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Current State of Fine Mineral Tailings Treatment: A Critical Review on Theory and Practice

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Highlights

- Presented facts on escalating generation of fine mineral tailings worldwide.
- Overview of coal, alumina, oil sands, and base metals tailings characteristics.
- Reviewed theoretical and industrial developments for tailings management.
- Determined numerous knowledge gaps between current theories and practices.
- Identified opportunities for improvement towards more sustainable practices.

Graphical Abstract

Evolution of fine mineral tailings treatment objectives.

Figures "Flocculated solids" and "Stackable solids" are adopted from Alamgir, et al. (2012), permission pending. The last figure "Reclaimed land" is adopted from Golder Associates (2009), permission pending.

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Abstract

The mining industry produces fluid fine mineral tailings on the order of millions of tonnes each year, with billions of tonnes already stored globally. This trend is expected to escalate as demand for mineral products continues to grow with increasingly lower grade ores being more commonly exploited by hydrometallurgy. Ubiquitous presence and enrichment of fine solids such as silt and clays in fluid fine mineral tailings prevent efficient solid-liquid separation and timely re-use of valuable process water. Long-term storage of such fluid waste materials not only incurs a huge operating cost, but also creates substantial environmental liabilities of tailings ponds for mining operators. This review broadly examines current theoretical understandings and prevalent industrial practices on treating fine mineral tailings for greater water recovery and reduced environmental footprint of mining operations.

1. Introduction

1.1. Fluid fine mineral tailings

Fluid fine mineral tailings refer to a mixture of waste by-products generated when recovering useful and precious minerals, metals, and other resources from the ores using mineral processing and hydrometallurgical processes. After selective extraction and beneficiation of the desired materials, the mill rejects and residuals are combined to form the tailings stream. In most cases the tailings are discharged in the form of a slurry into lagoons, engineered ponds and mine sites, where solids and process fluids separate under gravity. Given sufficient time, the nearly solids-free supernatant can be recycled into the extraction process to reduce freshwater intake and minimize waste volume. In very few instances the waste tailings has been discharged directly into the environment, although this practice is heavily declining and the practice is banned in many countries under more strict guidelines of zero discharge (Power, et al., 2011; Samal, et al., 2013). Discharge to tailings ponds remains an inexpensive and proven technology that has been widely adopted by the mineral industry (Watson, et al., 2010). However, this approach often does not provide a long term tailings management solution.

With the ever-growing demand for mineral products, coupled with deterioration and depletion of high-grade mineral ore deposits, mining of lower-grade ores that are more resource- and energy-intensive to process is becoming the norm (Crowson, 2012; Bethell, 2012; Nesbitt, 2007; Jones & Boger, 2012). In these cases, sub-micrometer ore grinding and classification become inevitable to achieve the necessary mineral liberation and hence recovery using conventional mineral processing and hydrometallurgical processes. Unfortunately, fine grinding has also led to the reduced selectivity by the production of undesired fine gangue mineral solids. These fine solids, often only a few microns in diameter, are extremely difficult to separate from the tailings water. As a result they contribute directly to the accumulation of an alarmingly large volume of fluid waste mineral tailings that requires safe containment.

For example, typical coal preparation plants discharge 75 to 120 kg of dry tailings per tonne of coal processed. These tailings are in the slurry form, with total solid contents ranging between 20-35% (w/w) (Ryu, et al., 2008; Beier & Sego, 2009; Murphy, et al., 2012). In 2002, the U.S. National Research Council estimated that 70-90 million tonnes of tailings were produced annually by these facilities in the United States alone (National Research Council, 2002). Global inventory of the highly alkaline by-product (red mud) from alumina production using the Bayer process has surpassed 2.5 billion tonnes in 2007 with a predicted growth of 120 million tonnes per year, at an estimated ratio of 1-1.5 tonnes of red mud per tonne of alumina product, or 4 tonnes per tonne of finished aluminum (Kumar, et al., 2006; Power, et al., 2011). Production of phosphoric acid, an essential ingredient for the fertilizer ammonium phosphate, generates on average 450% of its weight as phosphogypsum (phosphate tailings) (Zhang & Stana, 2012). Given a worldwide phosphoric acid production of 40 million tonnes in 2010, about 180 million tonnes of acidic phosphate tailings require proper disposal (International Fertilizer Industry Association, 2010). At the extreme, extraction of copper generates a vastly disproportional amount of tailings. According to studies by Gordon and Bridge, 128 to 196 tonnes of combined copper tailings would be generated to produce one tonne of copper (Gordon, 2002; Bridge, 2000). Using Gordon's data, Onuaguluchi and Eren estimated a worldwide production of 2 billion tonnes of copper tailings in 2011 (Onuaguluchi & Eren, 2012).

