settling and consolidation behaviour of unflocculated dispersion

Despite the low magnitude zeta potential (∼−7 mV) at pH 7.5 and 10^{-3} M KNO_3, pristine talc particles in 2–8 wt.% solid suspension, experienced a fairly high colloid stability. Without Mg(II) salt or flocculant addition, the suspension produced very low settling rate (<$0.1\ m\ h^{-1}$) and poor supernatant clarity (>12,000 $mg\ dm^{-3}$). The anisotropic, basal and edge faces charge character of the platy talc particles commonly lead to a variety of particle packing modes [21,22]. The main two modes result from edge–basal face (house of cards) and basal–basal face (band structure) particle interactions. These may lead to slow settling behaviour without flocculation aids, consistent with the current observation. Upon Mg(II) salt addition, coagulation which resulted in marginally improved dispersion clarification behaviour was achieved (Fig. 2). As the concentration of Mg(II) ions increased to 10^{-2} M, the settling rate increased from $0.1\ m\ h^{-1}$ to $0.4\ m\ h^{-1}$. Under higher ionic strength screening effect, the magnitude of the zeta potential was reduced (−3 mV), leading to coagulation presumably through a secondary minimum aggregation process. The aggregated particles settled faster in accordance with Stokes' Law, accompanied by greatly improved supernatant clarity.

Despite the poor suspension settling behaviour, the sediment bed formed after 24 h without the addition of Mg(II) ions or flocculant displayed relatively high consolidation behaviour (∼47 wt.% solid). This level of sediment consolidation is markedly greater than the 20–25 wt.% solid commonly observed for other mineral clay pulps (e.g., kaolinite and smectite) under similar conditions [5,11]. The strong consolidation ability of the pristine slurry, albeit preceded by slow settling rate, may be partly due to the hydrophobic character of the basal faces of the talc particles by which attractive, long-range hydrophobic forces may prevail in the presence of dissolved nano-bubbles to facilitate compact packing [23,24]. Although the sediment consolidation showed a noticeable decrease with increasing Mg(II) ion concentration, the decrease is statistically insignificant given the magnitude of the 95% CI error observed. This may be ascribed to deleterious effect of the adsorbed, hydrated Mg(II) ions on talc particles basal–edge face interactions and hence, aggregates equilibrium structure. At pH 7.5, hydrated Mg^{2+} ions' adsorption in the diffuse electrical double layer region around the otherwise hydrophobic talc particles will render the aggregates more hydrophilic, leading to increased intra-aggregate water content.

3.4. Adsorption kinetics

PEO adsorption rate showed a strong Mg(II) concentration and suspension conditioning time dependent for talc dispersions at pH 7.5 (Fig. 3). In general, the polymer adsorption was faster at higher supernatant Mg(II) ion concentration. Longer suspension conditioning time led to lower adsorption rate. It appears that where rapid adsorption occurred, a greater proportion of polymer adsorbed to the inner floc surfaces within the agglomerating floc, whilst the slower adsorbing polymer profiles more closely reflect adsorption at the exterior floc surface [10,25,26]. The fit of the experimental data to empirical zero-, first- and second-order adsorption kinetic models by least square regression analysis indicated that the initial adsorption behaviour was best represented by a first-order rate law (Eq. (4)). This suggests that the polymer molecules adsorbed at a rate proportional to their concentration in solution and the available particle surface area, where the molecules' mutual interactions in solution or at the particle surface were not influential in the adsorption process [10].

First-order rate constants estimated, following the fitting of the solution PEO concentration versus time data to a first-order integral power law below are given in Table 1.

$$C_t = C_0 e^{-kt} \tag{4}$$

where C_t and C_0 are the solution concentrations ($mg\ dm^{-3}$) at time t (s) and zero, respectively, and k is the rate constant (s^{-1}). The rate constants indicate that PEO adsorption was 65% more rapid onto

