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Optimising the dewatering behaviour of clay tailings through interfacial chemistry, orthokinetic flocculation and controlled shear

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Abstract

The effect of shear on dewatering behaviour and particle interactions of Na-exchanged smectite and kaolinite clay dispersions has been investigated at pH 7.5, using hydrolysable Ca(II) and Mn(II) ions as coagulants and high molecular weight anionic and non-ionic polyacrylamide (PAM A and PAM N, respectively) and polyethylene oxide (PEO) flocculants. Metal ion addition enhanced the flocculation performance by dramatically reducing the magnitude of the particle zeta potential and, in the case of smectite pulp, suppressing osmotic swelling. Under optimum orthokinetic flocculation conditions of controlled agitation rate and duration, PAM A and PEO-based flocs settled faster than those of PAM N whilst kaolinite pulps produced higher sedimentation rates than smectite pulps. The settling rates are nearly an order of magnitude greater than those observed under standard flocculant–pulp mixing/flocculation methods of inversion and plunging. The difference in the flocculant behaviour is attributed to the more expanded conformation of PAM A and PEO polymer chains in contrast to PAM N, whilst the lower yield stresses, reflecting inter-particle bridging and floc network structure strength that are conducive to faster clarification, were displayed by kaolinite pulps. Following shear, similar consolidation enhancement of ≈ 5–7 wt.% solid for both pulps was achieved at an optimum agitation range of 100–200 rpm. This was accompanied by decreased yield stress in the case of PAM A-based pulps, indicating non-reversible disruption of polymer mediated particle and floc network structure. In contrast, the yield stresses of PAM N and PEO flocculated dispersions indicated similar and stronger particle interactions, respectively, upon consolidation following shear. The findings show clear links between effect of shear, interfacial chemistry and polymer structure on pulp particle interactions and dewaterability.
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Keywords: Dewatering; Pulp consolidation; Smectite suspension; Kaolinite dispersion; Particle interactions; Rheology

1. Introduction

Optimising mineral waste tailings dewatering behaviour has both direct and indirect influence in improving “triple bottom line” sustainability outcomes for the mining and mineral processing industry [1–4], as recourse to Table 1 shows. By increasing water reclamation via improved thickening processes, the environmental impact of hydrometallurgical-based mineral extraction operations is minimised, whilst profitability and competitiveness are improved through cost savings, and ethical practice is attained. Clay minerals kaolinite and smectite pose a significant problem to effective pulp dewatering since the floc structures formed through flocculant assisted gravity thickening typically retain >88% water [5] due to the underlying interfacial chemistry and particle interactions.

In thickener operations, primary dewatering requires optimisation for good supernatant clarity and high settling rates. Typically, high molecular weight flocculants (e.g. polyacrylamides) are used for particle aggregation to amplify sedimentation rates. Coagulation alone achieved through dissolved salts (e.g. alum) or low molecular weight polyelectrolytes addition, whilst producing good supernatant clarity does not lead to rapid settling aggregates. Thus, to achieve desirable dewatering outcomes, both coagulation and flocculation are commonly used in conjunction. Polyacyrlamide (PAM) polymers used as flocculants adsorb onto clay mineral particles by hydrogen

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Table 1
Features of improved tailings dewatering on the "triple bottom line" approach to mining and mineral processing operations

	Environmental	Economic	Social/Ethical
Increased water recycling [1]	Increased environmental flows	Reduced acquisition and infrastructure cost	Responsible resource management
Reduced reagent usage	Reduced contamination risk [3]	Reduced acquisition cost	
Reduced energy consumption	Reduced greenhouse gas emissions	Reduced energy and pumping (capital) costs	Kyoto agreement compliance
Faster disposal site rehabilitation [4]	Improved ecosystem recovery, decreased erosion	Decreased assessment time [5]	Reduced geotechnical risk
Extended mine life cycle (low grade extraction)	Fewer mines for same output, waste recovery	Extended profitability of initial capital investment	Longer-term jobs, national/global exploitation efficiency