A notable example outside mineral processing is found in northern Alberta (Canada) where bitumen production by surface mining has been a thriving industry for over 50 years. Located north of Fort McMurray, tailings slurry impoundment has created substantial land disturbances, covering an area of at least 130 km^2 in 2011 (Masliyah, et al., 2011). To produce one barrel of crude bitumen, 3.3 m^3 of tailings is discharged, containing 1.5 m^3 of fluid fine tailings (mature fine tailings, MFT) that accumulate in the tailings pond after supernatant recovery (Masliyah, et al., 2011). These fluid fine tailings are stable at ~30% (w/w) solids content without further noticeable densification for centuries. If one assumes that the density of the crude bitumen is approximately the same as that of water, then approximately 11.6 tonnes of MFT would be generated per tonne of crude bitumen produced. Recently, the Alberta Energy Regulator (formerly Energy Resources Conservation Board, ERCB) published the latest crude bitumen production figure of 340 million barrels from surface mining activities in 2012 (Alberta Energy Regulator, 2013). That amounts to an increase of approximately 510 million cubic meters (627.3 million tonnes) of fluid fine tailings.

1.2. Accumulated tailings issues

The huge volumes of mineral tailings are conventionally discharged into natural or engineered depressions, surrounded by dams and dykes that are critical to the structural integrity of the containment pond. Unfortunately, over the years there have been several incidents of dam failures and the disastrous release of tailings, which are often a result of extreme weather and/or natural disasters (WISE Uranium Project, 2012). These dam failures are a result of both geotechnical problems of the containment structure and management of the stored tailings (Jones and Boger, 2012). Several failures of fine coal tailings ponds in the United States have been documented by the U.S. National Research Council. One such disaster in West Virginia resulted in 125 fatalities and substantial environmental and property damage (National Research Council, 2002). In Ajka, Hungary, the unprecedented release of ~700,000 m^3 of red mud slurry in October 2010 caused numerous fatalities as well as widespread farmland and waterborne contamination (Ruyters, et al., 2011). Between 1967 and 2005, eleven industrial accidents in the U.S. involving millions of cubic meters of phosphate tailings have been reported to damage or eliminate local aquatic biota (WISE Uranium Project, 2012). In the same time period many other mining industries, for example copper, iron, and zinc have witnessed failures leading to the destruction of properties, livelihood, and the local environment. Canada's oil sands industry has also received substantial negative public reception after much-publicized cases of wildlife deaths in the tailing ponds, though no major containment breaches of the oil sand tailings have been reported (Timoney & Lee, 2009).

In addition to the disastrous consequences of accidental tailings failures, the structures of operational tailings impoundment are also a cause of concern for mine operators. Fine solids in mineral tailings slurry require long settling time, which necessitates the use of large land areas to accommodate mine productivity. This situation is also magnified by the formation of stable particle networks (gels). Such network structure resists consolidation and traps a significant volume of process water that is not available for recycle. Also, certain clay minerals (such as montmorillonite) are able to absorb water into its internal structure, resulting in swelling and an increase in the apparent volume of discharged material. Those phenomena are responsible for poor water recovery from tailings, and directly contribute to increasing footprint of tailings containment structures. A growing number of studies conducted at mineral tailings containment areas suggest that mobilization of harmful

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substances by wind, evaporation, and seepage can affect air quality and underground water tables (Percy, et al., 2012; Timoney & Lee, 2009; Jones & Haynes, 2011; Jones & Boger, 2012). Stockpiling of mineral tailings can result in undesirable interactions with the environment (e.g. acid mine drainage), and this practice has also been linked to deformities, reproduction failures, and deaths of local flora and fauna (Renault, et al., 2000; Gentes, et al., 2006; Lee & Correa, 2005; Ramirez, et al., 2005). As the public grows increasingly aware of these environmental issues and disasters related to mineral tailings, mining projects are facing greater levels of scrutiny from government agencies in terms of sustainability and social responsibility. The familiar practice of containing mineral tailings slurry by conventional dam and dykes is no longer considered acceptable in many countries (Zhang & Stana, 2012).

