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Improved water recovery: A review of clay-rich tailings and saline water interactions

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ABSTRACT

The presence of clays can make dewatering of tailings from mineral processing challenging. This review focuses on the interaction of clays in tailings under different conditions, including the impact of high salinity. The surface chemistry and aggregation behaviour of clays in suspension are first discussed, and this is then extended to clay aggregation responses during polymer-induced flocculation, with a view to developing an understanding of how flocculant properties and applied shear can be optimised to enhance dewatering processes. There is increasing interest in polymer dosing to high solids tailings streams to enhance dewatering on deposition, and the demands for this process are contrasted against those for conventional flocculation at lower feed solid concentrations. The review concludes by highlighting a number of research challenges, which include that: (i) aggregate structures from polymer-assisted flocculation that are optimal for settling cannot also be assumed to be so for sediment consolidation; (ii) there is scope for reducing longer-term tailings impacts by choosing novel processing routes in the flowsheet design phase, but this requires insights on how tailings may behave after such processing

at a much earlier stage; and (iii) most flocculation studies suffer from inconsistent, ill-defined or inappropriate conditions during the preparative stages, which prevent definitive conclusions being drawn on how high salinity impacts upon tailings flocculation, despite evidence that it can change aggregate density.

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Review





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1. Introduction

The tailings generated from mineral processing can represent >95% of the total ore [1]. As ore grades decline, higher tonnages are processed, making tailings management more difficult [2]. This is reflected in higher costs, increased difficulties in returning water for further processing, and challenges in mine closure and rehabilitation. Both short and long-term tailings dewatering management are determined to a large degree by the phases present, and in particular by those of the smallest particle size.

Mineral tailings are heterogeneous mixtures of different solids suspended in process-contaminated water that often contains multiple soluble species. By convention, operators classify tailings solids size fractions as "sand", "silt", and "clay", where clay usually indicates particles <2 μ m. Wang et al. [3] has listed some examples of classification results and solids concentration for tailings across the mining industry sectors. Generally there are significant amounts of silt and clay materials in the fine fractions whose concentrations can vary considerably within an impoundment area. For example, the solid content of particles <4 μ m was up to 28% in a fresh coal tailings [4], 34% of particles <1 μ m were found in a copper tailings [5] and typical oil sand tailings contains 33% of particles <1 μ m [6].

Studies by De Kretser et al. [7], Sabah et al. [4], Ofori et al. [8] suggest the fines fraction of coal preparation tailings consist mostly of phyllosilicate minerals, such as kaolinite, illite, muscovite, mica, and mixed-layer illite/montmorillonite clays, along with quartz. This is very similar to phases identified within fluid fine tailings from oil sands processing, in which kaolinite is the dominant clay fraction, followed by illite, chlorite, and other mixed-layer clays, while the coarse fraction is mostly made up of quartz, K-feldspar, and bitumen-clay aggregates [3]. In comparison, tailings from the copper and other base metals industries are found to contain less clay minerals and higher proportions of metal oxides. Although differences exist in tailings composition, phyllosilicate minerals are ubiquitous, with the majority classified as clays and concentrated in the fines fractions, making the dewatering process challenging.

The flocculation of fine clay particles by polymers to enhance solidliquid separation efficiency has been extensively studied both at laboratory and industrial scale [9–11]. For aggregated particle structures, thickening and compression can be significantly affected by the strength and nature of clay interparticle forces and by particle packing [12], leading to poor solid-liquid separation and potentially higher operating and capital costs [13]. Consequences can be larger tailings storage facilities and increased risks of geotechnical failure. Despite legislative and environmental pressure for mines to recover more water and reduce the footprint of tailings storage facilities, there are currently limited economical and practical methods for significantly increasing the recovery of process water from clay-rich tailings [14,15].

The minerals industry is also increasingly using saline water in processing, which may further complicate tailings treatment. In some operations (e.g. for coal), salts are present in the sedimentary geology or are generated by weathering processes, causing process water salinity that increases on recirculation. Sites in water-sensitive environments may be required to use highly saline groundwater or seawater for processing [16]. Although many have studied tailings dewatering in fresh water or with low concentrations of single cationic salts, few have considered the impact of high salinity. Salts within process water are likely to affect the interactions of clay particles in tailings, altering dewatering responses relative to fresh water. A better understanding of such effects will assist operations to optimize tailings dewatering, especially when dealing with the depletion of available fresh water and increases in fines content.

This paper reviews clay dewatering in different suspension chemistry environments, with an emphasis on saline process water. It starts by providing background on the structure and properties of clay suspensions, followed by consideration of the dewatering response of clays to factors such as pH, water salinity, polymer addition and applied shear. The underlying mechanisms of clay flocculation in saline suspensions are also discussed, as well as the potential to enhance dewatering by dosing polymer at higher solids concentrations. The last section identifies research gaps and proposes possible strategies to manage clayrich tailings in saline water.

2. Properties of clays and their effects on the dewatering process

2.1. Crystalline structure

Clays are hydrous aluminium phyllosilicates, made of tetrahedral (T) and octahedral (O) sheets as the basic building blocks. The T and O sheets are chemically bonded in certain proportions through various forces and atoms to form the unit layer for different clay macrostructures. Based on the layer structures and their bonding forces, the most commonly occurring clays in ore deposits can be classified into three groups: the kaolinites, smectites, and illites [17]. For example, kaolinite is structured as repeating units of an O sheet bonded to a T sheet, whereas an O sheet is sandwiched between two T sheets for smectite and illite. Different clay layers could also alternate with each other to form mixed-layer clay minerals. Structures of the representative clay in each group are shown in Fig. 1 [18].

Kaolinite has a 1:1 layer structure, with sheets held together by van der Waals attractive forces and hydrogen bonds, the latter between hydroxyl groups in the O sheet of one layer and oxygens in the T sheet of the next. Water cannot penetrate due to strong hydrogen bonding between layers, and therefore kaolinite is generally non-swelling in water.

Unlike kaolinite, the smectite group has a 2:1 layer structure, and there is no possibility of hydrogen bonding, since both outer sheets are tetrahedral, meaning no exposed hydroxyl groups to interact with oxygens at the basal surfaces. The smectite sheets are therefore only loosely held together by weak van der Waals forces. Water molecules can penetrate the interlayer region, where resulting repulsive hydration forces lead to layer separation by 10–20 angstroms (crystalline swelling). Where the exchanged species are monovalent ions (e.g. Na⁺ or Li⁺), interlayer separations of up to several hundred angstroms (osmotic swelling) may result from high osmotic pressure that arises to overcome weak van der Waals' attractions [19]. The small particle size and inherent swelling properties of smectite lead to characteristically poor settling rates (e.g. $<0.1 \text{ mh}^{-1}$) and an increased shear yield stress at low sediment concentrations (<10 wt%), contributing to dewatering and consolidation issues [20].

Illite has a 2:1 layer structure similar to smectite, but the layers are tightly bonded by potassium ions that prevent water penetration. As a consequence, the swelling potential of illite itself is low [21]. Exceptions are for illite/smectie mixed layered structures, for which intercalated smectite layers are easily expanded [22].

Chlorites are often referred to as 2:1:1 clays since they are 2:1 structures with a hydroxide interlayer, either gibbsite-like $[Al(OH)_x]$ or



Fig. 1. Representation of structures for kaolinite, smectite, and illite clay groups (adapted with permission from UQ thesis copyright owner [18]).

brucite-like $[Mg(OH)_x]$ where x is <3, that is continuous across the interlayer sheet and octahedrally coordinated [23]. While observed in tailings, direct research on chlorite dewatering has been limited.

The properties of clays that make their presence within tailings a challenge for suspension dewatering include: 1) a layered structure, with one physical dimension in the nanometre range; 2) anisotropy (or directional-dependence) of the layers or particles; 3) the existence of external basal and edge surfaces, as well as internal (interlayer) surfaces; and 4) the relative ease with which the surfaces can be modified by adsorption, ion exchange, or grafting [24].

2.2. Surface chemistry

Clays expose two crystallographically-different surfaces through basal and edge faces. These present quite distinct electrical charge properties in aqueous suspension, having significant effects on their reactivity, dispersion and aggregation.

Basal surfaces of most clays have permanent, pH-independent negative charges, caused by isomorphous substitutions. For example, Si⁴⁺ in T sheets may be replaced by trivalent cations (Al^{3+} or Fe^{3+}), while Al^{3+} in O sheets may be replaced by divalent cations (Mg^{2+} or Fe^{2+}). Consequently, a charge deficiency occurs and a negative potential at the basal surface is created. Although this theory is widely accepted, Gupta and Miller [25] used colloidal force measurements to indicate the two basal surfaces of kaolinite can have positive or negative charge, with the silica tetrahedral face negative at pH > 4, and the alumina octahedral face negative at pH > 8 but positive at pH < 6. Tailings suspension pH will typically be >5, so for practical purposes such surfaces can be considered negatively charged.

In contrast, charge on the edges of clays will be more sensitive to pH [26]. The crystallite lattice is usually disrupted at the edges, and therefore a broken bond surface exposed. Additional polar sites at these edges are mainly octahedral Al-OH and tetrahedral Si-OH groups. Variable charge can therefore develop by adsorbing hydrogen or hydroxyl ions from an aqueous phase in accordance with the pH [27,28].

2.3. Aggregated structures

Owing to the different basal/edge surface characteristics, clay particles can interact with each other to form edge-edge (EE), edge-face (EF), and face-face (FF) aggregate structures [29,30], as shown in

Fig. 2. These associations are governed by the balance between van der Waals attraction and electrostatic forces that exist between charged double layers at clay platelet surfaces, the latter being either attractive or repulsive, depending on surface charge.

The FF network may form three-dimensional structures when the system's free energy is at its lowest [31]. The 'house-of-cards' EF network only forms when edges are positively charged, or in slightly alkaline media above the critical salt concentration, due to electrostatic attraction between edges and faces [19,32]. Such structures have lower density, usually characterized by non-Newtonian flow with high suspension viscosity. This is considered unfavourable for dewatering, as the structures retain water, slowing settling and consolidation rates.

Charge properties play important roles in the clay-clay/clay-mineral interactions, surface reactivity with reagents (e.g. polymer flocculants), and thereby the aggregate structures formed in suspensions. For example, the presence of bentonite (mainly composed of smectite) in tailings at even a low fraction (~10% by weight) can increase suspension viscosity and yield stress, even leading to gel formation [33–35]. The swelling nature and low permeability of these gels make the tailings very difficult to dewater and consolidate, fundamentally restricted by low mechanical strength and hydraulic conductivity. The presence of smectite can therefore create problems in tailings transport, as well as having long-term implications for the stability and rehabilitation of tailings storage facilities [7].

Gravity sedimentation is the primary method for separating tailings solids from water, but the nature of clays makes this inefficient without destabilization of the suspended clay solids by aggregation as a first step. Accelerated settling will result after clay aggregation, with the potential for enhanced properties of the sediment solids.

3. Effect of suspension chemistry on clay dewatering

Aggregation of clays for dewatering is initiated through coagulation, flocculation, or a combination of both processes [36–38]. Coagulation is achieved the manipulation of surface charge to enable particles to approach and interact with each other, either through areas or 'patches' of opposite charge (often formed by adsorbed salts or low molecular weight polymers) or a reduced magnitude of the effective charge (realised by increasing ionic strength or adjusting pH to near the isoelectric point (IEP)). Aggregation by flocculation is generally achieved



Fig. 2. Particle aggregate structures in clay suspensions: (a) dispersed; (b) FF; (c) EF; (d) EE (from [19], copyright (1999) with permission from Elsevier).

through high molecular weight (MW) synthetic polyelectrolytes (predominantly acrylamide/acrylate copolymers) that form bridges between particles. While intrinsically fragile, flocculated aggregates are typically stronger than coagulated aggregates, and flocculation will under most conditions lead to larger aggregates [39].

Both processes are sensitive to clay surface chemistry and suspension variables, such as ionic strength and pH. This is discussed below, with emphasis on the impact of ionic strength.

3.1. Coagulation of clays

3.1.1. pH effect

The charge density of clay basal and edge surfaces depends on the pH. Particles either aggregate or disperse, depending on the structure of the electric double layer formed on their surfaces [27,28]. Studies using synthetic clay suspensions of controlled pH have been considered.

Lagaly [40] claimed the microstructure of kaolinite slurries is EFdominated at low pH, with FF-dominated band-like structures formed at high pH. The EF aggregates form due to positively charged *Al*–OH sites at the edges interacting with negatively charged basal faces [28,41–44]. Zbik et al. [45] also observed high-void structures (mainly EE with some EF and FF) in the packing behaviour of kaolinite particles at pH 4 and 6, while more EE and compact FF structures form at pH 10. The EE mode of contact may occur under low ionic strength conditions when the pH is at the IEP of the edge surfaces [31].