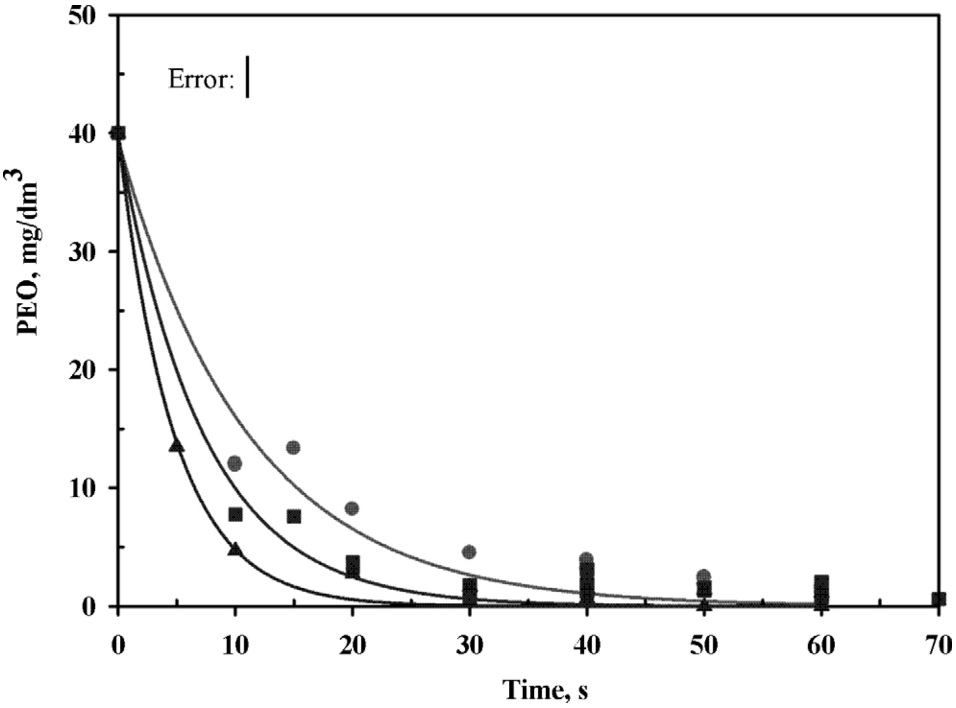

Fig. 3. Concentration of unabsorbed PEO as a function of time during flocculation of 8 wt.% talc dispersion after initial dose of 500 g polymer t^{-1} solid. (●: 18 h conditioning time, 2×10^{-4} M Mg(II), ■: 1 h conditioning time, 10^{-5} M Mg(II) and ▲: 1 h conditioning time, 10^{-2} M Mg(II)).

talc in 10^{-2} M than in 10^{-5} M Mg(II) solution condition, and 75% more rapidly onto talc for the suspension conditioned for 1 h than 18 h.

3.5. *Adsorption isotherms*

The adsorption density of PEO at aqueous–talc interface as a function of equilibrium polymer concentration in solution, suspension conditioning time and Mg(II) concentration at pH 7.5 is shown in Fig. 4. The polymer adsorption increased steadily with increasing equilibrium concentration up to 10 mg dm^3, after which a plateau was reached. All the isotherms exhibit high affinity behaviour, where a single plateau of the adsorbed amount is readily attained at relatively low equilibrium polymer concentration. At similar PEO dosages, adsorption densities which are an order of magnitude lower were observed for smectite and kaolinite clays [4,27]. It is pertinent to note that PEO dosages of 200–500 g t^{-1} solid used in flocculation and dewatering, correspond to ~20–30% surface coverage of plateau adsorption densities (Fig. 4). These data therefore suggest that the non-ionic PEO-flocculation mechanism is bridging [9,28]. Using the Langmuir and Freundlich models, the estimated adsorption parameters, given in Tables 2 and 3, clearly show that there is a noticeable variation of PEO adsorption density with suspension/solution conditions. The flocculant adsorption plateau density or adsorbent capacity decreased with increasing conditioning time or lower Mg(II) ion concentration for a given conditioning time (1 h). Based upon the Langmuir model fit, the calculated affinity constant (b) and $\Delta G^{\circ}_{\mathrm{ads}}$ values <0 confirm that the PEO adsorption onto the talc surface is readily favourable. The b values increased with increasing Mg(II) concentration in the suspension, confirming that the hydrophilic PEO display a higher affinity for the talc surface when more Mg ions are present. In all cases, the magnitude of adsorption free energy is bounded as $62 < |\Delta G^{\circ}_{\mathrm{ads}}| < 68\,\mathrm{kJ\,mol^{-1}}$. This suggests that the bonds underpinning the adsorption of PEO onto talc are more than twice as strong as that typically reported for hydrogen bonding ($|\Delta G^{\circ}_{\mathrm{ads}}| \sim 25\,\mathrm{kJ\,mol^{-1}}$) suggestive of chemisorption [4,15,29]. It therefore appears that substantial, specific adsorption of PEO takes place at talc–solution interface via Mg(II) sites mediation.

Comparison of the results of the Langmuir and Freundlich models analyses show that the former appears to provide a better fit to all the isotherms, as evident from the higher correlation factor

Table 1
Pseudo-first-order rate constants for PEO adsorption to talc particles.

Suspension and solution condition	k (mg dm^{-3} s^{-1})
1 h conditioning time, 10^{-2} M Mg(II)	0.212 ± 0.007
1 h conditioning time, 10^{-5} M Mg(II)	0.139 ± 0.005
18 h conditioning time, 2×10^{-4} M Mg(II)	0.090 ± 0.004

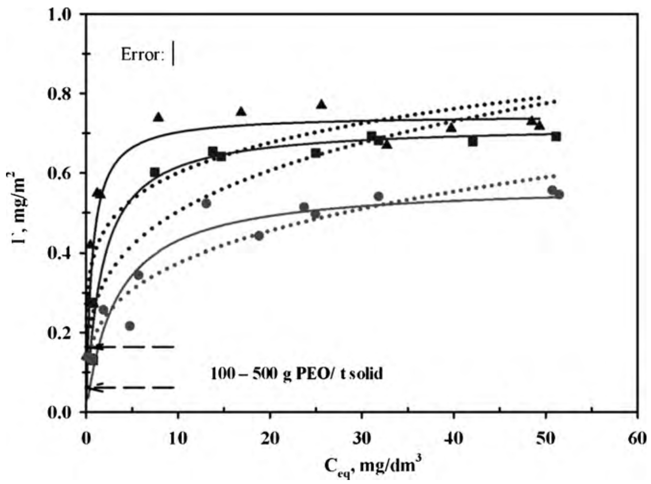

Fig. 4. Adsorption isotherms of PEO on talc particles as a function of suspension conditioning time and Mg(II) ion concentration (●: 18 h conditioning time, 2×10^{-4} M Mg(II), ■: 1 h conditioning time, 10^{-5} M Mg(II) and ▲: 1 h conditioning time, 10^{-2} M Mg(II)). The solid and dotted lines represent Langmuir and Freundlich isotherms plots, respectively.