bonding between silanol/aluminol groups at the clay surface and the polymer's primary amide and/or carboxylate functional groups [6,7]. More efficient dewatering of kaolinite has been achieved in recent years through prior manipulation of the surface chemistry by hydrolysable metal ion [8] and surfactant [9] addition before flocculation. Hydrodynamic (orthokinetic) conditions during flocculation significantly influence the size and structure of the flocs produced [10,11], impacting significantly on primary dewatering behaviour (i.e. settling rate) [12–14]. Secondary dewatering involves consolidation of sedimented flocs through compaction and release of inter- and intra-floccule pore water. Particle interactions and structure formation in clay mineral dispersions may result in high yield stresses which can significantly mitigate gravitational compaction of sedimented pulps [15–23]. Rake action in thickeners facilitates consolidation to a certain extent by modifying the particle interactions and increasing the effective sediment permeability [19], resulting in thickener underflow solid loadings of ~20–25 wt.%. Further consolidation in the tailings dam is not generally achieved even after several months due to the characteristically slow compaction rate of the clay pulp. Thus, a better fundamental understanding for enhancing the consolidation behaviour of flocculated clay dispersions is required.

Non-conventional, high molecular weight, non-ionic polymeric flocculant, polyethylene oxide (PEO) has been shown to exhibit 'shear sensitive' floc-structure behaviour [20,21], leading to higher pulp solid contents in the range 35–42 wt.% [21,22]. However, due to its high cost, PEO has not gained widespread application in tailings dewatering processes. Investigation has therefore been undertaken using non-ionic PAM as a possible low-cost analogue for non-ionic PEO by comparing its capacity for 'shear sensitive' behaviour with an anionic polyacrylamide of similar molecular weight.

The main aim of this study was to investigate the dewatering behaviour of flocculated kaolinite and smectite clay dispersions under industrially relevant conditions, focussing in particular on improvement in consolidation behaviour. This was achieved by coagulation with hydrolysable metal ions (Ca(II) and Mn(II)) before flocculation with anionic and non-ionic high molecular weight ($(4.5–5.0)\cdot 10^6$) PAM and PEO polymers. Optimum orthokinetic flocculation conditions were established for the various flocculant–clay dispersion combinations with respect to the resulting settling rates and final sediment volumes. Particle interactions and consolidation behaviour of the sedimented pulps were determined in the presence and absence of shear and comparison made between PAM and PEO flocculated pulps. Surface chemistry and particle interactions have been assessed via measurement of zeta potential and shear yield stress, respectively.

2. Experimental procedure

2.1. Materials and dispersion preparation

Colloidal Na-exchanged smectite (Activebond 23, 95% pure, 5% quartz) and kaolinite (K15GM, 99% pure, quartz and mica 1%) (Unimin Australia) were used in this work. The median particle size and BET specific surface area were 2.6 and 5.5 μm and 45.8 and 27.1 $m^2\cdot g^{-1}$ for smectite and kaolinite, respectively. The flocculants used were Na-acrylate (carboxyl-substituted) polyacrylamide copolymer (PAM A, 25% mol anionically charged), polyacrylamide homopolymer (PAM N, <2% mole anionically charged) (CIBA, Australia) and PEO with average molecular weights $4.96\cdot 10^6$, $4.59\cdot 10^6$ and $4.80\cdot 10^6$, respectively, determined from intrinsic viscosity data using the Mark–Houwink equation and constants estimated by McCarthy [18]. Dilute 0.025 wt.% polymer solutions gently mixed for 16 h were prepared and used within 3 days to minimise aging effects. All reagents were analytical grade and solutions were prepared in high purity Milli-Q water. KOH and HNO_3 were used to adjust pH whenever necessary. Solution species concentration was determined by Inductively Coupled Plasma (ICP) analysis.

Smectite and kaolinite dispersions were prepared at 8 wt.% solid in 10^{-3} M KNO_3 solution at an agitation rate of 500 rpm for 1 h and allowed to equilibrate acquiescently overnight. To facilitate formation and adsorption of Mn(II) hydrolysis products (e.g. $Mn(OH)^+$) at pH 7.5 [8], 10^{-3} M $MnCl_2$ was added from a 1 M stock solution to kaolinite suspensions 30 min prior to pH adjustment and flocculation tests. Smectite dispersions were prepared using the "controlled dispersion" method in the manner of de Kretser et al.

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