Bentonite suspensions, on raising pH from 4 to 8.5, went from open, EF- and EE-dominated structures to dense and FF-dominated [27]. The latter has the highest van der Waals interaction area, giving structures more resistant to shear breakage and erosion, and also more readily settled.

Highly charged montmorillonite (smectite group) particles form stable dilute suspensions at low ionic strength (0.01 M NaCl). The average particle size remains almost constant across the pH range, with only a slight increase below pH 7 [46]. In principle, positively charged plate edges can interact with negative basal faces below pH 6.5. However, EF heterocoagulation does not take place at such low ionic strengths because the edge surfaces of montmorillonite plates are thought to remain cloaked by spillover of the dominant basal face electrical double layer [27].

McFarlane et al. [14] concluded EF structures with high angle particle contacts are unlikely to be a major factor in highly colloidal smectite suspensions, where (a) the edge face area is considerably smaller than that of the basal face ($\approx 10\%$); (b) thin plate-like particles are able to bend normally to the interlayer orientation; and (c) pH is normally moderate-to-high and overall particle surface charge will be dominated by the negatively charged basal face. Despite this, structures in suspension will still have high voidage.

3.1.2. Ionic strength effect

The electrolyte concentration has a significant influence on the electrical double layer thickness for clay surfaces. At high ionic strength, electrostatic repulsion (or attraction) between particles is reduced because of double layer compression or ion shielding of surface charges, and this may induce the formation of denser FF aggregates [47].

Studies of ionic strength effects on clay coagulation have mostly been on commercially available clays in synthetic liquors. Nasser and James [47] found that kaolinite settling changed with both ionic strength and suspension pH. At pH 2, particles settled in a coagulated form regardless of ionic strength, however, under alkaline conditions (pH 9), particles were dispersed at low ionic strength (0.001 M NaCl) and coagulated at higher ionic strength (0.1 and 1 M NaCl), leading to low and high sediment volumes, respectively, on extended settling.

Several indirect measures of aggregate structure, such as rheology, have been applied to study the impact of ionic strength. Heath and Tadros [48] found that the yield stress, zero-shear viscosity, and shear modulus of bentonite suspensions increase with ionic strength, suggesting a change in aggregate structure from modified interaction forces. This was supported by scanning electron microscopy (SEM), showing that higher ionic strength changed structures from porous EF to EE, and ultimately to a much denser FF arrangement [49,50]. The degree of swelling for Na-montmorillonite can also be limited by increasing ionic strength to restrict double-layer repulsions [7]. Saline water could therefore assist in forming dense aggregates in bentonite suspensions, depending on the type of salts. Tombácz and Szekeres [27] also observed that more compact FF bentonite structures were induced by the presence of added salts on increasing pH from 4 to 8.5.

In studying inorganic cation effects, Stawinski et al. [50] found that bentonite aggregate size decreased as a function of Na⁺ and Ca²⁺ concentrations up to critical values, above which sizes then increased. In contrast, kaolinite aggregate size increased consistently with concentration. SEM showed both clays forming EF aggregates in distilled water. Adding a small amount of salt led to EE bentonite aggregates and EF kaolinite aggregates (with some FF associations). At high electrolyte concentrations, compact FF-dominated aggregates were formed with both clays.

Adding Ca^{2+} to improve dewatering efficiency is common in operations with tailings containing montmorillonite [29]. As a cation which can exchange with Na⁺ within clays, it has a twofold effect. Being divalent, Ca^{2+} has a higher neutralizing power than Na⁺, resulting in platelet coagulation at lower concentrations. More importantly, it promotes FF aggregation, as opposed to random aggregation [51].

Other multivalent cations show similar effects. Leong [52] reported that adsorbed Cu^{2+} and Al^{3+} ion hydrolysis within higher pH suspensions enables stronger aggregate formation, increasing yield stress by several orders-of-magnitude. McFarlane et al. [14] found that dispersion in 0.05 M Ca²⁺ or Mn²⁺ led to a marked reduction in particle zeta potential, complete suppression of swelling, the collapse of honeycomb network structures, and a related reduction in shear yield stress of smectite (but not kaolinite) suspensions.

Palomino and Santamarina [53] postulated EE, EF, and FF kaolinite aggregation to be a function of ionic strength and pH, producing a fabric map of particle associations in NaCl suspensions, based on sedimentation and rheological parameters (Fig. 3). Ionic concentration controls behaviour at high solids, i.e. above the transition or threshold NaCl concentration, *C*_{th}, that once exceeded, causes particles to approach each other spontaneously. As NaCl concentrations increase from low to high, particle associations shift from deflocculated-dispersed or EF to predominantly FF. In the transition region, EE association is expected and is independent of pH. Above this, the double layer is thin and van der Waals attraction dominates, with aggregation mainly FF. Conversely, the pH effect is greatest at low NaCl concentrations.

Gorakhki and Bareither [54] evaluated the effect of salinity and cation valence on kaolinite and bentonite sedimentation. Increased salinity led to higher bentonite sedimentation rates and final solids contents. In contrast, 100 mM salt was identified as a critical concentration whereupon kaolinite settling decreased, regardless of salt type, attributed to an increase in fluid density and viscosity. Recent studies on Q38, a commercial kaolinite, also showed high salinity slowing suspension settling rates [55,56], with crystallinity possibly a factor. Poorly crystallized kaolinite particles are disordered, leading to more complex surface structures and higher specific surface areas [57]. Due to the complex structure of Q38, more of the porous EF aggregates that easily trap water are thought to be generated in the presence of Ca²⁺, leading to slower settling in synthetic saline liquors.

Saline process waters from mine sites will typically have a much more complex composition than synthetic liquors used in the above studies. Their composition will depend on the ore being processed, the reagent suite, the water source and how it is managed on the site, as well as being affected by the climate [58]. Biotic constituents (e.g. microorganisms) may also be present.



Fig. 3. Postulated particle associations (preferred minimum energy configurations) for kaolinite in NaCl liquors. Mixed symbols represent changes in observed association mode due to boundary conditions (from [53], copyright (2005) with permission from Springer Nature).

3.2. Flocculation of clays

The size and settling rates of aggregates formed from clays by simple coagulation are quite low and almost always inadequate for any industrial solid-liquid separation applications requiring high throughputs. Coagulation may be sufficient to settle clays in wastewater clarification, but gravity thickening in mineral processing, continuous centrifugation and even filtration will often only be practical if additional aggregation is achieved.

High MW polymers facilitate particle aggregation (and thereby gravity settling) through a number of adsorption mechanisms that cause particles to 'bridge' together, e.g. through hydrogen bonding, charge patch neutralization, electrostatic, chemical, or other forms of bridges [37,59,60]. Bridging requires polymer chains to be adsorbed on surfaces with only limited functionality attachment per particle, the remainder for each polymer projecting into the surrounding solution (the 'tail' shown in Fig. 4), potentially available for contact and adherence to other particles [61,62]. While adsorption of individual polymer functionalities is weak, having multiple functionalities in an adsorbed segment ('train') leads to an effectively irreversible bond [63].

A polymer having a strong affinity for a surface does not necessarily assist in flocculation. It can cause surface saturation, preventing effective bridging when the proportion of loops and trains increases at the expense of tails, as illustrated in Fig. 5 [64]. In extreme cases, this can lead to the restabilisation of fine particle dispersions.



Fig. 4. Polymer adsorption on a surface (adapted from [62], copyright (1993) with permission from Springer Verlag London Limited).

The nature of aggregates formed by flocculation depends on factors that include the properties of the solids (surface charge, mineralogy, size, size distribution, shape, density), the liquid phase (viscosity, dielectric constant), the suspension (electric charge, pH, ionic strength, temperature), and the flocculant (MW, MW distribution, functionality, charge density, chain branching), with many of the conclusions that can be drawn from the literature summarized in Table 1. Clay flocculation is particularly affected by the distinct surface properties of the different particle faces, a significant point of differentiation from other phases that may be present within tailings, and there is therefore much greater potential for variations in particle packing behaviour in clay-rich tailings to influence consolidation in gravity thickening.

Common flocculants include synthetic water-soluble organic polyelectrolytes, for which the properties and physical forms can be controlled when polymerising selected monomers (e.g. acrylamide and ethylene oxide), or natural polymers (e.g. starches, guar gum, tannins and sodium alginate). The natural polymers are non-toxic, whereas some synthetic flocculants may be toxic, mainly from the potential for residual monomers to be present. The polymers applied in flocculating clays are discussed below and their properties also summarized in Table 1.

3.2.1. Cationic polymers

Cationic polyacrylamides (CPAM) are made by copolymerising acrylamide with quaternary ammonium derivatives of acrylamide. They contain 10 to 80 mol% of cationic monomer, although typically only 10% for higher MWs that can act as flocculants [76]. Methacrylate copolymers are also commercially produced. Poly(diallyl dimethyl ammonium chloride), better known as polyDADMAC, is usually of low-tomedium MW, but higher MW copolymers with acrylamide are available.

Cationic polymers are effective for aggregating low solid clay suspensions in wastewater clarification, generally by coagulation. Their main application as flocculants is in fine coal or coal tailings thickening [65]. They are not widely used in high throughput applications because they struggle to achieve high settling rates.

Cationic polymers adsorb onto negatively charged fine particles via a charge neutralization mechanism. When this occurs with higher MW CPAMs, there may still be tails that project beyond the surface, and collision with negative patches on other particles allows bridging aggregation [61]. In contrast, bridging by low MW CPAM is impeded by their



Fig. 5. Polymer conformation and adsorption on clay particles (adapted from [64], copyright (2006) with permission from Elsevier).

short macro-ion length, promoting coagulation but thereby only forming small aggregates.

Laird [66] found CPAM to be highly effective at flocculating Na- and Ca-saturated kaolinite, illite and quartz, regardless of electrolyte concentration, the presence of excess salt or saturating cations. It was slightly less effective at a basic pH (10.9) than under neutral (pH 5.9–8.2) or acidic (pH 3.4) conditions. Charge neutralization involving positive trimethyl ammonium groups on CPAM and negative surface sites was considered the dominant bonding mechanism. Nasser and James [64] also identified that optimum kaolinite flocculation by CPAM was through charge neutralization.

Polyethylenimine (PEI) is a polyamine that can be linear or branched; when not quaternised, its charge in solution is pH dependent, but likely to be cationic in most slurries. Leong et al. [101] observed that adding PEI of MW 70,000 to kaolinite significantly increased the yield stress at all pH values due to particle bridging to form stable aggregates. Avadiar et al. [102] also investigated the effect of branched PEI on kaolinite slurries at pH 8, finding low dosages of 0.004 and 0.04 dry weight percentages (dwb%) did not alter inter-particle forces and thus rheological and sedimentation behaviour. However, at 0.4 dwb% PEI, the yield stress was significantly higher and sedimentation was much enhanced, attributed to strong and voluminous aggregate formation by particle bridging. In comparison, branched PEI MW had negligible effects on slurry behaviour.

3.2.2. Anionic polymers

Water-soluble polymers of defined anionic character are synthesized by either partial hydrolysis of the acrylamide homopolymer or copolymerizing acrylamide with acrylic acid. Commercial anionic polyacrylamide (APAM) products cover a wide range of charge densities and MWs. The monomer sodium 2-acrylamido-2-methyl-propane sulphonate (AMPS) can be copolymerised with acrylamide to give products of comparable flocculation activity to APAM with many substrates, but at a lower MW [103]. As a stronger acid than acrylic acid, the AMPS functionality remains unprotonated at lower pH. Polymers containing AMPS are less sensitive to calcium and other divalent solution cations, however, they may be precipitated by aluminium at pH < 5 [76].

Anionic polymers are extensively used to flocculate clays within mineral processing applications. The polymer bridging mechanism is then of primary importance, with charge neutralization either not applicable or a minor factor [67]. High MW APAM is more effective than CPAM in flocculating negatively charged particles to give larger aggregates and faster settling. In addition, restabilisation of kaolinite colloids by excessive polymer adsorption is much less likely. The electrostatic repulsion between the polymer's COO⁻ pendant groups and negatively charged surfaces allows only limited points of polymer adsorption to each clay particle (even at basic pH values, some minor fraction of neutral surface sites will be available). At the same time, the polymer's expanded conformation arising from charge repulsion produces loops and tails, which, in conjunction with possible steric hindrance due to APAM chain branching, leads to the formation of loose, open, and fragile aggregates [67]. This effect has been found effective in flocculating negatively charged kaolinite dispersions [64].