Table 2
Langmuir adsorption isotherm parameters.

Suspension and solution condition	$\Gamma_{\mathrm{ads}}^{\mathrm{m}}$ (mg m^{-2})	b (dm^3 mol^{-1})	$\Delta G^{\circ}_{\mathrm{ads}}$ (kJ mol^{-1})	Correlation factor (R^2)
1 h conditioning time, 10^{-2} M Mg(II)	0.75 ± 0.02	$(1.28 \pm 0.26) \times 10^{10}$	−66.9 ± 0.5	0.91 ± 0.002
1 h conditioning time, 10^{-5} M Mg(II)	0.72 ± 0.02	$(4.70 \pm 0.26) \times 10^{9}$	−64.5 ± 0.5	0.94 ± 0.002
18 h conditioning time, 2×10^{-4} M Mg(II)	0.61 ± 0.02	$(2.38 \pm 0.26) \times 10^{9}$	−62.8 ± 0.5	0.89 ± 0.002

Table 3
Freundlich adsorption isotherm parameters.

Suspension and solution condition	n_{F}	k_{F} (dm^3 g$_{\mathrm{solid}}^{-1}$)	Correlation factor (R^2)
1 h conditioning time, 10^{-2} M Mg(II)	5.84 ± 0.87	0.41 ± 0.04	0.80 ± 0.002
1 h conditioning time, 10^{-5} M Mg(II)	3.73 ± 0.52	0.27 ± 0.04	0.87 ± 0.002
18 h conditioning time, 2×10^{-4} M Mg(II)	3.54 ± 0.39	0.19 ± 0.02	0.91 ± 0.002

(R^2) in Tables 2 and 3 (R^2 is the quotient of the covariance and the product of their standard deviations of the variables) [30]. For the suspension conditioned for 18 h, it is interesting to note that PEO adsorption onto talc particles may, alternatively, be represented as a Freundlich isotherm (comparable R^2 values in Tables 2 and 3). In this instance, the equally good fit of the data to Freundlich model, of which no maximum adsorption density exist with increasing equilibrium polymer concentration, possibly suggests that the talc surface adsorption sites' homogeneity begun to play an appreciable role after prolonged suspension conditioning. Previous studies of conventional polymers (i.e., Carboxymethyl cellulose, Dextrin, polyacrylamides, polysaccharides, guar, etc.) adsorption onto talc particles showed the isotherms to be more compliant with the Langmuir than Freundlich model [13,15,20,31,32]. The general observation of Langmuir adsorption behaviour implies that either the polymer only adsorbs predominantly onto one of the two talc particle surfaces or similar affinities prevailed between the polymers and both the edge and basal faces [14,32].

3.6. Settling behaviour of flocculated talc dispersion of 8 wt.% solid: effect of Mg(II) ion concentration, suspension conditioning time and PEO-flocculant dosage

The effect of Mg(II) ion concentration, suspension conditioning time and PEO dosage on settling rate of 8 wt.% talc dispersion is shown in Fig. 5. Significant increase in settling rate was observed upon increasing the PEO dosage, consistent with formation of larger flocs as a result of increasing polymer concentration and hence, bridging forces. Furthermore, the settling rates correlate inversely with the flocculant adsorption kinetics (rate constant, k, Table 1). Conditions which lead to faster adsorption kinetics resulted in lower settling rates. This is exemplified by tests performed at higher Mg(II) ions concentration which led to higher PEO adsorption rate and lower settling rate after 1 h conditioning (Fig. 5). Faster polymer adsorption onto clay particles is consistent with flatter polymer interfacial conformation and hence, ineffective polymer bridging [10,33]. Besides, when adsorption takes place very rapidly, the time available for microfloc growth is relatively shorter, leading to smaller, slower settling flocs [10,25]. The slowest polymer adsorption kinetics observed for 18 h, in contrast with 1 h, is conducive to a more extended interfacial conformation of the adsorbed polymer and greater microflocs interactions and hence, greater polymer bridging floc growth and better flocculation performance. The relationship between flocculant adsorption rate and floc settling behaviour is good agreement with the findings of previous studies [8,10,34,35].

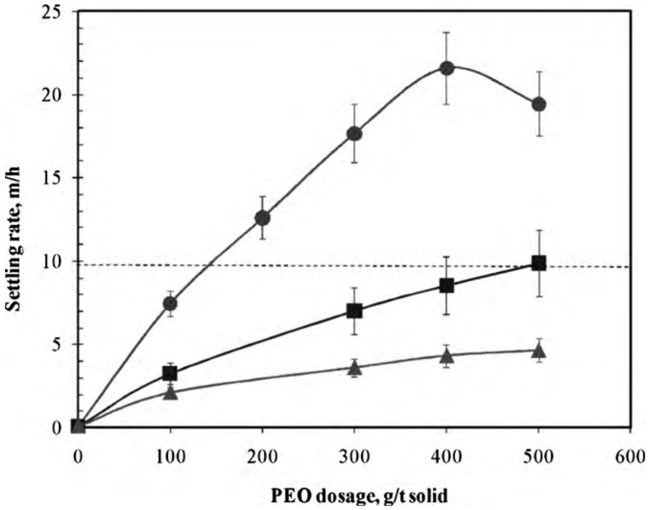

Fig. 5. Settling rate of 8 wt.% solid dispersion as a function of polymer dosage, suspension conditioning time and Mg(II) ion concentration (●: 18 h conditioning time, 2×10^{-4} M Mg(II), ■: 1 h conditioning time, 10^{-5} M Mg(II) and ▲: 1 h conditioning time, 10^{-2} M Mg(II)). The broken line indicates an acceptable 10 m h^{-1} norm in industry practice.

