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Improved dewatering behavior of clay minerals dispersions via interfacial chemistry and particle interactions optimization

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Abstract

Orthokinetic flocculation of clay dispersions at pH 7.5 and 22 °C has been investigated to determine the influence of interfacial chemistry and shear on dewatering and particle interactions behavior. Modification of pulp chemistry and behavior was achieved by using kaolinite and Na-exchanged (swelling) smectite clay minerals, divalent metal ions (Ca(II), Mn(II)) as coagulants and anionic polyacrylamide copolymer (PAM A) and non-ionic polyacrylamide homopolymer (PAM N) as flocculants. The pivotal role of shear, provided by a two-blade paddle impeller, was probed as a function of agitation rate (100–500 rpm) and time (15/60 s). Particle zeta potential and adsorption isotherms were measured to quantify the interfacial chemistry, whilst rheology and cryogenic SEM were used to investigate particle interactions and floc structure and aggregate network, respectively. Osmotic swelling, accompanied by the formation of "honeycomb" particle network structure and high yield stress, was produced by the Na-exchanged smectite, but not kaolinite, dispersions. Dispersion of the clay particles in 0.05 M Ca(II) or Mn(II) solution led to a marked reduction in particle zeta potential, complete suppression of swelling, honeycomb network structure collapse and a concomitant reduction in shear yield stress of smectite pulps. Optimum conditions for improved, orthokinetic flocculation performance of negatively charged clay particles, reflecting faster settling flocs comprised (i) coagulation, (ii) moderate agitation rate, (iii) shorter agitation time, and (iv) anionic rather than non-ionic PAM. The optimum dewatering rates were significantly higher than those produced by standard, manual-mixing flocculation techniques (plunging and cylinder inversion) commonly used in industry for flocculant trials. The optimum flocculation conditions did not, however, have a significant impact on the final sediment solid content of 20–22 wt%. Further application of shear to pre-sedimented pulps improved consolidation by 5–7 wt% solid. Higher shear yield stresses and greater settling rates were displayed by PAM A based than PAM N based pulps and this is attributed to the former's more expanded interfacial conformation and greater clay particles bridging ability. It appears that the intrinsic clay particles' physico-chemical properties and interactions limit compact pulp consolidation.

Keywords: Smectite; Kaolinite; Clay mineral flocculation; Polyacrylamide; Settling behavior; Sedimentation; Dewatering; Pulp consolidation

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1. Introduction

Clay (e.g., smectite and kaolinite) tailings arising from hydrometallurgical processing of mineral ores constitute ubiquitous yet problematic minerals in waste treatment and disposal [1–7]. Kaolinite and smectite clays are phyllosilicate minerals with unit cells comprising an alumina octahedral sheet and either one (kaolinite) or two (smectite) silica tetrahedral sheets [1]. A single particle therefore comprises several alternating layers stacked on top of one another. Due to isomorphous substitution (e.g., Al(III) replacing Si(IV) in the SiO_2 layer), the basal faces carry a permanent negative charge which is balanced by exchangeable cations (e.g., Na^+, Ca^{2+}) adsorbed at the particles' surfaces [3]. The degree of isomorphous substitution in smectite group minerals is characteristically high, in contrast to kaolinite. In aqueous suspensions of weakly exchanged smectite, water molecules penetrate the interlayer region where resulting repulsive hydration forces lead to separation of the layers by 10–20 Å

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(crystalline swelling) [2]. Where the exchanged species are monovalent ions such as Na^+ or Li^+, interlayer separations up to several hundred angstroms (osmotic swelling) may result due to high osmotic pressure which arises to overcome the weak van der Waals' attraction. The swelling behavior of smectite suspensions leads to characteristically poor settling rates (e.g., $<0.1\ m\,h^{-1}$), low sediment solid loading (<10 wt%) and increased shear yield stress, the latter which can mitigate compact consolidation. Under plant thickening conditions, flocculated kaolinite and smectite thickener underflow pulps typically consolidate to 20–22 wt% solid. Recent smectite dewatering studies have shown that improved consolidation may be achieved through "controlled dispersion," whereby the Na-smectite clay is dispersed in 0.02–0.05 M solutions of divalent metal ions (e.g., Ca(II), Mn(II)) [5–7]. Pulp solid content as high as 32 wt% was attained with divalent metal ions addition by de Kretser [5]; however, without flocculation the settling rates were remarkably low ($\approx 0.1\ m\,h^{-1}$). Upon exchanged of Na^+ with the divalent metal ion at sufficiently high ionic strength, osmotic swelling was suppressed, as is electrostatically repulsive particle interactions, allowing a more compact packing and hence, improved dewaterability to occur.