The adsorption of APAM to clay surfaces has been extensively investigated. Laird [66] claimed cation bridging (APAM-Ca²⁺-clay) was the major polymer bonding mechanism. Other mechanisms suggested include: (i) hydrogen bonding between electronegative APAM moieties and protonated non-bridging aluminol groups on kaolinite and illite edges; and (ii) hydrophobic bonding between the APAM carbon chain and kaolinite basal faces. Heller and Keren [69] reported that APAM adsorption usually happened on clay edge surfaces. The main driving force for adsorption may be hydrogen bonding with silanol and aluminol OH groups at the clay surfaces, particularly between edge faces and the polymer's amide (-CONH₂) groups (Lewis base) [70]. Others found that at neutral pH, the majority of particles are negatively charged and electrostatic repulsion may reduce the amount of APAM adsorbed on kaolinite [68,71]. It should be noted that only low adsorption levels are required to promote flocculation at the typical tailings particle sizes, and therefore flocculation performance will not necessarily be influenced by changes in plateau adsorption values.

Laird [66] found the flocculation efficacy of APAM varied with the saturating cation ($Ca^{2+} >> Na^+$), mineralogy (kaolinite > illite >> quartz), and treatment (acid > salt > H₂O > base), concluding cation bridging between APAM COO⁻ groups and negative clay surface sites explained much of the observed behaviour. Hydrogen bonding between electronegative APAM functional groups and protonated nonbridging aluminol groups on phyllosilicate edges was indicated under acidic conditions. Nasser and James [64] investigated the importance of APAM and CPAM charge density and MW in relation to surface chemistry, settling rates, aggregate sizes, and sediment compaction for kaolinite at neutral pH. At optimum polymer dosages, aggregate sizes and settling rates were greater for APAM than CPAM. Optimum flocculation for APAM flocculants was linked to only a small reduction in the zeta potential.

3.2.3. Nonionic polymers

Starch-based and nonionic synthetic polymers are commonly used to enhance dewatering; the latter are often preferred in the presence of multivalent cations or at high ionic strength, conditions that may adversely influence APAM performance [72]. The homopolymer of acrylamide PAM is nominally nonionic, although most commercial products contain up to 1% anionic character.

Heath and Tadros [48] found sodium montmorillonite flocculation by poly(vinyl alcohol) (PVA) was by particle bridging, the optimum dosage being 2–3% PVA (based on the clay content). The structures formed were rigid and shear-resistant, but sensitive to pH, which needed to be controlled carefully.

Polyethylene oxide (PEO) has been widely examined for clay flocculation [19,67,104]. Hydroxyl groups on kaolinite edges interact with ether oxygens on PEO chains, forming hydrogen bonds and giving bridging flocculation [105]. Mpofu et al. [67] claimed that for kaolinite dispersions at low ionic strength, PEO produces better inter-particle bridging, greater settling rates and higher aggregate compaction upon shear than APAM. Polymer specific adsorption and conformational

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Table 1

Table 1	(continued)
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Drivers	Key effect summary	Reference
рН	Higher pH assists kaolinite and bentonite to go from EE-, EF-dominated structures to denser FE aggregates	[14,27,40]
	EF structures are less likely to be a major factor in smectite	[14,27,46]
Ionic strength	Higher salinity generally favours denser FF aggregates for both	[7,27,47,49,50]
	Lower crystallinity kaolinite more likely to form lower density EF aggregates at high	[55,56]
	Effective ions initiating clay aggregate structure changes: Na ⁺ , Ca ²⁺ , Cu ²⁺ , Al ³⁺ and Mn ²⁺ .	[14,29,50–52]
Cationic polymer flocculant	Charge neutralization is major adsorption/aggregation mechanism.	[61,64]
	Cationic polymers not widely used beyond fine coal or coal tailings thickening, due to small aggregates and low settling rates	[65]
	CPAM more effective in neutral and acidic than basic conditions for flocculating Na- and Ca-saturated kaolinite, illite and quartz	[66]
Anionic polymer flocculant	Polymer bridging mechanism of primary importance; APAM more effective than CPAM, forming open and fragile	[67]
	APAM adsorption to clays very dependent on surface structure and adsorbed/exchanged	[66,68–71]
	APAM efficacy varied with mineralogy (kaolinite > illite >> quartz), saturating cation (Ca ²⁺ >> Na ⁺), and liquor (acid > salt > $H_2\Omega$ > base)	[66]
Nonionic polymer flocculant	Bridging by starch-based and nonionic synthetic polymers; latter often preferred at high salinity or if multivalent cations present.	[72]
	2–3% PVA can effectively flocculate sodium montmorillonite.	[48]
	PEO may be a better flocculant than APAM for smectite at low salinity, giving greater consolidation	[67]
Polymer flocculant solution activity	Powder and emulsion products need ageing during make-up to reach maximum activity	[73–76]
	Long chain polymer solutions are shear-sensitive. Activity can be strongly affected	[77-79] [65.72.80-82]
Salt effect on polymer	by water quality used in make-up. Salinity induces higher APAM	[83]
flocculation	adsorption onto kaolinite due to polymer conformational changes.	r1
	Hydrolysis of added Mn^{2+} or Ca^{2+} to $Mn(OH)^+$ or $Ca(OH)^+$ increases kaolinite settling rates on flocculation by APAM	[84]
	Salinity favoured APAM adsorption and reduced particle	[85]

Drivers	Key effect summary	Reference
	repulsion, resulting in enhanced aggregation and settling. High salinity gives compressed chain conformations that may limit bridging and hindered	[56,72,86]
	settling at higher dosages. Molecular dynamics predicts competing effects of salinity – increased polymer adsorption but raduced conformation	[87]
	Salinity favours EF clay structures prior to flocculation	[55,56]
	Controlling initial coagulated clay size may impact on	[88]
Shear during polymer flocculation	flocculated aggregate density. "Tapered shear" favours initial mixing of flocculant and	[89–91]
	Subsequent aggregate growth. Optimum dewatering conditions may be established with respect to applied mixing intensity, time, polymer type,	[39,92–97]
Shear during sedimentation/consolidation	MW, cations and device. Aggregate structure densification confirmed from rake action.	[98]
	Raking assists in water release from aggregate structures and improves suspension consolidation.	[67,71,99,100]

effects are believed responsible for differences in the shear-sensitivity of nonionic PEO and APAM flocculated kaolinite aggregates and their subsequent dewatering.

Zhang et al. [106] studied the effect of a polycarboxylate ether (PCE) *comb*-type polymer on the viscosity and interfacial properties of kaolinite. At pH 3.4, a higher viscosity was attributed to strong electrostatic interactions between the clay's oppositely-charged basal and edge faces. At pH 8.3, suspension viscosity initially rose with added PCE but then decreased at higher dosages. At low dosages, hydrogen bonding led to network structures and hence an increased suspension viscosity. However, at high dosages, clay particles were fully covered by PCE, and steric repulsions then resulted in dispersion. These findings suggest that polymer type and application conditions can have competing effects on the settling behaviour of clays.

3.2.4. Factors affecting polymer flocculant activity

The acrylamide/acrylate copolymers used as flocculants in most mineral processing/hydrometallurgical applications are high MW, long chain polyelectrolytes that are relatively slow to dissolve and achieve a solution state optimal for flocculation. It is therefore important to ensure the properties of these aqueous solutions are optimised prior to dosing for flocculation.

The flocculant products used to treat tailings are typically received in either powder or emulsion form, with subsequent solution make-up conditions affecting their activity. The former need to be wetted carefully to avoid gels of agglomerated polymer that are unlikely to disperse [73]; even under ideal conditions, some powders take several days to reach maximum activity, after which they slowly reconform to reduced solution dimensions and lose activity [74,75]. Powder product dissolution by stirring is favoured for concentrations of 0.25–0.50%, with the high viscosity believed to provide internal friction that aids the rate of dissolution and chain dispersion [76]. Optimal ageing maximised the discrete polymer concentration available for flocculation, leading to an increase in aggregate size without appearing to impact the aggregate structure (density).

Products in an emulsion form (where concentrated aqueous flocculant drops are dispersed in an organic phase, with the emulsion then inverted by shear during make-up) are easier to prepare as concentrated solutions that rapidly attain a usable activity, but still may not reach their maximum appreciably quicker than powder products. This is attributed to slow disentanglement of highly agglomerated polymer chains, affected by the polymer MW [75]. In practice, ageing times rarely exceed 4–8 h, often a compromise due to storage capacity; where powder stock solution ageing times are less than an hour, required dosages can rise sharply, then putting even greater pressure on ageing times.

The polymer solutions are also shear-sensitive, further complicating flocculant make-up and application. While applying low shear is an important part of make-up, excessive shear adversely affects activity. High speed stirring and the action of pumps leads to a permanent loss of MW [77–79]. In contrast, transport through pipes is found to induce entanglement of the polymer chains that may be reversible [79]. In practice, both outcomes can lead to higher required dosages or the inability to achieve the desired settling rates in high throughput units.

Flocculant activity can also be affected by the guality of water used during make-up. Henderson and Wheatley [65] claimed the presence of Ca²⁺ and Mg²⁺ in flocculant solutions did not influence subsequent clay flocculation, arguing the 1:1 complexes formed with carboxylate functionalities have a minor effect on polymer conformation. In contrast, Cu^{2+} could chelate to two carboxylates, leading to a much more compact conformation. Rey [80] observed a significant loss of flocculant activity with a predominantly clay tailings from make-up and subsequent dilution in increasing liquor Ca²⁺ concentrations; Peng and Di [81] attributed a similar Ca²⁺ effect to polymer coiling and precipitation on clay surface. However, these results are far from convincing due to the inevitable poor control of applied shear in conventional batch cylinder or jar tests. Witham et al. [72] studied how water quality (and in particular multivalent cations) in make-up and dilution liquors impact upon flocculant activity in continuous flocculation within a Couette device providing greater control of residence time and mixing. While solution iron was found highly detrimental to performance for dilute flocculant solutions, the impact of divalent Ca²⁺ and Mg²⁺ was more subtle, only affecting settling rates at higher dosages, an effect masked under stronger applied shear conditions that favour some degree of aggregate breakage. Such effects increased with the flocculant's anionic character and the cation concentration.

For many polymers in solution, increasing salinity will result in a reduced hydrodynamic radius due to the interaction between the salt and active functional groups on the polymer chain, rendering it impaired or inactive for flocculation. As this interaction is unavoidable, flocculation under high salinity remains a difficult challenge to overcome. Dao et al. [82] therefore sought to synthesize ABA block copolymers (i.e. 100% polyacrylate chain at each end and 100% polyacrylamide inbetween), for which the conformation may be less sensitive to salt than the random copolymers, which may then offer advantages for flocculating clays in highly saline liquors [107].

3.2.5. Salt effect on polymer flocculation

The flocculation efficiency of a polymer with clays can be affected by salt ions in the tailings suspensions. Studies have covered experimental conditions of clays and water from different sources and can be generally differentiated into two categories: synthetic clay suspension with controlled water composition (Condition 1); and systems using real tailings and process water (Condition 2). Contrasting observations from different experimental systems enables a better understanding of how clay-rich tailings are flocculated in saline process waters. The different experimental categories used are specified in the discussion below.

Siffert and Bocquenet [83] found APAM adsorption onto kaolinite was higher in strongly saline water than in pure water (Condition 1), with polymer uptake inversely proportional to its degree of hydrolysis. The latter was explained in terms of conformational changes induced by salts. Adsorption in CaCl₂ solution was greater than in the same concentration of NaCl. In the presence of the surfactant sodium dodecylbenzenesulfonate, polymer adsorption was reduced in NaCl solutions but unaffected in CaCl₂ solutions, as the latter induced surfactant precipitation.

Mpofu et al. [84] reported how prior addition of divalent cations $(Mn^{2+} \text{ or } Ca^{2+})$ that undergo hydrolysis to a monovalent complex $(Mn(OH)^+, Ca(OH)^+)$ resulted in increased settling rates for kaolinite flocculation by APAM (Condition 1). The adsorbed cations facilitated polymer bridging due to both electrical double-layer compression and zeta potential reduction, allowing close approach of particles and increasing the positive sites available to bind with APAM carboxylate functionalities. Hydrogen bonding may also occur between the polymer's amide groups, OH groups at the clay surface, and hydration layers surrounding surface adsorbed cations. The adsorption density of APAM depended on pH and cation solution concentrations. That their flocculation tests were at a single high concentration (8 wt%) and dosed with quite concentrated flocculant (0.1 wt%) makes the relative impacts on settling rates questionable.