In the U.S. for example, the Florida Department of Environment Protection (FDEP) established guidelines for phosphate tailings disposal (DEP 62-673.220), which has been adopted by an increasing number of government regulators worldwide (Zhang & Stana, 2012). In essence, the FDEP requires several modifications to the conventional containment structure by using: a) composite liner, b) leachate control, and c) perimeter underdrain, with specified material properties. Top soil cover of specified nature is applied for closure of the disturbed area. This improved tailings containment setup limits the extent of contamination from the seepage. However it does little to prevent slurry overflow, structural failures, and large land area requirements.

In an effort to reduce the inventory and production of oil sands tailings, the Energy Resources Conservation Board issued in 2009 Directive 074 which required operators to convert fresh and legacy tailings to deposits of trafficable material strengths (ERCB, 2009). Recognizing the evolving and often site-specific nature of tailings management practices, the ERCB has given operators the freedom to choose their own best practice, and outlined progressive evaluation criteria that are based on the amount of fine solids captured. According to the performance assessment report issued in June 2013, operators have not been able to meet these criteria despite ongoing efforts and improvements, due to numerous issues with operations and reliability (Alberta Energy Regulator, 2012).

1.3. Current tailings treatment objectives

The status quo of mineral tailings management thus appears as follows. In response to the progressive government regulations and public sentiment, mine operators are more willing to address the environmental and social impacts of legacy tailings and conventional tailings management practices. However, current mineral tailings consumption technologies are usually costly, perform less robust than desired, and suffer from limited throughput, which is particularly the case for managing the growing volume of copper, oil sands, and bauxite tailings. These factors elevate the risk associated with tailings management programs using alternative technologies that differ from the less expensive and more established "dam and dyke" approach, and discourages their execution. On the other hand, mine operators are unwilling to reduce production rates due to plant economics and generally rising demand for products, thus leading to an overall excess and accumulation of fluid mineral fine tailings.

To break this impasse, actions must be taken to target the heart of the tailings problem – fine solids, and to better understand and combat the two undesirable fundamental phenomena that are associated with it – slow consolidation and water capture, using efficient, reliable, and economical processes. This review broadly examines current scientific understandings and prevalent practices of fluid mineral fine tailings densification (thickening) and dewatering,

and the scope of this work is by no means comprehensive. Rather, the authors wish to highlight some of the difficulties and aims to provide some insights into future technological developments and advancements in this challenging yet essential area.

2. Theoretical Considerations

2.1. Tailings solids and stability

Mineral tailings are heterogeneous mixtures of different solids suspended in process-contaminated water that often contains multiple soluble species. Characterization of solids in mineral tailings is often considered in terms of grain size, mineralogy, and morphology. All three factors and their interactions with the aqueous species directly contribute to the observed bulk behaviour of a given tailings slurry.

Size classification

By convention, mining operators classify the size fractions of solid constituents in tailings as "sand", "silt", and "clay" based on a variety of methods and standards. Exact cut-off sizes for these classes can vary by applications. Table 1 provides some general guidelines used in the mining industry.

Table 1: Grain size classification criteria

Methods and Standards	Classification Criteria			Reference
	Sand ("Coarse")	Silt ("Fines")	Clay ("Fines")	
Wentworth (1922)	> 63 μm	4 – 63 μm	< 4 μm	(Sabah & Cengiz, 2004)
ISO 14688-1	> 63 μm	2 – 63 μm	< 2 μm	(ISO, 2002)
Unified Soil Classification System (USCS)	> 75 μm	< 75 μm (Distinguished by plasticity)		(ASTM, 2011)
Canadian Oil Sands Classification System	> 44 μm	2 – 44 μm	< 2 μm	(Masliyah, et al., 2011)

Table 2 lists some examples of classification results and solids concentration (if available) for tailings across different sectors of the mining industry. Generally there are significant amounts of silt and clay materials whose concentrations can vary considerably within an impoundment area. Fines enrichment becomes increasingly pronounced at locations further away from the slurry discharge point (Gräfe, et al., 2011), and may be minimized by alternative discharge methods as demonstrated in, for example, Al and Blowes (1999).