3.7. Effect of dispersion solid loading and PEO-flocculant dosage on dewatering behaviour

The effect of initial suspension solid content (2, 4 and 8 wt.%) on the dewatering behaviour was determined by flocculation in background solution of 10^{-3} M KNO_3 with PEO dosage in the range 100–500 g t^{-1} solid. The settling rates, supernatant clarity and consolidation with respect to the solid concentration of the suspension are shown in Figs. 6–8 as a function of PEO dosages, respectively.

Fig. 6 shows that the settling rate increased significantly with decreasing initial suspension solid loading and increasing PEO concentration. On the other hand, the supernatant clarity became poorer with increasing polymer concentration and decreasing initial slurry solid content, as indicated in Fig. 7. However, the more concentrated suspension was more amenable to effective dewatering over 24 h than the dilute one. Flocculated, 8 wt.% solid content dispersion produced not only a better supernatant clarity after 20 min, but also ≈4 wt.% solid greater sediment consolidation than the faster settling, lower solid content (2 and 4 wt.%) suspensions. How the initial solid content-dependent supernatant clarity observed compares with the acceptable industry norm of <50 mg solid dm^{-3} solution is demonstrated by the chain broken line in Fig. 7. Previous dewatering studies intimated that high settling rate and poor supernatant clarity were ascribe to poor flocculation performance involving bimodal floc size distribution [36–38].

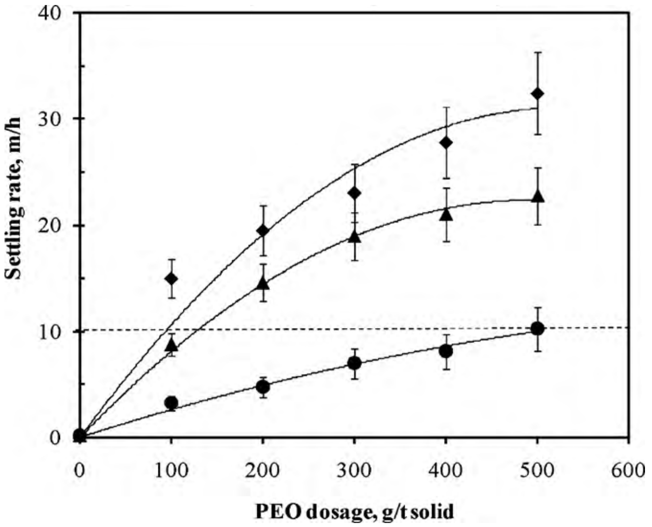

Fig. 6. Settling rate of flocculated talc suspension at 10^{-3} M KNO_3 and pH 7.5 conditioned for 1 h as a function of PEO dosage and talc suspension solid concentration (♦ = 2 wt.%, ▲ = 4 wt.% and ● = 8 wt.% solid). The chain broken line indicates an acceptable 10 m h^{-1} norm in industry practice.

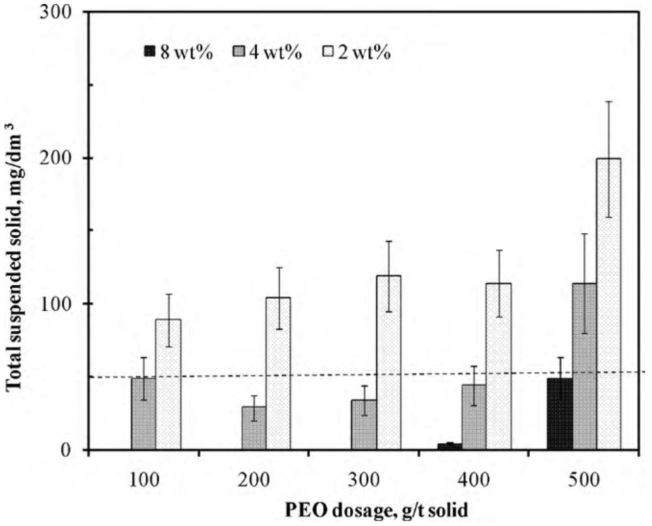

Fig. 7. Supernatant clarity of flocculated talc suspension at 10^{-3} M KNO_3 and pH 7.5 as a function of PEO dosage and suspension solid concentration. The broken line indicates the maximum acceptable limit of 50 mg dm^{-3} in industry practice.