Ajao et al. [108] proposed a detailed mechanism for natural microbial extracellular polymeric substances (EPS) as flocculants for saline and non-saline kaolinite suspensions coagulated with Ca^{2+} (Condition 1). At high salinity, hydrogen-bonds are easily formed between amides (of EPS-protein) or hydroxyl groups (of EPS-polysaccharide) and kaolinite surface hydroxyl groups after electric double layer suppression, thus forming EPS particle bridges (Fig. 6a). A similar mechanism was reported for APAM flocculation of both saline mine tailings and kaolinite [109]. However, in non-saline kaolinite suspensions coagulated with 100 mg/L Ca^{2+} , the ionic strength (0.0075 mol/L) was possibly too low for significant suppression of DLVO-type electrostatic repulsions to favour hydrogen-bonding, making divalent cation bridging more likely to control flocculation. Despite electrostatic repulsions, Ca^{2+} can bridge between the polymer's anionic groups and negative kaolinite surface sites (Fig. 6b).

Zhang et al. [110] reported that carbonate minerals, especially gypsum, can release Ca^{2+} and Mg^{2+} to increase the hardness of recycled water, resulting in higher settling rates for flocculated coal tailings and



Fig. 6. Proposed kaolinite flocculation mechanisms with EPS in (a) saline suspension (hydrogen bonding after double layer suppression), (b) non-saline suspension coagulated with 100 mg/L Ca^{2+} (divalent cation bridging mechanism) (from [108], copyright (2018) with permission from Elsevier).

better supernatant clarity (Condition 2). In studying coal tailings flocculation by NPAM, APAM and Al(OH)₃-polyacrylamide (Al-PAM) in both freshwater and saline solutions, Ji et al. [85] found APAM gave the best settling. Representations of how ionic strength impacts on the adsorbed polymer conformations are shown in Fig. 7. In fresh water, relatively short-range hydrogen bonding between amides on APAM and Si-O-Si and Si-OH surface groups may be inhibited by long-range electrostatic repulsions, and hence adsorption and bridging were relatively weak. At increased salt concentrations, both the particle electrical double layer and the APAM conformation were much compressed (Fig. 7a). Hydrogen bonds could therefore be more easily formed to enhance polymer bridging; together with reduced electrical repulsion among the particles, aggregation rates and settling enhanced compared to tailings in fresh water. Ionic strength had a negligible effect on conformation for both NPAM and Al-PAM polymers (Fig. 7b) due to their neutral charge.

Saline water may also have a negative impact for some flocculants. Wang et al. [86] investigated the influence of suspension salinity (viz., addition of NaCl and CaCl₂) on kaolinite flocculation with chitosan graft polyacrylamide (chi g PAM), also conducting surface and atomic force measurements on model substrates (Condition 1). Initial settling rates declined with increasing NaCl and CaCl₂ concentrations (from 0.01 to 1 M). High salinity led to relatively weak adsorption and more compressed conformations for chi-g-PAM on both silica and alumina surfaces (both represented within kaolinite), as well as weakening bridging interactions between mica surfaces (a silicate structure similar to kaolinite). Liu et al. [56] also observed high salinity assisted settling of APAM-flocculated bentonite and illite but hindered that of the kaolinite Q38. The bridging effect was best above a threshold dosage level for illite but tailed-off for both kaolinite and bentonite, suggesting other factors may come into play.

Quezada et al. [87] used molecular dynamics to simulate the impact of NaCl concentration on the conformation of an anionic polymer and its adsorption on a quartz surface at pH values above its IEP. Increased salinity was predicted to lead to two competing effects, as shown in Fig. 8: (i) increased polyelectrolyte adsorption would favour initial aggregateforming collisions due to counter-ion effects on surface interactions; while (ii) the polyelectrolyte's reduced radius-of-gyration may then limit the aggregate size achieved. This modelling is consistent with experimental observations for the performance of long-chain watersoluble polymer flocculants in highly saline liquors [72,111].

An interesting insight from the simulations by Quezada et al. [87] is that the predicted adsorption density of the anionic polymer onto quartz rose by several orders of magnitude over the range of NaCl concentrations considered. Such adsorption at a low ionic strength for anything other than a low pH would only take place in the presence of adsorbed multivalent cations. High solution Na⁺ levels serve to both adsorb on the surface and shield the —COO⁻ groups on APAM, enabling polyelectrolyte and quartz interactions. Given quartz is a common phase in tailings slurries, salinity may be an important factor in promoting co-flocculation.

While high settling rates result from increased aggregate size, sediment consolidation may then diminish due to the more porous structures and how they pack [9]. Liu and Peng [55] reported that kaolinite flocculation with PEO formed more compact aggregates in fresh water than in synthetic saline liquors matching concentration from a mine site, with the dominant EF associations in the latter leading to slower settling. Liu et al. [56] also attributed distinct settling responses for kaolinite, bentonite, and illite flocculated in synthetic saline liquors to distinct aggregate structures, confirmed by cryo-SEM images of 5 wt% kaolinite flocculated with 200 g/t APAM at low- and high-salinity. Large FF structures at low-salinity (Fig. 9a) suggested adding APAM triggered strong kaolinite aggregation. In contrast, less dense, slower settling EF aggregates dominated at high-salinity (Fig. 9b). Adjusting solution and particle chemistry conditions to control aggregate structures can therefore influence solid-liquid separation, although this is rarely targeted in tailings applications.

Wilkinson et al. [88] found the initial size of coagulated bentonite was a bigger factor than ionic strength in determining flocculated aggregate structures. At high ionic strength, a low coagulated clay size led to rod-like flocculated aggregates typically observed only at low ionic strength and a highly networked internal structure. A larger coagulated size at the same high ionic strength resulted in more regular, compact aggregates. Controlling initial effective clay sizes should therefore be given more consideration in applications where higher aggregate densities are sought.

3.2.6. Effect of applied shear conditions

3.2.6.1. Shear during polymer flocculation. The applied hydrodynamic shear is known as a key factor during polymer-induced flocculation, with the potential for profound impacts on settling rates and, to a lesser extent, sediment consolidation. Flocculation under lower shear favours large, fast settling aggregates, while very high shear will normally result in irreversible aggregate degradation, although smaller aggregates will give some additional long-term sediment consolidation [8,112]. Higher mean shear rates actually accelerate both aggregate growth and breakage, but higher exponents in the breakage response limit the sizes attained [76]. The peak aggregate size will decline with increasing shear rate, and the degree of aggregate breakage at reaction times beyond this peak will increase.



Fig. 7. Representation of ionic strength impacts on flocculant conformation and adsorption on negatively-charged particle surfaces: (a) APAM, (b) PAM and Al-PAM (from [85], copyright (2013) with permission from Elsevier).



Fig. 8. Simulated response of a short-chain APAM to changes in salinity and its interaction with quartz (red represents oxygen, blue spheres are sodium cations). Water molecules are not shown for clarity of flocculant-surface interactions (from [87], copyright (2018) with permission from Elsevier). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The importance of considering both the applied shear intensity and duration was highlighted by Owen et al. [91] in experiments with staged shear (i.e. from high to low in different pipe diameters), finding the residual activity of surface adsorbed flocculant at short reaction times allowed subsequent growth under reduced shear [91]. Such growth was absent at reaction times beyond the peak due to flocculant then being effectively deactivated, and hence the settling rate differential was much greater than expected on the basis of aggregate size measured within the pipe. This is a clear illustration of how "tapered shear" (i.e. shear is initially high but then decreases) favours flocculant mixing and initial bridging collisions, but then provides milder conditions to maximize aggregate growth. The concept is well understood in water treatment applications [89,90], but also forms the basis for optimal flocculation in mineral processing.

Flocculation of kaolinite [92,98] and smectite [94] with ionic and nonionic PAM polymers indicated optimum dewatering conditions may be established with respect to both the applied mixing intensity and time. Yeung et al. [93] observed such optimums in hydrodynamic conditions did not coincide with those for maximum aggregate strength, claiming densification under shear may contribute to strength. Using hydrocyclones for dewatering is ineffective for particles <20 µm, and the high shear generated doesn't favour large aggregates from flocculation, but Franks et al. [96] found 90% of aggregates formed from dosing an ultrahigh MW APAM to submicron tailings (in conjunction with a low MW cationic coagulant) were still >38 µm. Yalcin and Brunet [95] claimed good hydrocyclone performance for a "shear resistant flocculant", which was actually a cationic of lower MW than the anionic products studied; shear-resistance most likely reflected forming smaller aggregates and more chains provided by a lower MW polymer.

McFarlane et al. [14] studied orthokinetic flocculation of kaolinite and smectite by applying shear with a two-blade paddle impeller, achieving significantly higher settling rates than produced by manual plunger mixing or cylinder inversions, although inadequate flocculant dilution makes that conclusion questionable. Their optimum conditions involved pre-coagulation, moderate agitation rates, shorter agitation times and using APAM rather than NPAM, the latter due to APAM's more expanded conformation favouring particle bridging.

Impellers like that used by McFarlane et al. [14] provide inadequate control over the applied shear to then isolate its effect on flocculation, a criticism applicable to most studies in this area. Costine et al. [97] addressed this by continuous flocculation under tightly controlled mixing in a Couette device with a vertical flow-through arrangement that enabled operator-independent settling rate measurements. They considered the influence of applied mixing (intensity and duration), solids concentration, and liquor chemistry on the MW (as measured by intrinsic viscosity) response of seven 30% anionic PAM polymers when flocculating a standard kaolin slurry at pH 8. Lower MWs were more dosage-effective under mild mixing, producing denser, faster-settling aggregates than equivalent sizes produced with higher MWs. However, larger sizes possible with



Fig. 9. Cryo-SEM micrographs of 5 wt% kaolinite flocculated with 200 g/t APAM in (a) low-salinity and (b) high-salinity water at 10000× (with sublimation at -100° for 5 min) (from [56], copyright (2018) with permission from Elsevier).

higher MWs gave access to faster settling after intense mixing. While <0.01 M Na⁺ in slurries favoured some pre-coagulation, Fig. 10 shows Ca²⁺ adversely affected settling rates even at <0.002 M, with the effects of a reduced bridging capacity most apparent for lower MWs. Comparisons of aggregate density from flocculating at low and high ionic strength (the latter in the presence of divalent cations) show denser structures for the latter, in part reflecting higher dosage requirements [39]. An advantage of raising aggregate density is a higher optimum solids concentration for flocculation, given solids dilution is normally sought prior to flocculation in tailings thickeners.

3.2.6.2. Shear during sedimentation and consolidation. Applied hydrodynamic shear can also have a strong influence on structures postformation as they pass through a thickener, at solids concentrations both below and above the gel point, ϕ_{g} (the concentration at which particles/aggregates are touching, above which a network structure develops). Flocculated clay aggregate structures are initially highly porous, with intra- and inter-aggregate water seen in networks at or above ϕ_{g} both needing to be released to achieve better dewatering. Farrow and Swift [113] characterized the size and free settling rate of aggregates at high dilution, demonstrating that samples taken from a diamond mine tailings thickener underflow were smaller but denser than those formed in the feedwell. Farrow et al. [98] extended this to sampling flocculated kaolinite from a continuous raked pilot column, confirming aggregate densification after raking was well above that seen from compressive dewatering in the bed alone.

Application of shear or compression to pre-sedimented, PEOflocculated suspensions are reported to give improved consolidation [67]. The better efficacy of PEO was attributed to a more extended and flexible (or elastic) configuration that favours more compressible aggregates when under load, a behaviour rarely displayed by comparatively inelastic APAMs. Gladman et al. [99] noted that low constant shear applied to settling aggregates induced some level of structural densification, such that higher solids concentrations were achieved without detrimental impacts on rheology, i.e. ϕ_g increased. Similar effects are claimed for the extra shear aggregates experience on rolling down sloped walls [100], as seen in lamella thickeners. There are no known results comparing how such effects are impacted by salinity, but the effect will be greatest for initial aggregates that are the most porous.

Rake structures projecting high into the settling zone could promote this effect, although the challenge is ensure most of the settling material is influenced. Hoyland and Day [114] claimed faster consolidation from the gentle mixing of a rotating picket, but with insufficient detail to separate this from effects on the bed solids. The concept was enhanced and applied to industrial tailings with Outotec's Shear Enhanced Thickening (SET) technology [115,116], where a radial arm higher up on the rake shaft had a series of 'shearing elements' along its length, angled with respect to the vertical plane – increasing element spacing with radial distance was critical towards giving uniform shear.

Rakes are a feature in almost every gravity thickener to move settled bed solids to the underflow discharge. Rotation rates are slow («1 rpm) to prevent bed disruption re-entraining settled solids. For porous aggregates formed from clay-bearing tailings, raking of compressed beds at low shear also assists in water release. Rakes and associated structures like vertical pickets produce channels for released water to rise [112], which can be critical given that permeability is reduced under consolidation. Du et al. [57] suggested that raking assisted dewatering by rearrangement of EE to FF structures for highly crystalline kaolinite. However, this did not apply to poorly ordered kaolinite Q38, with its ragged, broken nano sized edges on the basal surfaces thought to resist EF structure transformation at low raking shear forces. As a result, EF structures still dominate Q38 aggregates, leading to settled beds of lower density than high-crystallinity kaolinite [71].