Table 2: Examples of grain size distributions for mineral tailings of different origin

Industry	Examples	Grain Size Distributions	Reference
Coal	Fresh tailings from Tuncbilek, Turkish Coal Enterprises, Turkey	Solids: 5.85% (w/w) > 63 μm: 10% 4 – 63 μm: 62% < 4 μm: 28%	(Sabah, et al., 2004)
	Sediment tailings from Coal Valley Resources Inc., Alberta, Canada	Solids: 50-55% (w/w) > 63 μm: 3% 4 – 63 μm: 31% < 4 μm: 66%	(Beier & Sego, 2009)
	Diluted tailings from BMA plant, Central Queensland, Australia	Solids: 35% (w/w) > 63 μm: 35.4% 38 – 63 μm: 6.2% < 38 μm: 58.4%	(Alam, et al., 2011)
	Tailings from Colombian washing coal plant, Columbia	Solids: 5% (w/w) > 75 μm: 19.5% 37 – 75 μm: 8.6% < 37 μm: 71.9%	(Barraza, et al., 2013)
Alumina	Aluminum Corporation of Shandong Ltd., China	Solids: 60.2-66.8% (w/w) > 23 μm: none 5 – 23 μm: 90.3% < 5 μm: 9.7%	(Wang, et al., 2008b)
	Etibank Seydisehir Aluminum Plant, Konya, Turkey	> 23 μm: 10% (w/w) 5 – 23 μm: 40% < 5 μm: 50%	(Kalkan, 2006)
	Literature review	Solids: 20-80% (w/w) Range: 0.1 – 200 μm Average: 2 – 100 μm < 5 μm: 50%	(Gräfe, et al., 2011)
Phosphate	Bunge Brazil SA, Araxá, Brazil	> 75 μm: 60.7% (w/w) 37 – 75 μm: 25.0% < 37 μm: 14.3%	(Oliveira, et al., 2011)

Phosphate (cont'd)	Phosphate concentration plant, Guizhou Province, China	> 75 μm: 14.0% (w/w) 37 – 75 μm: 28.5% < 37 μm: 57.5%	(Xu, et al., 2012)
	The Mosaic Company, United States	Fresh tailings solids: 3% (w/w) (settles and stabilizes to ~20%) < 19.95 μm: 90% < 8.96 μm: 50% < 1.73 μm: 10%	(Tao, et al., 2008)
Copper	El Teniente-Codelco copper mine, Chile	> 75 μm: 66.1% (w/w) 38 – 75 μm: 30.0% < 38 μm: 3.9%	(Hansen, et al., 2005)
	Abandoned processing facility, Lefke, Cyprus	> 48 μm: 50% (w/w) 1 – 48 μm: 16% < 1 μm: 34%	(Onuaguluchi & Eren, 2012)
	Carén tailings, El Teniente copper mine, Chile	Solids: 55% (w/w) > 63 μm: 11% 2 – 63 μm: 68% < 2 μm: 21%	(Smuda, et al., 2008)
Oil Sands	Tailings pond MFT, Alberta, Canada	Solids: 40% (w/w) > 44 μm: 4% 2 – 44 μm: 78% < 2 μm: 19%	(Farkish & Fall, 2013)
	Mature fine tailings from Syncrude Canada Ltd., Alberta, Canada	Solids: 34% (w/w) > 44 μm: 4% 6.5 – 44 μm: 46% < 6.5 μm: 50%	(Alamgir, et al., 2012)
	Typical fine tailings sample	Solids: 30-40% (w/w) > 44 μm: 10% 1 – 44 μm: 57% < 1 μm: 33%	(Voordouw, 2013)