3.8. *Consolidation of flocculated dispersion of 4 and 8 wt.% solid: effect of shear*

Consolidation of the PEO-flocculated pulp was 9 wt.% solid loading lower than that of the unflocculated pulps (~47 wt.% solid) as shown in Fig. 9. The decrease in the extent of consolidation of the flocculated sediments is believed to be due to the formation of large, open flocs resulting from expanded, interfacial conformation and strong interparticle bridging force of the adsorbed PEO chains. Upon shear of unflocculated pulp sediment at 100 rpm for 10 min, an increase of ~8 wt.% in solid loading resulted. The applied shear facilitated the re-arrangement and compaction of the weakly charged particles in the sediment, permitting the water trapped to escape [9,39,40]. Similar agitation of PEO-flocculated sediments on the other hand, showed a more dramatic increase of 12–16 wt.% to ~50 ± 2 wt.% solid loading as Fig. 9(A) shows. The dispersion flocculated at 4 wt.% solid loading showed a slightly lower (~3–5 wt.%) sediment consolidation behaviour than that of the 8 wt.% solid

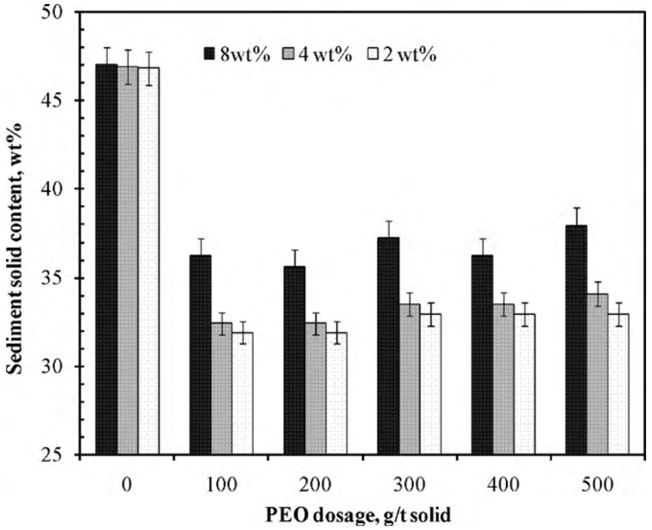

Fig. 8. Final consolidation behaviour of flocculated talc suspension at 10^{-3} M KNO_3 and pH 7.5 as a function of PEO dosage and suspension solid concentration.

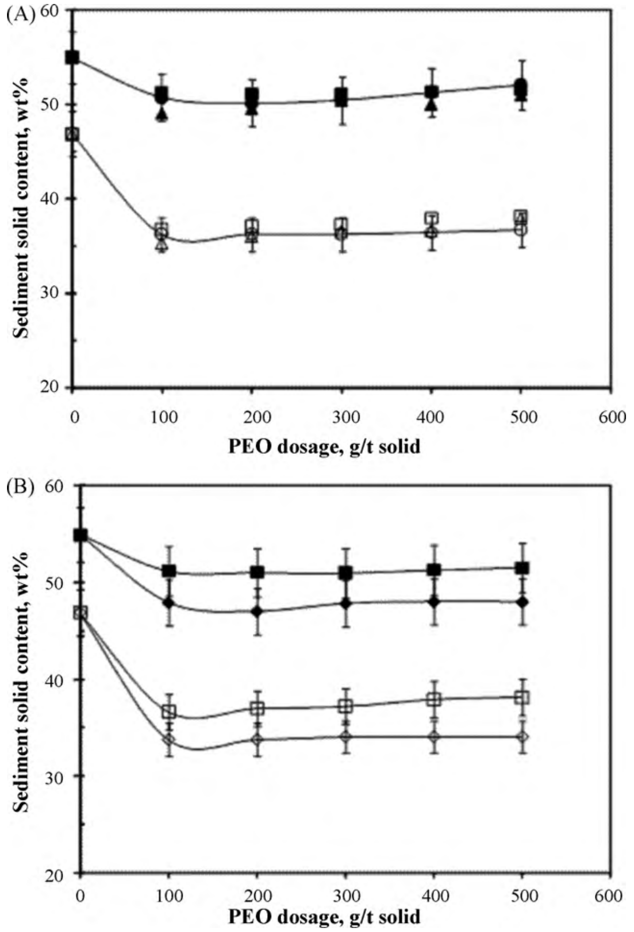

Fig. 9. Final consolidation behaviour of unflocculated and flocculated talc suspensions (A) initially at 8 wt.% solid as a function of polymer dosage, suspension conditioning time and Mg(II) ion concentration (●: 18 h conditioning time, 2×10^{-4} M Mg(II), ■: 1 h conditioning time, 10^{-5} M Mg(II) and ▲: 1 h conditioning time, 10^{-2} M Mg(II)). (B) Initially at 8 wt.% (■) and 4 wt.% (♦) solid as a function of polymer dosage, before (unfilled symbols) and after (filled symbols) pulp shear.

(Fig. 9B). Seemingly, at a given polymer dosage leading to <50% particle surface coverage, a more compact packing of flocculated particles is achieved during consolidation when higher numbers of floc particles are bridged by attachment to the available polymer loops and tails as the dispersion solid content is increased.

4. Discussion

Weakly charged talc particles in aqueous suspensions are observed to display poor settling behaviour without and with the addition of Mg(II) ions as a coagulant. The resulting settling rate was two orders of magnitude <10 m h^{-1} threshold required in industry gravity thickening/dewatering practice. Non-ionic PEO-flocculant adsorption rates which fostered floc formation, growth and size enlargement, determined the resulting settling behaviour. The highest PEO affinity and adsorption rate constants observed in the presence of the highest amount of Mg(II) ions in solution suggests that the bonding between PEO's ether oxygen and electropositive Mg(II) species adsorbed onto talc particles play an important role in the polymer adsorption mechanism [20,41,42]. Such interactions have been described in terms of hydrogen bonding: PEO's ether oxygen (Lewis base)–protonated clay surface Si(OH), Al(OH), Mg(OH) sites (Bronsted acid) or PEO's chemisorptions via complexation with clay surface exposed metal ions (e.g., Mg(II)) [4,21,41,43]. Regarding the present PEO adsorption mechanism, whilst it is believed that hydrogen bonding plays a role, the contribution of chemisorption appears to be pivotal judging from the higher values of the adsorption densities and $\Delta G^{\circ}_{\text{ads}}$ when compared with hydrogen bond driven PEO adsorption onto kaolinite and smectite clays [4]. Spectroscopic investigations are currently being performed to unravel the exact adsorption mechanism.