Mechanical shear within beds was identified by Spehar et al. [117] as enhancing the rate and extent of aggregate densification in both a laboratory-based fluidisation rig and a pilot-scale thickener. From this, Scales et al. [118] developed thickener models incorporating the shear



Fig. 10. Effect of calcium concentration on settling rates of 60 g L⁻¹ kaolin slurries as a function of APAM dosage and intrinsic viscosity ([η]). Flocculant (0.005%) dosed into a continuous flow Couette device at 250 rpm with a residence time of 16.5 s (from [97], copyright (2018) with permission from Elsevier).

effect on aggregate structures through a shear rate dependent densification rate and final extent of densification. The model can predict quantitatively thickener underflow solids fluxes for a given flocculation condition without resorting to extensive pilot trials.

3.2.7. Other considerations

While there is almost always scope to optimize polymer-assisted flocculation in industrial tailings applications for faster settling, the greatest practical challenge confronting operators is to actually maximize suspension consolidation and the solids concentration discharged from thickener underflows. Tailings operations typically seek an underflow value from design studies as their main performance measure, despite the known variability of such concentrations strongly indicating that targeting a single underflow value for thickener control is unreliable [119]. Such targets are even more questionable when mineralogy varies, in particular when the type and proportion of clay within the tailings change.

It cannot be assumed that aggregate structures conducive to enhanced settling behaviour will also be optimal for sediment consolidation and underflow properties. There are undoubtedly situations where this is the case, such as (for example) where very ineffective feedwell flocculation leads to excessive flocculant dosages and low underflow solids concentrations from sediment networking, with improved flocculation then assisting in reaching underflow target values [120,121]. Such changes are more likely in applications with high fines or clay contents; flocculant dosages are inevitably much lower when feed particle size distributions are dominated by coarser phases, and hence flocculation impacts on sediments and underflows may then be only incremental.

As discussed above, processing tailings with significant clay contents at high ionic strength is likely to change the balance between precoagulation and final polymer-bridging flocculation to an aggregate size giving the required settling response. Any enhancement to the extent of coagulation for fines or ultrafines will lead to improved fines capture (i.e. better overflow clarity) and lower flocculant dosages to achieve moderate settling rates, with the possibility of some performance limitations if high settling rates are required. However, enhanced fines capture prior to flocculation will likely result in lower effective density of "core" aggregate structures that persist through to an underflow, and may then incrementally reduce the solids concentrations attained.

3.3. Enhanced dewatering by high polymer dosing at high solids

Concentrating tailings solids by thickening allows high volumetric throughputs, but conventional thickeners typically produce low yield stress underflows that need to be stored in tailings dams. Modern paste thickeners offer more powerful rake mechanisms and greater bed depths that then lead to high yield stress underflows [122]. While additional short-term water return from paste thickening may be small, the reduced tailings moisture, combined with effective deposition practices, leads to quicker drying to a load-bearing state, as seen with bauxite residues produced via the Bayer Process [123].

Such advantages may not be fully realised with clay-based tailings, given the highly porous flocculated aggregate structures formed, as already discussed. Pastes from high clay tailings can be deposited, but liquefaction (where shocks such as earthquakes lead to pastes becoming fluid) can then be a concern. For tailings from Canadian oil sands, a combination of residual bitumen, high pH and clay mineralogy results in slurries that are difficult to thicken conventionally, but also do not consolidate over time [124]. As a consequence, there are huge volumes of legacy tailings requiring further treatment prior to rehabilitation.

Adding polymer at high dosages (significantly greater than applied in thickener feedwells) to high solids tailings streams can generate much enhanced dewatering relative to that achieved from thickening alone, and is the subject of several patents [125,126]. McColl and Scammell [125] describe such dosing to a pipeline containing thickener underflow, mixing within to form "super-aggregates" – essentially a continuous network rather than individual aggregates. On deposition, the tailings exhibit a lava-like flow, channels quickly appear and water is rapidly released. The mixing is not specified, but it is stressed the effect cannot be achieved by flocculating in a thickener, as the material produced would then not be conducive to pumping.

Strong interest within the Canadian oil sands industry has seen fullscale applications, with considerable research into novel polymers and optimised dosing. However, the mechanism by which enhanced dewatering is achieved by polymer dosing at high solids is still poorly understood. Wells et al. [127] describe the process as "inline flocculation", reflecting reagents normally being dosed directly into pipe flow prior to deposition. Such a name is not ideal, as it implies it can only be done in that manner, and flocculation can still occur inline without enhanced dewatering on deposition. In addition, calling the process "flocculation" leads to assumed parallels with the conventional process that are not necessarily valid, as will be discussed below. Despite this, the term has gained wider acceptance, and will be used here.

Wells et al. [128] not only highlight the need for the process to be done at high solids, but also the importance of the correct applied shear regime. Flocculant must be added under high shear, with subsequent tapered shear to give the optimum discharge properties. Fig. 11 represents the main stages and the likely impact on performance measures. The stages are: (i) flocculant mixing and adsorption, with the start of aggregate growth; (ii) "aggregate rearrangement", when it is claimed aggregate growth and breakage are in balance; and finally (iii) "aggregate breakdown" which sees a reduced yield stress and the greatest water release. Extending the mixing too long leads to "overshear", and while the yield stress continues to reduce, little additional water is released.

Potential points of differentiation between "inline flocculation" and polymer-bridging flocculation at typical feedwell solids concentrations are summarized in Table 2, with Fig. 12 a representation (not to scale) of how the two processes may differ. Flocculant chains are not represented to simplify the images.

Self-similar fractal structures are maintained in polymer-bridging flocculation, from the initial particle aggregates through to subsequent growth by clustering. The aggregates are weak, reflecting the open structures and limited binding points, and so the response to shear applied after formation is breakage, with little actual densification. Some liquor is inevitably released, but the structures retain most.

With inline flocculation, initially formed core aggregates will be denser, due to closer particle proximity at higher solids concentrations. Clustering of such aggregates will also be influenced by the higher dosages, with additional bridges giving some further networking within clusters. The second step in Fig. 12 represents internal cluster rearrangement, with relaxation/contraction of multiple bridging chains possibly leading to densification. When the overall cluster breaks down to these internal clusters, a greater proportion of the originally encapsulated liquor is released, but any subsequent breakage releases less liquor.

Liquor is observed to be "ejected" or "squeezed" out of the networks, possibly the result of intense force/pressure inside such structures as newly-formed aggregates effectively compete with liquor for limited space. Aggregates may be held in position by a large number of bridging structures (a combination of high dosages and close proximity causing cross-aggregate bridging), hence the simplest route to creating more space is to eject unbound liquor. The "pressure" may also be responsible for aggregates effectively "collapsing" into each other and densifying, creating the beaching effect on deposition. The network structures were demonstrated by Adkins et al. [129] as an important point of differentiation from conventional flocculation.

Long mixing times (>30 s) are needed to achieve the sought-after continuous networked structures. This is unlike conventional flocculation, where solids contents are reasonably low and residence times



Fig. 11. The impact of mixing time on the main stages and performance responses for "inline flocculation" (from [128], image reproduced with kind permission of Australian Centre for Geomechanics, 14th International Paste and Thickened Tailings Seminar, Perth, Australia, 2011; www.acg.uwa.edu.au).

<5 s can give optimal aggregation. It is also suspected that the shear for inline flocculation after dosing should be close to laminar and not fully turbulent, as the aggregates formed are already exposed to intense breakage events due to the high particle concentration. A turbulent mixing zone will only exacerbate aggregate breakage.

Information on flocculant choice is not extensive, complicated by (i) high flocculant concentrations being needed, and hence the dosed solution's rheology becomes an issue, and (ii) poor small-scale procedures to compare products. The polymer chemistries used in full-scale applications appear similar to those used in feedwells, the main difference being in MW. Not surprisingly, lower MWs can favour mixing, but the presence of some higher MW components can be beneficial [130]. Given the strong interest in oil sands tailings applications, there are numerous studies of novel flocculant chemistries (e.g. [131–133], but evidence of their practical advantages over conventional chemistries has been unconvincing.

While adsorbed divalent cations on tailings particle surfaces also appears to be beneficial to inline flocculation, there is no published context available as to the likely impact of high ionic strength. From what is already known for flocculation at lower solids concentrations, increasing the liquor ionic strength may favour flocculant solution distribution through high solids suspensions, but if the polymer solution conformation is then in any way diminished, it would be doubtful that the necessary highly aggregated networking of tailings solids could be achieved.

4. Knowledge gaps and recommendations

Hart and Boger [134] suggested manipulating surface chemistry as an important area of future research for tailings dewatering. The rationale behind their statement is not in dispute, given the potential changes in clay aggregate structures as a consequence of varying surface properties. However, in most mineral processing applications, the state of particles and liquors within a thickener feed is determined by upstream (and sometimes downstream) requirements, with minimal scope for adjustment. Large volumetric flows rarely make pH or liquor composition adjustment viable when the primary objective is better tailings dewatering, although exceptions are known [135,136].

There may be far greater scope to reduce longer-term tailings impacts through choices made in the design phase for mineral processing,

Table 2

Contrasting feedwell flocculation vs. inline flocculation (from [39], copyright (2017) with permission from Cambridge University Press).

Aspect	Polymer-bridging flocculation	Inline flocculation
Flocculant mixing and adsorption	Adsorption is rapid, with effective surface coverage typically <20%.	Initial adsorption rapid, but at high dosages surface coverages may be >50%, slowing adsorption. Some unadsorbed?
Initial aggregation	High fraction of available surface makes bridging collisions effective; higher dosages increase collision efficiency. Lower solids concentrations reduce growth rates, but lower viscosity and shear-induced breakage.	High surface coverage lowers collision efficiency (fewer adsorption sites). High solids increases collision rate, but raises shear-induced breakage. High viscosity slows aggregation.
Adsorbed flocculant conformation	Polymer adsorbs irreversibly in a series of "trains"; bridging through tails, ~30–50% of polymer mass. Non-bridging tails rapidly reconform back to surface, losing bridging capacity.	Surface crowding limits extent of trains (esp. after initial adsorption) and bridging links. Is some adsorption irreversible? Tails may be less likely to reconform, retaining some activity.
Aggregate size	Limited by applied shear and dosage. Large sizes form, but there is an optimum solids concentration, above which size decreases.	Determined by solid concentration/viscosity, with limited impacts of applied shear (in terms of maximum size) and dosage.
Aggregate breakage	Breakage is irreversible – bridging chains are generally halved to shorter tails unlikely to bridge.	Sheared chains may retain bridging capacity at close aggregate proximity. Weak adsorption may allow chain detachment. Both reflected in a degree of reversible breakage (like coagulation).
Aggregate structure	Initial fractal aggregates further flocculated by clustering. Multiple bridges may exist. Large aggregates weak, but small core structures persist to underflow.	Initial aggregates small and dense. Clusters have many bridges, rearrangement of which may further densify. High level clusters are broken, but core persists.
Applied shear	Feedwell mean shear rates $40-80 \text{ s}^{-1}$, residence times $10-40 \text{ s}$; higher shear favourable during initial mixing (i.e. 2–5 s).	Mean shear rate 20–40 s ^{-1} (?), residence times 20–100 s.
Aggregate response to shear	Extended shear during flocculation favours breakage over densification. Low shear post-flocculation may give densification.	Initial "rearrangement" may involve substantial internal densification, followed by breakage – both may release water.



Initially formed particle aggregates come together as clusters, but still maintaining the same overall fractal structure.





Application of shear is more likely to break off aggregate fragments than lead to significant densification. Core particle aggregates may not be affected.



clustering forms a structure with more networked connections.

Under shear, clusters within the network contract, possibly from relaxation of the larger number of bridging chains. Subsequent breakage of these networks should then lead to the release of significant liquor from within.

Fig. 12. Representation of possible aggregate structures for polymer-bridging and inline flocculation processes, and the influence of shear forces (from [39], copyright (2017) with permission from Cambridge University Press).

rather than during operation or post-closure [137]. Edraki et al. [2] argued an integrated approach for tailings research linked to better processing options would have beneficial environmental outcomes, allowing consideration of processes that may not necessarily have short-term cost benefits but could reduce environmental problems and thereby have long term value.

Corder et al. [138] observed that while many organisations have internal sustainable development (SD) tools, there was not "a practical systematic, rigorous and standardised approach to capture SD opportunities in project management systems." They developed the SUSOP® framework, analogous to the HAZOP (Hazard and Operability Studies) safety approach, to identify and evaluate sustainability opportunities and risks early in the project life-cycle. Case studies included considering effluent management options for a mineral processing operation at the pre-feasibility phase [139]. Such an approach could provide the basis for a step-change in current practice, although it should be noted that the SD focus in relation to mineral processing waste streams has been on potential contamination within aqueous effluent streams, e.g. arsenic levels from flotation circuits [140], for which relevant, robust data is readily acquired. While there are well-established procedures to quantify the long-term geotechnical behaviour of polymeramended tailings (e.g. [141]), there is less clarity on how to quantify short- and medium-term tailings thickening and deposition behaviour (where polymer effects are greatest), such that novel processing options can be usefully assessed early.