Solids mineralogy and morphology

Many researchers have studied and characterized the solids mineralogy and morphology for some of the tailings samples listed in Table 2. Characteristics of the process water obtained from the tailings slurries were also widely published. Results presented (de Kretser, et al., 1997; Sabah, et al., 2004; Ofori, et al., 2011) suggest that coal preparation tailings in the fines fraction consist mostly of phyllosilicate minerals, such as kaolinite, illite, muscovite, mica, and mixed-layer illite/montmorillonite clays, along with quartz. Residual coal particles are detected predominately in the coarse fraction (Sabah, et al., 2004). This particular combination of fine solids is very similar to those identified from the oil sands fluid fine tailings, in which kaolinite is the dominant clay fraction, followed by illite, chlorite, and other mixed-layer clays (Masliyah, et al., 2011). However, the coarse fraction of oil sands fluid fine tailings is mostly quartz, K-feldspar, and bitumen-clay aggregates. Solids in both coal and oil sands tailings are entrained in slightly alkaline process waters, with pH ranging between 7.5-8.5 and 7.7-8.8, respectively (de Kretser, et al., 1997; Allen, 2008). Concentrations of sodium ion between the two mineral tailings are generally similar (Ryu, et al., 2008; Alam, et al., 2011; Allen, 2008) although higher levels (in excess of 960 ppm) have been reported for coal tailings (Ofori, et al., 2011). Process water from oil sands tailings contains lower amounts of calcium, magnesium, chloride and sulfate ions, thus coal tailings are, in general, more saline than its counterpart from oil sands (Allen, 2008; Ofori, et al., 2011; Sabah, et al., 2004; Alam, et al., 2011).

In comparison, mineral tailings from the alumina, phosphate and copper industries are found to contain less clay minerals and higher proportions of metal oxides. It is often unclear which types of mineral are enriched in either the coarse or fines fractions. The nature of the process water from these tailings is closely linked to the type of the extraction process used. Details are presented in Table 3.

Table 3: General characteristics of alumina, phosphate and copper tailings

Industry	Composition of solids	Characteristics of liquid	Reference
Alumina	Oxides of iron (III), titanium, silicon, calcium, sodium, and residual aluminum.	Elevated pH (10.3-11.3) and sodium ions (average 2332 mg/L)	(Gräfe, et al., 2011; Kalkan, 2006; Poulin, et al., 2008; Wang, et al., 2008a)
Phosphate	Oxides of calcium, iron (III), silicon (quartz and mica), residual P_2O_5, and magnesium oxide (dolomite) in some cases.	Limited available data; generally acidic; concentrated in anions such as sulfite (SO_3^{2-}).	(Oliveira, et al., 2011; Abdel-Aal, 2000; Xu, et al., 2012; Zhang and Stana, 2012)
Copper	Quartz, K-feldspars, biotite, chlorite, mica, muscovite, gypsum, and dolomite, with residual amounts of copper and other metals.	pH 9.2-10.2 for alkaline flotation of sulfide ores; neutral pH reported for porphyry deposit tailings; limited water salinity data.	(Smuda, et al., 2008; Liu, et al., 2013; Hansen, et al., 2005)

Although differences exist in the composition of these tailings, the ubiquitous presence of phyllosilicate minerals is evident. Among these phyllosilicate minerals, the majority is classified as clay minerals and concentrated in the fines fractions. These materials originate from weathering of ores and have tetrahedral sheets of silicon and oxygen as the basic building block. Other types of layers are chemically bonded parallel to each tetrahedral sheet to form the unit layer for a variety of clays. For example, kaolinite is structured as repeating units of an octahedral aluminum-hydroxyl sheet bonded to the tetrahedral silicon-oxygen sheet, as illustrated in Figure 1 by Konan, et al. (2007), whereas the octahedral Al-OH sheet is sandwiched between two tetrahedral Si-O sheets for montmorillonite and illite. Clays have a large surface area to volume ratio that facilitates a variety of interactions with themselves as well as with aqueous species in the slurry (Singer & Munns, 1996; Giese, 2002).
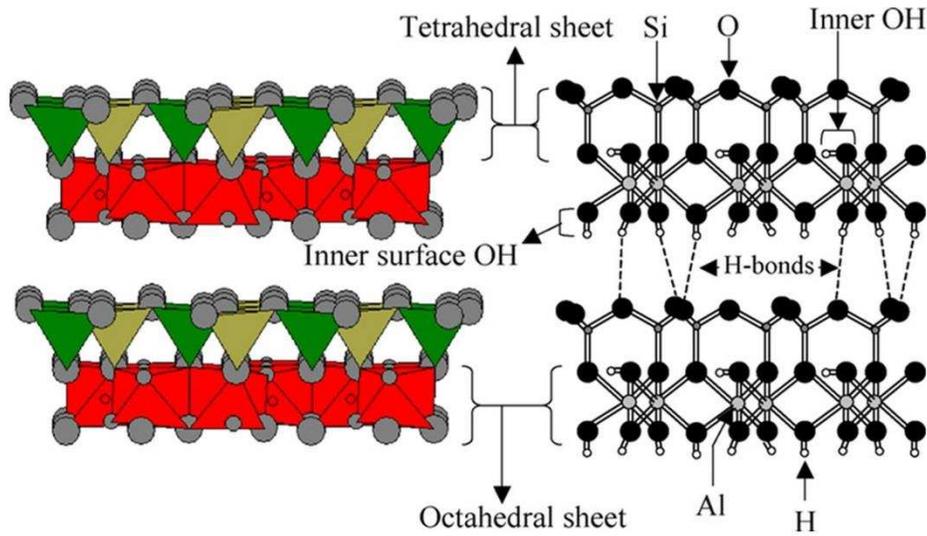