The lower affinity of PEO for the talc particle surface after prolonged homogenization of 18 h may be partly attributed to longer shear-induced delamination of the platy talc particles. This would result in the reduction of hydrophilic brucite edge face surface area. One may expect greater adsorption of PEO to take place at the brucite edges at Mg–OH and Si–OH sites than at the siloxane basal faces. Increased bonding facilitated by the addition of Mg(II) ions amplified the affinity and adsorption rate of PEO onto talc particle surface. This will result in a flatter polymer interfacial conformation where the shorter polymer loops and tails which emerge are less conducive to bridging flocculation [44]. Thus, the leaching of Mg(II) ions from talc edge faces after longer conditioning time leasing to a lower adsorption density, attest to the pivotal contribution of hydroxylated (brucite) layer or surface Mg(II) sites in fostering the adsorption process [20]. Addition of Mg(II) ions to the suspension would not only lead to suppression of leaching of lattice Mg ions but also result in their proliferation at talc particle surface.

Flocculation at different solid loadings under orthokinetic condition has significant influence on the rate of flocculant–particle and particle–particle adsorption/collisions, as well as the effective polymer dosage requirement. For the more dilute talc dispersions, lower particle–polymer molecule collision rate and fast polymer adsorption reduced the opportunities for homogeneous bridging flocculation and microflocs (i.e., smaller, primary flocs) growth to larger flocs formed. This not only resulted in several fast settling flocs formation but also small flocs and very fine particles experiencing negligible gravitational force and hence, remained in the supernatant. The lower settling rate and higher supernatant clarity observed at higher suspension solid loading may be rationalized as follows. Higher particle concentration facilitated greater collisions between the polymer chains and bridging of a larger number of particles by the polymer chains via multi-segment adsorption. As the solid volume fraction increased, the particles and their floc interact more closely and interfere with each other. Therefore, the settling rate attenuates with increasing hindrance, which in turn, enable the formation of microflocs and slower growth of the supra-flocs (i.e., larger aggregates of microflocs) [38,45]. The hindered settling flocs produced a filtering effect where the remaining unflocculated fine particles and smaller non-settling flocs were trapped or captured.

The possible contribution of long-range hydrophobic attraction induced by the presence of nano-bubbles on hydrophobic talc surface may not be discounted [23,46–48]. The contact angle measured at the basal of the talc particles is ≈85°, indicative of a strongly hydrophobic surface. The entrapment of air bubbles after perennial homogenization may lead to the formation of nanoscale gas bubbles on hydrophobic talc basal faces enabling long-range attraction of the two approaching particles. Such hydrophobic attraction suggests that gaseous phase plays an important role in the initial particle aggregation step, prior to polymer bridging flocculation [23].

For 4 wt.% talc dispersion which conditioned for 1 h, 200 g t^{-1} solid was required to achieve settling rate of ~15 m h^{-1} with relatively good supernatant clarity (<50 mg dm^{-3}). On the other hand, for 8 wt.% solid dispersion, similar settling rate may be achieved with equivalent PEO dosage provided that the dispersion was conditioned for 18 h prior to flocculation. In comparison with 8 wt.% solid dispersion conditioned for 1 h, 500 g t^{-1} solid was required to achieve settling rate of ~10 m h^{-1} instead. Thus, the PEO dosage requirement may vary markedly with suspension pre-treatment and solid loading conditions.

In spite of the strong influence of polymer dosage, Mg(II) ion concentration and suspension conditioning time on settling rate, these factors had no noticeable effect on the extent of sediment consolidation, consistent with the finding of reported clay mineral dewatering studies [4,10]. The sediment bed formed after 24 h without the addition of flocculant displayed ~9 wt.% higher in consolidation compared with the consolidation of the PEO-flocculated pulp. This is due to the formation of space-filling of 'hard flocs' under atmospheric pressure loading, such robust flocs are produced by polymer bringing forces arising from multi-segment polymer adsorption onto the talc particles. The dramatic increase in consolidation to 52 ± 2 wt.% solid achieved upon further agitation, mimicking rake and picket action in the consolidation zone at the bottom of the thickener, shows how shear or loading force is essential for reconformation of the adsorbed polymer chains for compact packing of the flocs, leading to their densification [49,50]. For comparison, a consolidation test was performed by flocculation with a conventional carboxylate-substituted PAM co-polymer of similar molecular weight. At the same pH and flocculant dosage of 500 g t^{-1} solid, 36 and 42 wt.% sediment solid loadings were observed, without and with shear, respectively. The difference in behaviour is due to the shear-responsive, interfacial reconformation and subsequent floc restructuring ability of the more-flexible PEO polymer. This remarkable compaction of shear-induced PEO-flocculated talc dispersions agrees well with reported smectite/kaolinite studies [4,21].