An example where this may apply is in considering alternative lixiviants to cyanide for gold recovery. Leaching with cyanide requires the pH to be maintained at >10, with a high pH (and residual cyanide) persisting through to the tailings. Alternatives such as thiosulfate can offer the opportunity to leach at a neutral pH [142], providing a shift in tailings surface chemistry that is not readily achieved in a cyanide-based system. The SD implications should be significant, but even the SUSOP® approach will struggle to properly capture these without access to appropriate characterisation of how the physical behaviour of the tailings (with and without polymer treatment) would change. This characterisation is normally only available after extensive testwork, by which time flowsheets are invariably locked in. The challenge is to facilitate insights on how tailings may behave after novel processing routes at a much earlier stage.

An effective strategy to minimise tailings dewatering issues is to produce fewer fines. Low grade, finely disseminated ore bodies can push operations to finer grind sizes, but inefficiencies in this process can lead to overgrinding and excessive fines formation. Technologies do exist to achieve the required liberation without generating significant fractions <10 μ m [143]. However, grinding will usually have limited impact on the subsequent suspension particle size of clay phases, and hence will have most impact for ores when other gangue phases dominate.

From the available literature on how coagulants and flocculants impact on clay dewatering (Section 3), the following general observations can be made:

- Clay aggregate structures following flocculation are inevitably more open and water-retaining than those formed from particles with regular shapes and homogenous surfaces, however, optimising the flocculation process can increase aggregate density.
- ii) Suspension pH, solids concentration, ionic strength, mineralogy, polymer type, make up conditions, dosage, water quality and applied shear can all interact in a complex fashion to affect clay dewatering. While there are numerous studies of enhancing tailings dewatering using flocculants [3,38,144–146], few quantify the solid-liquid separation process in predictive modelling, and none success-fully capture key factors such as polymer dosage, clay mineralogy and water salinity. There are increasing examples of data-based modelling of performance outputs in preference to modelling of the underlying physical processes (e.g. [147]), and while these have potential in control when appropriate sensor data is available (which is rare), they are unlikely to offer important fundamental insights.

A major barrier to fully predictive modelling and even the ability to draw-out deeper insights into tailings flocculation is that inconsistent, ill-defined or inappropriate conditions are frequently applied when studying the process. Given the multiple overlapping stages involved in achieving aggregation and the fragile, timedependent structures formed, the lack of sophistication in preparative procedures is often surprising in what is otherwise detailed research. Many groups inappropriately apply jar test (i.e. stirred beaker) procedures from wastewater treatment to tailings-related studies, despite them being intended only for low solid or coagulation applications [8,148-152]. Reaction times in such vessels of several minutes may be appropriate at low solids, but rarely are at high solids. The consequences can be excessive dosages and the masking (or even reversal) of performance trends. Such issues currently prevent any definitive conclusions being drawn on how high salinity impacts upon tailings flocculation.

Cylinder testing, with mixing achieved by inversion or with plungers, does at least provide a degree of control over the duration of mixing that is more appropriate for tailings flocculation, but the challenge is ensuring reproducible mixing. Flocculation during continuous flow through a Couette device [153] enables high reproducible, rapid screening of conditions and products, and others have applied similar designs (e.g. [154,155]). Rulyov et al. [156] produced a smaller 'ultraflocculator' device that applies very higher shear and shorter residence times, which may be more appropriate to flocculation in filtration than feedwell applications.

Couette devices may not be fully turbulent under the conditions of interest and therefore extracting mean shear rates for modelling aggregation kinetics is not trivial. Options for residence time control under shear are also limited. Turbulent pipe flow allows reaction time control to a fraction of a second and the ready estimation of mean shear rates [157], although the initial version with a linear 22 mm ID pipe required slurry flow rates of at least 20 L min⁻¹. Grabsch et al. [103] scaled this down to 7.7 mm ID with lengths coiled to a diameter of 0.3 m, greatly reducing the experimental footprint and required flow rates (1 to 3 L min⁻¹). Secondary flow effects within helical coils can affect calculated shear rates and raise the Reynolds numbers required for turbulence, but in this case the coil is too large and the flow velocities too low for this to be significant. Essential to the success of this approach is the ability monitor realtime of aggregate dimensions at all solids concentrations (i.e. no need for sample dilution). Such studies have made use of focused beam reflectance measurement probes (FBRM, Mettler-Toledo) to produce reaction profiles of aggregate dimensions vs. time, but other instruments giving comparable information are known.

5. Conclusion

Mineral processing tailings typically contain significant fractions of colloidal and ultrafine particles that are mainly clays. Their layered structures lead to distinct basal face and edge surfaces, the aqueous suspension properties of which are readily modified to influence whether aggregation is by edge-edge, edge-face or faceface interactions, with the first two producing higher aggregate porosity. Clays therefore cause significant problems in tailings dewatering, often in the form of slow settling rates and poor consolidation. The impact of water chemistry on the interactions of clays within tailings was reviewed, with an emphasis on salinity effects and optimising polymer-induced flocculation to enhance dewatering. The latter includes contrasting conventional low solids flocculation for gravity settling with polymer dosing to high solids tailings prior to deposition. The review process highlighted a number of research challenges, from optimising the microscopic properties of the aggregates formed, through to how the practical impacts of such optimisation on long-term tailings behaviour can be captured early enough to influence the selection of mineral processing options. While there is evidence to suggest salinity alters flocculated aggregate density, ill-defined or inappropriate conditions in most published flocculation testwork represents the main barrier to deeper insights on the implications for tailings behaviour.

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References

- J.S. Adiansyah, M. Rosano, S. Vink, G. Keir, A framework for a sustainable approach to mine tailings management: disposal strategies, J. Clean. Prod. 108 (2015) 1050–1062.
- [2] M. Edraki, T. Baumgartl, E. Manlapig, D. Bradshaw, D.M. Franks, C.J. Moran, Designing mine tailings for better environmental, social and economic outcomes: a review of alternative approaches, J. Clean. Prod. 84 (2014) 411–420.
- [3] C. Wang, D. Harbottle, Q. Liu, Z. Xu, Current state of fine mineral tailings treatment: a critical review on theory and practice, Miner. Eng. 58 (2014) 113–131.
- [4] E. Sabah, H. Yüzer, M.S. Çelik, Characterization and dewatering of fine coal tailings by dual-flocculant systems, Int. J. Miner. Process. 74 (2004) 303–315.
- [5] O. Onuaguluchi, Ö. Eren, Recycling of copper tailings as an additive in cement mortars, Constr. Build. Mater. 37 (2012) 723–727.
- [6] G. Voordouw, Interaction of oil sands tailings particles with polymers and microbial cells: first steps toward reclamation to soil, Biopolymers 99 (2013) 257–262.
- [7] R. De Kretser, P.J. Scales, D.V. Boger, Improving clay-based tailings disposal: case study on coal tailings, AICHE J. 43 (1997) 1894–1903.
- [8] P. Ofori, A.V. Nguyen, B. Firth, C. McNally, O. Ozdemir, Shear-induced floc structure changes for enhanced dewatering of coal preparation plant tailings, Chem. Eng. J. 172 (2011) 914–923.
- [9] A. Mierczynska-Vasilev, M. Kor, J. Addai-Mensah, D.A. Beattie, The influence of polymer chemistry on adsorption and flocculation of talc suspensions, Chem. Eng. J. 220 (2013) 375–382.
- [10] P. Mpofu, J. Addai-Mensah, J. Ralston, Interfacial chemistry, particle interactions and improved dewatering behaviour of smectite clay dispersions, Int. J. Miner. Process. 75 (2005) 155–171.
- [11] I. Cengiz, E. Sabah, S. Ozgen, H. Akyildiz, Flocculation of fine particles in ceramic wastewater using new types of polymeric flocculants, J. Appl. Polym. Sci. 112 (2009) 1258–1264.
- [12] G.J. Sparrow, S.W. Ihle, Dewatering Clay Slimes: an Approach to the Problem, CSIRO Division of Mineral Chemistry, Report IR/126, 1978 57.
- [13] H.J.L. Wright, J.A. Kitchener, The problem of dewatering clay slurries: factors controlling filtrability, J. Colloid Interface Sci. 56 (1976) 57–63.
- [14] 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 (2006) 116–127.
- [15] M. Rahman, Dewatering of phosphatic clay waste by flocculation, Chem. Eng. Technol. 23 (2000) 457–461.

- [16] B. Wang, Y. Peng, The effect of saline water on mineral flotation a critical review, Miner. Eng. 66 (2014) 13–24.
- [17] W.A. Deer, R.A. Howie, J. Zussman, An Introduction to the Rock-Forming Minerals, Longmans, London, 1966.
- [18] M. Zhang, The Effect of Clay Minerals on Copper and Gold Flotation, University of Queensland, School of Chemical Engineering, 2016.
- [19] P.F. Luckham, S. Rossi, The colloidal and rheological properties of bentonite suspensions, Adv. Colloid Interf. Sci. 82 (1999) 43–92.
- [20] G.E. Morris, M.S. Zbik, Smectite suspension structural behaviour, Int. J. Miner. Process. 93 (2009) 20–25.
- [21] R.E. Grim, Clay Mineralogy, McGraw-Hill, 1968.
- [22] J. Środoń, Nature of mixed-layer clays and mechanisms of their formation and alteration, Annu. Rev. Earth Planet. Sci. 27 (1999) 19–53.
- [23] D.L. Sparks, 2 inorganic soil components, in: D.L. Sparks (Ed.), Environmental Soil Chemistry (Second Edition), Academic Press, Burlington 2003, pp. 43–73.
- [24] F. Bergaya, G. Lagaly, Chapter 1 general introduction: Clays, clay minerals, and clay science, in: B. Faïza, L. Gerhard (Eds.), Developments in Clay Science, Elsevier 2013, pp. 1–19.
- [25] V. Gupta, J.D. Miller, Surface force measurements at the basal planes of ordered kaolinite particles, J. Colloid Interface Sci. 344 (2010) 362–371.
- [26] S.L. Swartzen-Allen, E. Matijevic, Surface and colloid chemistry of clays, Chem. Rev. 74 (1974) 385–400.
- [27] E. Tombácz, M. Szekeres, Colloidal behavior of aqueous montmorillonite suspensions: the specific role of pH in the presence of indifferent electrolytes, Appl. Clay Sci. 27 (2004) 75–94.
- [28] E. Tombácz, M. Szekeres, Surface charge heterogeneity of kaolinite in aqueous suspension in comparison with montmorillonite, Appl. Clay Sci. 34 (2006) 105–124.
- [29] H.V. Olphen, An Introduction to Clay Colloid Chemistry, Second edition National Academy of Sciences, Washington, DC, 1977.
- [30] A. McFarlane, K. Bremmell, J. Addai-Mensah, Microstructure, rheology and dewatering behaviour of smectite dispersions during orthokinetic flocculation, Miner. Eng. 18 (2005) 1173–1182.
- [31] B. Rand, I.E. Melton, Particle interactions in aqueous kaolinite suspensions: I. effect of pH and electrolyte upon the mode of particle interaction in homoionic sodium kaolinite suspensions, J. Colloid Interface Sci. 60 (1977) 308–320.
- [32] G. Lagaly, Chapter 5 colloid clay science, in: B.K.G.T. Faïza Bergaya, L. Gerhard (Eds.), Developments in Clay Science, Elsevier 2006, pp. 141–245.
- [33] H. Olphen, Forces Between Suspended Bentonite Particles, Clays and Clay Minerals: Proceedings of the Conference, Pergamon Press, Symposium Publications Division, 1956 204.
- [34] R. Goh, Y.K. Leong, B. Lehane, Bentonite slurries-zeta potential, yield stress, adsorbed additive and time-dependent behaviour, Rheol. Acta 50 (2011) 29–38.
- [35] P.I. Au, Y.K. Leong, Rheological and zeta potential behaviour of kaolin and bentonite composite slurries, Colloids Surf. A Physicochem. Eng. Asp. 436 (2013) 530–541.
 [36] J. Gregory, Particles in Water: Properties and Processes, CRC Press, 2005.
- [37] J. Gregory, C.R. O'Melia, Fundamentals of flocculation, Crit. Rev. Environ. Sci. Technol. 19 (1989) 185–230.
- [38] R. Hogg, Flocculation and dewatering, Int. J. Miner. Process. 58 (2000) 223-236.
- [39] P. Fawell, Solid–liquid separation of clay tailings, in: A.J. McFarlane, C. Klauber, D.J. Robinson, M. Gräfe (Eds.), Clays in the Minerals Processing Value Chain, Cambridge University Press, Cambridge 2017, pp. 327–380.
- [40] G. Lagaly, Principles of flow of kaolin and bentonite dispersions, Appl. Clay Sci. 4 (1989) 105–123.
- [41] H. Van Olphen, An Introduction to Clay Colloid Chemistry, For Clay Technologists, Geologists, and Soil Scientists, Interscience, Wiley, New York, 1963.
- [42] F. Bartoli, R. Philippy, The colloidal stability of variable-charge mineral suspensions, Clay Miner. 22 (1987) 93–107.
- [43] H. Zhao, P.F. Low, J.M. Bradford, Effects of pH and electrolyte concentration on particle interaction in three homoionic sodium soil clay suspensions, Soil Sci. 151 (1991) 196–207.
- [44] D. Penner, G. Lagaly, Influence of anions on the rheological properties of clay mineral dispersions, Appl. Clay Sci. 19 (2001) 131–142.
- [45] M.S. Zbik, R.S.C. Smart, G.E. Morris, Kaolinite flocculation structure, J. Colloid Interface Sci. 328 (2008) 73–80.
- [46] R. Keren, D.L. Sparks, The role of edge surfaces in flocculation of 2:1 clay minerals, Soil Sci. Soc. Am. J. 59 (1995) 430–435.
- [47] M.S. Nasser, A.E. James, Settling and sediment bed behaviour of kaolinite in aqueous media, Sep. Purif. Technol. 51 (2006) 10–17.
- [48] D. Heath, T.F. Tadros, Influence of pH, electrolyte, and poly(vinyl alcohol) addition on the rheological characteristics of aqueous dispersions of sodium montmorillonite, J. Colloid Interface Sci. 93 (1983) 307–319.
- [49] J. Chen, J.H. Cushman, P. Low, Rheological behavior of Na-montmorillonite suspensions at low electrolyte concentration, Clay Clay Miner. 38 (1990) 57–62.
- [50] J. Stawinski, J. Wierzchos, M.T. Garcia-Gonzalez, Influence of calcium and sodium concentration on the microstructure of bentonite and kaolin, Clay Clay Miner. 38 (1990) 617–622.
- [51] R. Kjellander, S. Marcelja, R.M. Pashley, J.P. Quirk, Double layer correlation forces restrict calcium clay swelling, J. Phys. Chem. 92 (1988) 6489–6492.
- [52] Y.K. Leong, Yield stress and zeta potential of nanoparticulate silica dispersions under the influence of adsorbed hydrolysis products of metal ions-cu(II), Al(III) and Th(IV), J. Colloid Interface Sci. 292 (2005) 557–566.
- [53] A.M. Palomino, J.C. Santamarina, Fabric map for kaolinite: effects of pH and ionic concentration on behavior, Clay Clay Miner. 53 (2005) 211–223.
- [54] M.H. Gorakhki, C.A. Bareither, Salinity effects on sedimentation behavior of kaolin, bentonite, and soda ash mine tailings, Appl. Clay Sci. 114 (2015) 593–602.