Figure 1: Two unit layers of kaolinite (adopted from Konan, et al., 2007. Permission pending.)

Slurry stability

Mineral solids suspended in slurries physically and chemically interact with the carrier fluid and dissolved species. These interactions directly dictate the suspension bulk properties, such as stability of the solids dispersion, slurry viscosity, as well as shear and compressional yield stresses.

All solid particles in a slurry are subjected to gravitational settling at steady-state (or terminal) velocities v_∞ that can be estimated by Stoke's law for dilute suspensions. The Stoke's law established relations between the settling velocity with the gravitational field strength g, characteristic particle size D_P, particle density ρ_P, as well as carrier fluid density ρ_f and viscosity μ_f.

$$v_\infty = \frac{g D_P^2 (\rho_P - \rho_f)}{18\mu_f} \tag{1}$$

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Actual particle settling velocities will be lower than those predicted by Eq. (1) due to non-spherical particle shapes and, at sufficient particle concentrations, hindrance effects from the neighboring particles. Nevertheless, Stoke's law is commonly used as a first-hand approximation to describe particle settling in stagnant media, such as tailings impoundments. From Eq. (1) it is clear that particles in the coarse fraction (i.e. sand) settle much faster than silts and clays. Consequently, this differential settling results in the segregation of these two size fractions and formation of fluid fines tailings in the disposal areas (Masliyah, et al., 2011; Gräfe, et al., 2011).

Suspended fine solids generally settle at negligible velocities and remain stable for extended periods of time, due to increasingly pronounced colloidal interactions and diminishing role of gravity with decreasing particle size. Stability of the fines suspension is reasonably well described by the DLVO theory that considers two principal colloidal forces. The ubiquitous and attractive van der Waals force acts between particles in close proximity, enabling particles to "stick" upon contact and remain in intimate contact. Counteracting the attractive force is a repulsive force caused by the overlap of electrical double layers surrounding the neighboring particles. This repulsive force is termed as electrical double layer repulsion. Unlike the attractive force that is only material specific, the double layer force is both material and solution dependent (electrolyte type, concentration and pH), with the repulsive potential decreasing with increasing conductivity which supresses the charge/potential surrounding the particles, known as charge screening.

Fine solids, especially clays when dispersed in an aqueous fluid can attain surface charge through a variety of mechanisms. Isomorphous substitution, where structural cations (e.g., Si^{4+}, Al^{3+}) are exchanged by dissolved cations of equal or, more commonly, lower valence (e.g. Al^{3+}, Mg^{2+}, K^+), resulting in a net negative charge on the basal surfaces of the clay particle. Many researchers had considered that surface charges on both the tetrahedral Si-O layer and octahedral Al-OH layer to be relatively constant regardless of pH (Singer & Munns, 1996; Giese, 2002), although recent research has challenged that notion and found that Al-OH layer has a pH-dependent (although less pH-sensitive as compared to the edge or metal oxide surfaces) surface charge for kaolinite (Gupta & Miller, 2010) and muscovite (Yan, et al., 2011), see Figure 2. Protonation or de-protonation of oxides and hydroxide groups can occur at the broken edges of the layers, which results in a more pH-dependent surface charge (Singer & Munns, 1996). When the surfaces of a fine solid particle become charged in an aqueous environment via those mechanisms, it attains a surface potential and attracts a fixed (Stern) layer of counter ions (if available) on the particle surface, enveloped by a diffuse ionic layer that forms the basis of an electric double layer in such a manner that the particle appears electrically neutral in the bulk, i.e., at a large distance into the bulk. The surface potential is usually estimated by the potential at the boundary between the Stern and diffuse layers, known as zeta potential and often determined from electrophoretic mobility measurements. Thickness of the double layer, κ^{-1}, is defined as the distance from the particle surface into the aqueous phase at which the surface potential decays to 1/e of its magnitude. The value of electrical double layer thickness is inversely related to the concentration c_i and valence Z_i of the dissolved i^{th} counter ions as shown in Equation (2).