5. Conclusions

The influence of suspension conditions, interfacial chemistry, PEO adsorption behaviour and shear on orthokinetic flocculation dewatering performance of talc dispersions had been investigated. Higher Mg(II) ion concentration and shorter suspension conditioning time, whilst leading to enhanced flocculant adsorption, were found to be less conducive to a better flocculation performance and improved dewaterability. Conditions which facilitate relatively slower flocculant adsorption produce better dewatering behaviour. Higher settling rate accompanied by poor supernatant clarity was observed at lower (e.g., 2 and 4 wt.%) than higher (8 wt.%) solid loading. Longer conditioning time (e.g., 18 h) is essential for producing acceptably high settling rate at higher dispersion solid loading. The present work demonstrates how judicious selection of talc suspension treatment conditions may lead to dramatic enhanced dewaterability using shear-responsive PEO as flocculant.

Acknowledgements

The financial support from the Australian Research Council, AMIRA International, and State Governments of South Australia and Victoria is gratefully acknowledged.

References

[1] Position paper for Australia's water reform agenda. Minerals Council of Australia, 2004.
[2] D.J. Venter, J.C.J. Boshoff, Y. Pather, The impact of elevated blanket drain installation on tailings dam operations, in: Proceedings of the Sixth International Conference on Tailings and Mine Waste, Taylor & Francis, Fort Collins, CO, USA, 1999.
[3] K.E. Bremmell, J. Addai-Mensah, Interfacial-chemistry mediated behavior of colloidal talc dispersions, J. Colloid Interface Sci. 283 (2) (2005) 385–391.
[4] P. Mpofu, J. Addai-Mensah, J. Ralston, Flocculation and dewatering behaviour of smectite dispersions: effect of polymer structure type, Miner. Eng. 17 (3) (2004) 411–423.
[5] P. Mpofu, J. Addai-Mensah, J. Ralston, Interfacial chemistry, particle interactions and improved dewatering behaviour of smectite clay dispersions, Int. J. Miner. Process. 75 (3–4) (2005) 155–171.
[6] A. Ozkan, Coagulation and flocculation characteristics of talc by different flocculants in the presence of cations, Miner. Eng. 16 (1) (2003) 59–61.
[7] P. Mpofu, J. Addai-Mensah, J. Ralston, Influence of hydrolyzable metal ions on the interfacial chemistry, particle interactions, and dewatering behavior of kaolinite dispersions, J. Colloid Interface Sci. 261 (2) (2003) 349–359.
[8] J. Gregory, Particles in Water: Properties and Processes, 1st ed., Taylor & Francis Group, 2006.
[9] J. Bratby, Coagulation and Flocculation in Water and Wastewater Treatment, 2nd ed., IWA Publishing, London, 2006.
[10] A. McFarlane, K.Y. Yeap, K. Bremmell, J. Addai-Mensah, The influence of flocculant adsorption kinetics on the dewaterability of kaolinite and smectite clay mineral dispersions, Colloid Surf. A 317 (1–3) (2008) 39–48.
[11] A. McFarlane, K. Bremmell, J. Addai-Mensah, Improved dewatering behavior of clay minerals dispersions via interfacial chemistry and particle interactions optimization, J. Colloid Interface Sci. 293 (1) (2006) 116–127.
[12] B.J. Scheiner, A.G. Smelley, D.A. Stanley, A novel technique for dewatering waste slurries containing clay particles, in: Flocculation, Sedimentation and Consolidation, American Institute of Chemical Engineers, New York, 1985.
[13] G.E. Morris, D. Fornasiero, J. Ralston, Polymer depressants at the talc–water interface: adsorption isotherm, microflotation and electrokinetic studies, Int. J. Miner. Process. 67 (1–4) (2002) 211–227.
[14] R.J. Hunter, Foundations of Colloid Science, Oxford University Press, 2001.
[15] P. Jenkins, J. Ralston, The adsorption of a polysaccharide at the talc–aqueous solution interface, Colloids Surf. A 139 (1) (1998) 27–40.
[16] J. Nuysink, L.K. Koopal, The effect of polyethylene oxide molecular weight on determination of its concentration in aqueous solutions, Talanta 29 (6) (1982) 495–501.
[17] B.H. Hameed, A.A. Ahmad, N. Aziz, Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash, Chem. Eng. J. 133 (1–3) (2007) 195–203.
[18] X. Yao, S. Tan, Z. Huang, D. Jiang, Dispersion of talc particles in a silica sol, Mater. Lett. 59 (1) (2005) 100–104.
[19] G.D. Saldi, S.J. Köhler, N. Marty, E.H. Oelkers, Dissolution rates of talc as a function of solution composition, pH and temperature, Geochim. Cosmochim. Acta 71 (14) (2007) 3446–3457.
[20] G. Liu, Q. Feng, L. Ou, Y. Lu, G. Zhang, Adsorption of polysaccharide onto talc, Miner. Eng. 19 (2) (2006) 147–153.
[21] A.J. McFarlane, K.E. Bremmell, J. Addai-Mensah, Optimising the dewatering behaviour of clay tailings through interfacial chemistry, orthokinetic flocculation and controlled shear, Powder Technol. 160 (1) (2005) 27–34.