- [55] D. Liu, Y. Peng, Reducing the entrainment of clay minerals in flotation using tap and saline water, Powder Technol. 253 (2014) 216–222.
- [56] D. Liu, M. Edraki, L. Berry, Investigating the settling behaviour of saline tailing suspensions using kaolinite, bentonite, and illite clay minerals, Powder Technol. 326 (2018) 228–236.
- [57] J. Du, R.A. Pushkarova, R.S.C. Smart, A cryo-SEM study of aggregate and floc structure changes during clay settling and raking processes, Int. J. Miner. Process. 93 (2009) 66–72.
- [58] W. Liu, C.J. Moran, S. Vink, A review of the effect of water quality on flotation, Miner. Eng. 53 (2013) 91–100.
- [59] 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 (2005) 27–34.
- [60] J. Kitchener, Principles of action of polymeric flocculants, Br. Polym. J. 4 (1972) 217–229.
- [61] M. Pearse, J. Barnett, Chemical treatments for thickening and filtration, Filtr. Sep. 17 (1980) 465–468.
- [62] G. Fleer, M.C. Stuart, J.M. Scheutjens, T. Cosgrove, B. Vincent, Polymers at Interfaces, Springer Science & Business Media, 1993.
- [63] J. Lyklema, The colloidal background of flocculation and dewatering, in: B.M. Moudgil, B.J. Scheiner (Eds.), Flocculation and Dewatering: Proceedings of the Engineering Foundation Conference Held at the Sheraton Palm Coast Resort, Engineering Foundation, Palm Coast Florida, New York 1989, pp. 1–20.
- [64] M.S. Nasser, A.E. James, The effect of polyacrylamide charge density and molecular weight on the flocculation and sedimentation behaviour of kaolinite suspensions, Sep. Purif. Technol. 52 (2006) 241–252.
- [65] J. Henderson, A. Wheatley, Factors effecting a loss of flocculation activity of polyacrylamide solutions: shear degradation, cation complexation, and solution aging, J. Appl. Polym. Sci. 33 (1987) 669–684.
- [66] D.A. Laird, Bonding between polyacrylamide and clay mineral surfaces, Soil Sci. 162 (1997) 826–832.
- [67] 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 (2003) 247–268.
- [68] L. Nabzar, E. Pefferkorn, R. Varoqui, Polyacrylamide-sodium kaolinite interactions: flocculation behavior of polymer clay suspensions, J. Colloid Interface Sci. 102 (1984) 380–388.
- [69] H. Heller, R. Keren, Anionic polyacrylamide polymer adsorption by pyrophyllite and montmorillonite, Clay Clay Miner. 51 (2003) 334–339.
- [70] P. Mpofu, J. Addai-Mensah, J. Ralston, Flocculation and dewatering behaviour of smectite dispersions: effect of polymer structure type, Miner. Eng. 17 (2004) 411–423.
- [71] J. Du, G. Morris, R.A. Pushkarova, R. St. C. Smart, Effect of surface structure of kaolinite on aggregation, settling rate, and bed density, Langmuir 26 (2010) 13227–13235.
- [72] M. Witham, A. Grabsch, A. Owen, P. Fawell, The effect of cations on the activity of anionic polyacrylamide flocculant solutions, Int. J. Miner. Process. 114 (2012) 51–62.
- [73] R. Hecker, P. Fawell, A. Jefferson, The agglomeration of high molecular mass polyacrylamide in aqueous solutions, J. Appl. Polym. Sci. 70 (1998) 2241–2250.
- [74] A.T. Owen, P.D. Fawell, J.D. Swift, J.B. Farrow, The impact of polyacrylamide flocculant solution age on flocculation performance, Int. J. Miner. Process. 67 (2002) 123–144.
- [75] A. Owen, P. Fawell, J. Swift, The preparation and ageing of acrylamide/acrylate copolymer flocculant solutions, Int. J. Miner. Process. 84 (2007) 3–14.
- [76] P. Fawell, S. Adkins, A. Costine, Chapter 6: Reagents, Paste and Thickened Tailingsa Guide, Third edition Australian Centre for Geomechanics, Perth, 2015 87–108.
- [77] N.D. Sylvester, M.P. Toure, Effect of shear on polymer aided flocculation of suspensions, Ind. Eng. Chem. Prod. Res. Dev. 17 (1978) 347–351.
- [78] J.P. Scott, P.D. Fawell, D.E. Ralph, J.B. Farrow, The shear degradation of highmolecular-weight flocculant solutions, J. Appl. Polym. Sci. 62 (1996) 2097–2106.
- [79] A.T. Owen, T.V. Nguyen, P.D. Fawell, The effect of flocculant solution transport and addition conditions on feedwell performance in gravity thickeners, Int. J. Miner. Process. 93 (2009) 115–127.
- [80] P.A. Rey, The effect of water chemistry on the performance of anionic polyacrylamide-based flocculants, flocculation and dewatering, engineering foundation, N. Y. (1988) 195–214.
- [81] F.F. Peng, P. Di, Effect of multivalent salts—calcium and aluminum on the flocculation of kaolin suspension with anionic polyacrylamide, J. Colloid Interface Sci. 164 (1994) 229–237.
- [82] V.H. Dao, N.R. Cameron, K. Saito, Synthesis, properties and performance of organic polymers employed in flocculation applications, Polym. Chem. 7 (2016) 11–25.
- [83] B. Siffert, Y. Bocquenet, Polyacrylamide adsorption onto kaolinite in the presence of sodium dodecylbenzenesulfonate in saline medium, Colloids Surf. A Physicochem. Eng. Asp. 11 (1984) 137–143.
- [84] P. Mpołu, 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 (2003) 349–359.
- [85] Y. Ji, Q. Lu, Q. Liu, H. Zeng, Effect of solution salinity on settling of mineral tailings by polymer flocculants, Colloids Surf. A Physicochem. Eng. Asp. 430 (2013) 29–38.
- [86] S. Wang, L. Zhang, B. Yan, H. Xu, Q. Liu, H. Zeng, Molecular and surface interactions between polymer flocculant chitosan g polyacrylamide and kaolinite particles: impact of salinity, J. Phys. Chem. C 119 (2015) 7327–7339.
- [87] G.R. Quezada, R.I. Jeldres, P.D. Fawell, P.G. Toledo, Use of molecular dynamics to study the conformation of an anionic polyelectrolyte in saline medium and its adsorption on a quartz surface, Miner. Eng. 129 (2018) 102–105.