$$\kappa^{-1} = \sqrt{\frac{\varepsilon kT}{e^2 N_A \sum_i Z_i^2 c_i}} \qquad (2)$$

where ε is the permittivity of suspending media, k is the Boltzmann constant, T is the system temperature, e is the elemental charge, and N_A is the Avogadro number. On close approach, two similarly charged particles will experience increasing repulsion as their electrical double layers overlap.
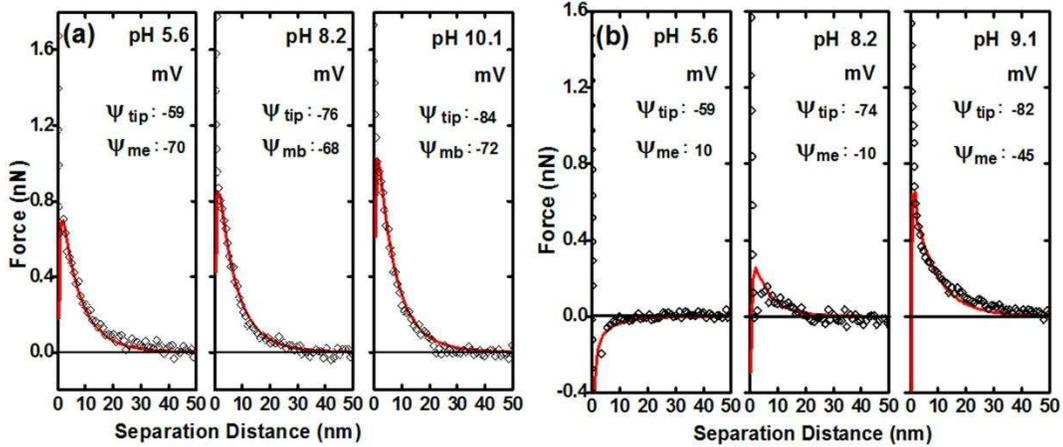

Figure 2: Typical AFM interaction forces on muscovite in 1 mM KCl solution of varying pH confirm the pH independent surface potential of the Si-O basal plane (a) (pH 5.6 – 10.1), and the pH dependent Al-OH/Si-O edge surface (b) with charge reversal measured between pH 5.6 (positive) and pH 8.2 (negative). The layered structure of muscovite, octahedral layer of gibbsite sandwiched between Si-O-Si tetrahedral layers, was suitably prepared for AFM measurement by cleaving the basal plane and exposing the edge surface using an ultramicrotome cutting technique. Adopted from Yan, et al. (2011). Permission pending.

However, given the pH-dependence and anisotropy of surface charge for the irregular-shaped clay minerals, as well as their interactions with a myriad of dissolved species in typical industrial process water, additional non-DLVO interactions and complex dispersion stability behaviours can be expected and have indeed been reported (Masliyah, et al., 2011; Johnson, et al., 2000). Hydration and steric interactions stemming from adsorbed layers of water and macromolecules increase the mutual repulsion between suspended particles, while surfactant-modified or naturally hydrophobic particle surfaces experience an additional attraction to surfaces of similar nature – hydrophobic force (Israelachvili, 2011). The total interaction potential between two suspended particles can be calculated in terms of interaction energies with respect to their separation distance, as shown by Masliyah, et al. (2011) for two spheres experiencing van der Waals and double layer interactions. A more thorough treatment involving "hard-sphere" and steric interactions is presented by Tadros (2011). Often, as two suspended particles approach each other, an energy barrier to the primary energy minimum, which corresponds to permanent particle attachment or strong aggregation, can be observed. In addition, a secondary energy minimum also exists before the energy barrier that results in weak and reversible aggregation (Elimelech, et al., 1995). In addition, Tadros (2011) showed the effect of electrosteric stabilization where no primary energy minimum exists. Magnitude of the energy barrier directly corresponds to the stability of the dispersion in a quiescent environment. For an energy barrier of 20kT and a given κ^{-1}, only one in an estimated 1 million inter-particle collisions due to thermal motion of two identical 1 μm particles can result in a successful aggregation (Elimelech, et al., 1995). In this case, collisions between

particles are highly inefficient for aggregation, and suspended particles are stabilized by their strong mutual repulsion at constant temperature.