In aqueous environments, the characteristic anisotropic charge and platy shape of clay mineral particles may lead to a variety of particle packing behavior. The main two types of packing behavior result from edge face–basal face ("house of cards") and basal face–basal face ("band structure") interactions [2–4]. The house of card structure, attributed to high angle positive edge face and negative basal face attraction, is unlikely to be predominant in highly colloidal smectite pulps where: (a) the total edge face area is considerably smaller ($\approx 10\%$) than the basal face; (b) thin plate-like particles are able to bend normally to the interlayer orientation; and (c) pH is moderate to high and the basal face negative charge significantly dominates the overall particle surface charge. Nevertheless, structures that contain the large voids, reminiscent of house of cards, commonly form in smectite pulps. Likewise, the interactions and packing behavior of kaolinite particles which have lower aspect ratios than smectite lead to the formation of house of cards and band structures, respectively, below and above pH 7 [4].

Coagulation and high molecular weight (e.g., $>1 \times 10^6$ Da) polymer flocculation of colloidally stable mineral dispersions are commonly used for rapid sedimentation, enabling supernatant recycling to upstream processes. As a result of their structural characteristics and pulp chemistry, conducive to an enhanced colloid stability at neutral to high pH, clay dispersions retain large volumes of water, displaying high flocculant demand and poor pulp compaction behavior. These, thus present intractable dewatering and impoundment challenges to the minerals industry. Coagulation invariably facilitates the screening of repulsive electrical double layer interactions which enables closer approach of particles and predominance of attractive van der Waals forces. High molecular weight polymer flocculation, on the other hand, significantly amplifies gravity settling, facilitated by particle aggregation through a number of bridging mechanisms (e.g., hydrogen bonding, charge patch neutralization, electrostatic, chemical, etc.). By prior addition of hydrolyzable metal ions (Mn(II) or Ca(II)) at concentrations and pH where the divalent metal ions undergo hydrolysis to the monovalent complexes ($Mn(OH)^+$, $Ca(OH)^+$) form, Mpofu et al. [7] subsequent flocculation with anionic PAM resulted in good settling rates ($10\ m\,h^{-1}$) and modest pulp consolidation of 26 wt% solid.

Floc formation is regarded as a series of simultaneous processes during which particle–polymer collision and adsorption, followed by further particle collision, take place allowing bridges between particles and aggregates to form [8]. Certain polymer re-conformation at the particle–solution interface may mitigate aggregation by limiting the extension of the polymer chains, loops, trains and tails, and prevent further particle bridging. In some cases, a good pulp–flocculant dispersion provided by right shear or agitation conditions are warranted to facilitate further adsorption onto more particles before an equilibrium re-conformation may be reached [9]. Irreversible floc rupture and/or eroding may also occur at a shear rate greater than that necessary for aggregation, if too high agitation intensity is applied. Yeung et al. [10] observed that the optimum individual mineral dispersions floc strengths were dependent upon agitation speed. Re-aggregation of disrupted flocs has been observed in some studies [11], however, this was attributed to a charge patch mechanism, which does not commonly reflect most bridging situations. Flocculation studies of kaolinite [12,13] and smectite [14] pulps with ionic and non-ionic and polyacrylamide polymers indicated that optimum dewatering conditions may be established with respect to agitation rate (e.g., 750 rpm) and time (e.g., 15 min). Further development in clay tailings consolidation enhancement has been achieved by the use of non-conventional, non-ionic polyethylene oxide (PEO) flocculant [6,15]. Dramatic improvements in pulp compaction or consolidation (>35 wt% solid) resulted from application of shear or compression to pre-sedimented, PEO flocculated pulps. The better efficacy of this flocculant was attributed to the capacity for the polymer chains to undergo irreversible and unhindered bridging under external loads, a behavior rarely displayed by ionic polyacrylamides. Recourse to other studies [13] suggests that high molecular weight non-ionic PAM might be capable of similar shear-responsive pulp compaction behavior.

A review of several dewatering studies [1–16] indicates that to date, the greatest challenge which persistently confronts the efficacy of chemical additive-assisted tailings dewatering methods, however, resides in pulp consolidation, specifically enhanced rapid compaction, rather than faster settling behavior. Whilst optimization of conventional polymeric flocculants type and dosage may improve flocculation performance, there is no guarantee that optimum floc structure for conducive to enhanced settling behavior will also facilitate compact consolidation. To increase thickener under-