- [88] N. Wilkinson, A. Metaxas, E. Brichetto, S. Wickramaratne, T.M. Reineke, C.S. Dutcher, Ionic strength dependence of aggregate size and morphology on polymer-clay flocculation, Colloids Surf. A Physicochem. Eng. Asp. 529 (2017) 1037–1046.
- [89] J. Nan, W. He, Characteristic analysis on morphological evolution of suspended particles in water during dynamic flocculation process, Desalin. Water Treat. 41 (2012) 35–44.
- [90] M. Yukselen, K. O'Halloran, J. Gregory, Effect of tapering on the break-up and reformation of flocs formed using hydrolyzing coagulants, Water Sci. Technol. Water Supply 6 (2006) 139–145.
- [91] A. Owen, P. Fawell, J. Swift, D. Labbett, F. Benn, J. Farrow, Using turbulent pipe flow to study the factors affecting polymer-bridging flocculation of mineral systems, Int. J. Miner. Process. 87 (2008) 90–99.
- [92] 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 (1997) 73–85.
- [93] A. Yeung, A. Gibbs, R. Pelton, Effect of shear on the strength of polymer-induced flocs, J. Colloid Interface Sci. 196 (1997) 113–115.
- [94] A. Sworska, J.S. Laskowski, G. Cymerman, Flocculation of the Syncrude fine tailings: part II. Effect of hydrodynamic conditions, Int. J. Miner. Process. 60 (2000) 153–161.
- [95] T. Yalcin, S. Brunet, in: J.S. Laskowski (Ed.), Testing of Flocculant-Assisted Hydrocyclone on Québec Cartier Mining Company's Iron Ore Tailings, Particle Size Enlargement in Mineral Processing-Proceedings of the Fifth UBC-McGill Biennial International Symposium on Fundamentals of Mineral Processing (Hamilton, Ontario), CIM, Montreal 2004, pp. 289–301.
- [96] G.V. Franks, P.D. Yates, N.W.A. Lambert, G.J. Jameson, Aggregate size and density after shearing, implications for dewatering fine tailings with hydrocyclones, Int. J. Miner. Process. 77 (2005) 46–52.
- [97] A. Costine, J. Cox, S. Travaglini, A. Lubansky, P. Fawell, H. Misslitz, Variations in the molecular weight response of anionic polyacrylamides under different flocculation conditions, Chem. Eng. Sci. 176 (2018) 127–138.
- [98] J.B. Farrow, R.R.M. Johnston, K. Simic, J.D. Swift, Consolidation and aggregate densification during gravity thickening, Chem. Eng. J. 80 (2000) 141–148.
- [99] B. Gladman, R. De Kretser, M. Rudman, P. Scales, Effect of shear on particulate suspension dewatering, Chem. Eng. Res. Des. 83 (2005) 933–936.
- [100] S. Usher, P. Scales, Predicting settler/clarifier behaviour: the role of shear effects, Filtration 9 (2009) 308–314.
- [101] Y.-K. Leong, J. Teo, E. Teh, J. Smith, J. Widjaja, J.-X. Lee, A. Fourie, M. Fahey, R. Chen, Controlling attractive interparticle forces via small anionic and cationic additives in kaolin clay slurries, Chem. Eng. Res. Des. 90 (2012) 658–666.
- [102] L. Avadiar, Y.-K. Leong, A. Fourie, Effects of polyethylenimine dosages and molecular weights on flocculation, rheology and consolidation behaviors of kaolin slurries, Powder Technol. 254 (2014) 364–372.
- [103] A. Grabsch, P. Fawell, S. Adkins, A. Beveridge, The impact of achieving a higher aggregate density on polymer-bridging flocculation, Int. J. Miner. Process. 124 (2013) 83–94.
- [104] J.V. O'Gorman, J.A. Kitchener, The flocculation and de-watering of kimberlite clay slimes, Int. J. Miner. Process. 1 (1974) 33–49.
- [105] S. Mathur, B.M. Moudgil, Adsorption mechanism(s) of poly(ethylene oxide) on oxide surfaces, J. Colloid Interface Sci. 196 (1997) 92–98.
- [106] L. Zhang, Q. Lu, Z. Xu, Q. Liu, H. Zeng, Effect of polycarboxylate ether comb-type polymer on viscosity and interfacial properties of kaolinite clay suspensions, J. Colloid Interface Sci. 378 (2012) 222–231.
- [107] V.H. Dao, N.R. Cameron, K. Saito, Synthesis of ultra-high molecular weight aba triblock copolymers via aqueous RAFT-mediated gel polymerisation, end group modification and chain coupling, Polym. Chem. 8 (2017) 6834–6843.
- [108] V. Ajao, H. Bruning, H. Rijnaarts, H. Temmink, Natural flocculants from fresh and saline wastewater: comparative properties and flocculation performances, Chem. Eng. J. 349 (2018) 622–632.
- [109] B. Bolto, J. Gregory, Organic polyelectrolytes in water treatment, Water Res. 41 (2007) 2301–2324.
- [110] Z. Zhang, H. Nong, L. Zhuang, J. Liu, Effect of water hardness on the settling characteristics of coal tailings, Energy Sources Part A 39 (2017) 1317–1322.
- [111] R.I. Jeldres, E.C. Piceros, W.H. Leiva, P.G. Toledo, N. Herrera, Viscoelasticity and yielding properties of flocculated kaolinite sediments in saline water, Colloids Surf. A Physicochem. Eng. Asp. 529 (2017) 1009–1015.
- [112] M.J. Pearse, Factors affecting the laboratory sizing of thickeners, in: P. Somasundaran (Ed.), Proc. Int. Symp. on Fine Particles Processing AIME, New York 1980, pp. 1619–1642.
- [113] J.B. Farrow, J.D. Swift, Improving thickener technology, fifth AUSIMM extractive metallurgy conference, Australas. Inst. Min. Metall. (1991) 227–232.
- [114] G. Hoyland, M. Day, An evaluation of picket fenses for assisting the consolidation of sewage sludges, Water Pollut. Control. 85 (1986) 291–303.
- [115] C. Loan, I. Arbuthnot, Innovative Technology for Optimised Thickening Sedimentation, XXV International Mineral Processing Congress 2010, Brisbane, QLD Australia, 2010 3663–3674.
- [116] C.L. Loan, N. Lawler, I. Arburthnot, Industrial scale results from shear enhanced thickening technology, Proceedings: 11th AusIMM Mill Operators' Conference 2012, Hobart, Australia 2012, pp. 341–346.
- [117] R. Spehar, A. Kiviti-Manor, P. Fawell, S.P. Usher, M. Rudman, P.J. Scales, Aggregate densification in the thickening of flocculated suspensions in an un-networked bed, Chem. Eng. Sci. 122 (2015) 585–595.
- [118] P.J. Scales, A.H. Crust, S.P. Usher, Thickener modelling-from laboratory experiments to full-scale prediction of what comes out the bottom and how fast, in: R.J. Jewell, A.B. Fourie (Eds.),Paste 2015: Proceedings of the 18th

International Seminar on Paste and Thickened Tailings, Cairns Australia 2015, pp. 3–12.

- [119] B. Pirouz, S. Javadi, K. Seddon, Thickener performance variability: Underflow solids concentration and flowrate, in: A. Wu, R. Jewell (Eds.), Proceedings of the 20th International Seminar on Paste and Thickened Tailings, University of Science and Technology Beijing, Beijing 2017, pp. 29–40.
- [120] T. Nguyen, J. Farrow, J. Smith, P. Fawell, Design and development of a novel thickener feedwell using computational fluid dynamics, J. South. Afr. Inst. Min. Metall. 112 (2012) 939–948.
- [121] A. Chryss, A. Fourie, A. Monch, D. Nairn, K. Seddon, Towards an integrated approach to tailings management, J. South. Afr. Inst. Min. Metall. 112 (2012) 965–969.
- [122] D. Bedell, S. Slottee, F. Shoenbrunn, P. Fawell, Chapter 7 thickening, in: R.J. Jewell, A.B. Fourie (Eds.), Paste and Thickened Tailings - a Guide (Third Edition), Australian Centre for Geomechanics, Perth 2015, pp. 113–136.
- [123] D.J. Cooling, Improving the sustainability of residue management practices Alcoa World Alumina Australia, Proceedings of the 10th International Seminar on Paste and Thickened Tailings 2007, pp. 3–16.
- [124] H.A. Kaminsky, T.H. Etsell, D.G. Ivey, O. Omotoso, Distribution of clay minerals in the process streams produced by the extraction of bitumen from Athabasca oil sands, Can. J. Chem. Eng. 87 (2009) 85–93.
- [125] P. McColl, S. Scammell, M. Philip, S. Stephen. 2004. Treatment of mineral material, especially waste mineral slurries transferring material with dispersed particulate solids as fluid to deposition area by combining with material aqueous solution of water-soluble polymer. Patent WO2004060819-A1; WOEP000042 07 Jan 2004 and numerous country patents.
- [126] N. Gaillard, F. Poncet. 2010. Treating sludge from mining or mineral industry before spreading out into soil, comprises contacting the sludge with a branched flocculant such as a water soluble organic polymer having a specified anionicity for a specified duration. Patent FR2937635-A1; US2010105976-A1; CA2682542-A1.
- [127] P. Wells, L. Charlebois, J. Diep, B. Moyls, O. Omotoso, A. Revington, M. Weiss, In-line flocculation, in: R. Jewell, A. Fourie (Eds.), Paste and Thickened Tailings: A Guide (Third Edition), Australian Centre for Geomechanics, Nedlands, Australia, Perth 2015, pp. 229–241.
- [128] P. Wells, A. Revington, O. Omotoso, Mature fine tailings drying-technology update, Proceedings of the 14th International Seminar on Paste and Thickened Tailings 2011, pp. 155–166.
- [129] S.J. Adkins, J. Bellwood, A. Beveridge, M. Edgar, I.A. Flanagan, Difference between secondary flocculation and rigidification via Rheomax®-enhanced tailings disposal technology, in: R.J. Jewell, A.B. Fourie, P.S. Wells, D. van Zyl (Eds.), Proceedings of the 17th International Seminar on Paste and Thickened Tailings, Infomine, Vancouver 2014, pp. 187–197.
- [130] A. Costine, F. Benn, P. Fawell, M. Edraki, T. Baumgartl, J. Bellwod, Understanding factors affecting the stability of inline polymer-amended tailings, in: R. Jewel, A. Fourie (Eds.),Paste 2018-21st International Seminar on Paste and Thickened Tailings, 2018.
- [131] D.R. Vedoy, J.B. Soares, Water-soluble polymers for oil sands tailing treatment: a review, Can. J. Chem. Eng. 93 (2015) 888–904.
- [132] D. Zhang, T. Thundat, R. Narain, Flocculation and dewatering of mature fine tailings using temperature-responsive cationic polymers, Langmuir 33 (2017) 5900–5909.
- [133] L. Botha, S. Davey, B. Nguyen, A.K. Swarnakar, E. Rivard, J.B. Soares, Flocculation of oil sands tailings by hyperbranched functionalized polyethylenes (HBfPE), Miner. Eng. 108 (2017) 71–82.
- [134] B. Hart, D. Boger, Tailings waste minimisation, rheology, and the triple bottom line, Proceedings of the International Seminar on Paste and Thickened Tailings, Australian Center for Geomechanics, University of Western Australia, Nedlands Wa, Australia 2005, pp. 5–27.
- [135] A. Read, C. Hollick, Selective flocculation techniques for recovery of fine particles, Miner. Sci. Eng. 8 (1976) 202–213.
- [136] M. Loan, O. Newman, R. Cooper, J. Farrow, G. Parkinson, Defining the paragoethite process for iron removal in zinc hydrometallurgy, Hydrometallurgy 81 (2006) 104–129.
- [137] B. McLellan, G. Corder, D. Giurco, S. Green, Incorporating sustainable development in the design of mineral processing operations-review and analysis of current approaches, J. Clean. Prod. 17 (2009) 1414–1425.
- [138] G. Corder, B. McLellan, S. Green, Incorporating sustainable development principles into minerals processing design and operation: SUSOP®, Miner. Eng. 23 (2010) 175–181.
- [139] G. Corder, B. McLellan, P. Bangerter, D. Van Beers, S. Green, Engineering-in sustainability through the application of SUSOP®, Chem. Eng. Res. Des. 90 (2012) 98–109.
- [140] M. Edraki, T. Huynh, T. Baumgartl, L. Huang, M. Andrusiewicz, K. Tungpalan, M. Tayebi-Khorami, E. Wightman, S. Palaniandy, E. Manlapig, Designer tailings-an integrated model for tailings management, Proceedings, Life of Mine 2014 Conference, Brisbane 2014, pp. 16–18.
- [141] D. Reid, A. Fourie, Laboratory assessment of the effects of polymer treatment on geotechnical properties of low-plasticity soil slurry, Can. Geotech. J. 53 (2016) 1718–1730.
- [142] O. Sitando, G. Senanayake, X. Dai, A. Nikoloski, P. Breuer, A review of factors affecting gold leaching in non-ammoniacal thiosulfate solutions including degradation and in-situ generation of thiosulfate, Hydrometallurgy 178 (2018) 151–175.
- [143] S. Palaniandy, M. Powell, Addressing Water Scarcity in Mining Through Improved Comminution Practices, AusIMM Bulletin, 2014 48.
- [144] A.-M. Jonas, Enhanced flocculation and dewatering of clay mineral dispersions, Powder Technol. 179 (2007) 73–78.
- [145] N. Alam, O. Ozdemir, M.A. Hampton, A.V. Nguyen, Dewatering of coal plant tailings: flocculation followed by filtration, Fuel 90 (2011) 26–35.

- [146] M. Dash, R.K. Dwari, S.K. Biswal, P.S.R. Reddy, P. Chattopadhyay, B.K. Mishra, Studies on the effect of flocculant adsorption on the dewatering of iron ore tailings, Chem. Eng. J. 173 (2011) 318-325.
- [147] C. Qi, A. Fourie, Q. Chen, X. Tang, Q. Zhang, R. Gao, Data-driven modelling of the flocculation process on mineral processing tailings treatment, J. Clean. Prod. 196 (2018) 505-516.
- [148] D.C. Hopkins, J.J. Ducoste, Characterizing flocculation under heterogeneous turbulence, J. Colloid Interface Sci. 264 (2003) 184–194.
- [149] E. Sabah, Z. Erkan, Interaction mechanism of flocculants with coal waste slurry, Fuel 85 (2006) 350-359.
- [150] S. Barany, R. Meszaros, L. Marcinova, J. Skvarla, Effect of polyelectrolyte mixtures on the electrokinetic potential and kinetics of flocculation of clay mineral particles, Colloids Surf. A Physicochem. Eng. Asp. 383 (2011) 48–55.
 [151] R.A. Garcia, S.A. Riner, G.J. Piazza, Design of a Laboratory Method for rapid evalua-
- tion of experimental flocculants, Ind. Eng. Chem. Res. 53 (2014) 880-886.

- [152] V. Vajihinejad, J.B. Soares, Monitoring polymer flocculation in oil sands tailings: a population balance model approach, Chem. Eng. J. 346 (2018) 447–457.
- [153] J. Farrow, J. Swift, A new procedure for assessing the performance of flocculants, Int. J. Miner. Process. 46 (1996) 263–275.
- [154] M. Gagnon, G. Simard, A. Charette, G. Péloquin, Characterization of red mud aggregate populations generated under shear conditions, CIM Bull. 95 (2002) 87-91
- [155] N. Wilkinson, C.S. Dutcher, Taylor-Couette flow with radial fluid injection, Rev. Sci. [156] N. Rulyov, B. Korolyov, N. Kovalchuk, Application of ultra-flocculation for improv-
- [157] A.R. Heath, P.D. Fawell, P.A. Bahri, J.D. Swift, Estimating average particle size by focused beam reflectance measurement (FBRM), Part. Part. Syst. Charact. 19 (2002) 84-95