[22] P.F. Luckham, S. Rossi, The colloidal and rheological properties of bentonite suspensions, Adv. Colloid Interface Sci. 82 (1–3) (1999) 43–92.
[23] M. Zbik, R.G. Horn, Hydrophobic attraction may contribute to aqueous flocculation of clays, Colloids Surf. A 222 (1–3) (2003) 323–328.
[24] X.H. Zhang, N. Maeda, J. Hu, Thermodynamic stability of interfacial gaseous states, J. Phys. Chem. B 112 (44) (2008) 13671–13675.
[25] A.J. McFarlane, Orthokinetic Flocculation, Optimized Particle Interactions and Dewatering of Clay Mineral Dispersions, Ian Wark Research Institute, University of South Australia, 2006.
[26] M.J. McGuire, J. Addai-Mensah, K.E. Bremmell, The effect of polymer structure type, pH and shear on the interfacial chemistry, rheology and dewaterability of model iron oxide dispersions, Colloids Surf. A 275 (1–3) (2006) 153–160.
[27] P. Mpofu, J. Addai-Mensah, J. Ralston, Temperature influence of nonionic polyethylene oxide and anionic polyacrylamide on flocculation and dewatering behavior of kaolinite dispersions, J. Colloid Interface Sci. 271 (1) (2004) 145–156.
[28] P. Mpofu, J. Addai-Mensah, J. Ralston, Investigation of the effect of polymer structure type on flocculation, rheology and dewatering behaviour of kaolinite dispersions, Int. J. Miner. Process. 71 (1–4) (2003) 247–268.
[29] J. Wang, P. Somasundaran, Adsorption and conformation of carboxymethyl cellulose at solid–liquid interfaces using spectroscopic, AFM and allied techniques, J. Colloid Interface Sci. 291 (1) (2005) 75–83.
[30] W.M. Harper, Statistics T.M.E.h. series, 3rd ed., Macdonald and Evans, Plymouth, 1977.
[31] A. Mierczynska-Vasilev, J. Ralston, D.A. Beattie, Adsorption of modified dextrins on talc: effect of surface coverage and hydration water on hydrophobicity reduction, Langmuir 24 (12) (2008) 6121–6127.
[32] D.A. Beattie, L. Huynh, G.B. Kaggwa, J. Ralston, Influence of adsorbed polysaccharides and polyacrylamides on talc flotation, Int. J. Miner. Process. 78 (4) (2006) 238–249.
[33] V. Chaplain, M.L. Janex, F. Lafuma, C. Graillat, R. Audebert, Coupling between polymer adsorption and colloidal particle aggregation, Colloid Polym. Sci. 273 (10) (1995) 984–993.
[34] R. Hogg, The role of polymer adsorption kinetics in flocculation, Colloids Surf. A 146 (1–3) (1999) 253–263.
[35] D.K. Sengupta, J. Kan, A.M. Al Taweel, H.A. Hamza, Dependence of separation properties on flocculation dynamics of kaolinite suspension, Int. J. Miner. Process. 49 (1–2) (1997) 73–85.
[36] R. Hogg, Flocculation and dewatering, Int. J. Miner. Process. 58 (1–4) (2000) 223–236.
[37] P.T. Spicer, W. Keller, S.E. Pratsinis, The effect of impeller type on floc size and structure during shear-induced flocculation, J. Colloid Interface Sci. 184 (1) (1996) 112–122.
[38] L.S. Kotlyar, B.D. Sparks, Y. LePage, J.R. Woods, Effect of particle size on the flocculation behaviour of ultra-fine clays in salt solutions, Clay Miner. 33 (1) (1998) 103–107.
[39] R.H. Perry, D.W. Green, Perry's Chemical Engineers' Handbook, McGraw-Hill, 1997.
[40] J.B. Farrow, R.R.M. Johnston, K. Simic, J.D. Swift, Consolidation and aggregate densification during gravity thickening, Chem. Eng. J. 80 (1–3) (2000) 141–148.
[41] S. Mathur, B.M. Moudgil, Adsorption mechanism(s) of poly(ethylene oxide) on oxide surfaces, J. Colloid Interface Sci. 196 (1) (1997) 92–98.
[42] H. Du, J.D. Miller, A molecular dynamics simulation study of water structure and adsorption states at talc surfaces, Int. J. Miner. Process. 84 (1–4) (2007) 172–184.
[43] K.P. Ananthapadmanabhan, E.D. Goddard, Aqueous biphase formation in polyethylene oxide–inorganic salt systems, Langmuir 3 (1) (1987) 25–31.
[44] S. Bratskaya, S. Schwarz, J. Laube, T. Liebert, T. Heinze, O. Krentz, C. Lohmann, W.-M. Kulicke, Effect of polyelectrolyte structural features on flocculation behavior: cationic polysaccharides vs. synthetic polycations, Macromol. Mater. Eng. 290 (8) (2005) 778–785.
[45] L. Svarovsky, Solid–liquid Separation, Butterworth–Heinemann, 2000.
[46] J.W.G. Tyrrell, P. Attard, Images of nanobubbles on hydrophobic surfaces and their interactions, Phys. Rev. Lett. 87 (17) (2001) p176104.
[47] X.H. Zhang, A. Khan, W.A. Ducker, A nanoscale gas state, Phys. Rev. Lett. 98 (13) (2007) 136101–136104.
[48] P. Attard, Nanobubbles and the hydrophobic attraction, Adv. Colloid Interface Sci. 104 (2003) 75–91.
[49] B.P. Makogon, E.N. Bykova, S.I. Klenin, I.L. Povkh, Instability in polyethylene oxide solutions in a hydrodynamic field, J. Eng. Phys. Thermophys. 54 (2) (1988) 161–164.
[50] P. Pang, P. Englezos, Phase separation of polyethylene oxide (PEO)–water solution and its relationship to the flocculating capability of the PEO, Fluid Phase Equilib. 194–197 (2002) 1059–1066.