Although the efficiency of particle collisions is a major determining factor for aggregate formation, the total number of successful aggregations formed per unit time is a product of both the collision efficiency and frequency of collisions in the same time frame. Application of additional collision frequency via increased kinetic energy, as well as lowering the magnitude of the energy barrier can greatly improve the formation rate of aggregates, which increases the apparent particle size D_P. As indicated in Eq. (1), the rate of particle sedimentation can be improved, and the suspension is subsequently destabilized as the apparent particle size increases due to particle aggregation. Techniques to destabilize fine solids suspensions will be discussed in detail in section 2.2.

Slurry rheology

Suspended solids in a slurry are known to alter the rheological properties of the slurry, whose effects are strongly dependent on the net interaction between particles (Tadros, 2011; Harbottle, et al., 2011a; Harbottle, et al., 2011b). Strong net repulsive interactions amongst the fine solids result in a stable dispersion with minor modifications to slurry viscosity. In this case, no shear yield stress is developed. On the other hand, if the solids experience strong net attractive interactions (i.e. at primary interaction energy minimum without energy barriers), they will readily aggregate into a single, tightly-bound solid mass, leading to very high shear yield stress of the slurry. However, it is often the case in which the particles, or a fraction of the particles are weakly interacting, more so for clays due to their pH-dependent and anisotropic distribution of surface charges. Consequently, the solids aggregate at larger separation distances where the secondary interaction energy minimum occurs to form loose and porous aggregates. For clays, a "card house" structure is often observed at intermediate pH and for low aspect ratio clays, where the dominant inter-particle orientation consists of basal plane-edge surface interaction due to anisotropic surface charge characteristics of basal planes and edge surfaces, as shown in Figure 3 (Johnson, et al., 2000; Gupta, et al., 2011; Yan, et al., 2013). At high pH, the charge repulsion between the negatively charged basal plane and edge surface is sufficient to stabilize the particles in the suspension. However, as the pH is lowered the edge surface undergoes charge reversal leading to a net attraction between the basal plane and edge surface. The strength of the attraction is shown to increase as the pH is lowered from pH 8 to pH 5.6. Clay anisotropy should be carefully considered to provide meaningful interpretation of slurry/sediment rheology (Yan, et al., 2013).
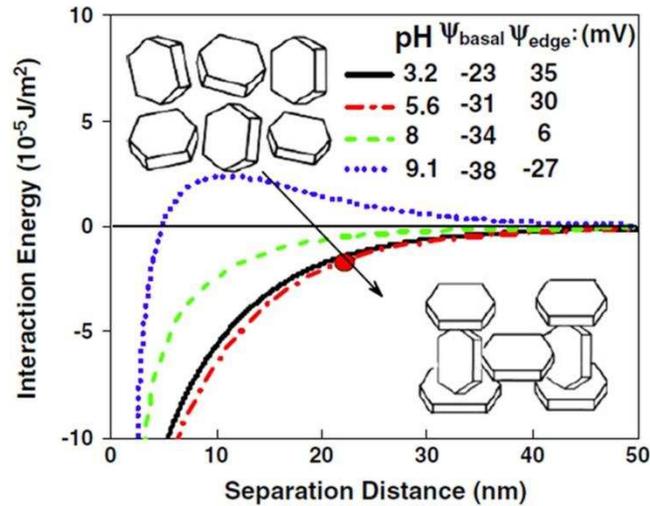
Figure 3: Interaction energies associated with the preferred "card house" structure of clays. Basal-edge attachments are favored across a wide spectrum of system pH values (adopted from Yan, et al., 2013. Permission pending.)

Since the aggregation process is reversible, a few interesting rheological behaviors are observable: a) the slurry viscosity decreases with increasing shear, as more loose aggregates are fractured than formed per unit time; b) when at rest, a shear yield stress is developed as the aggregates obtain structural integrity; and c) under constant shear, the competing processes of shear fracturing and weak aggregation reaches steady state, thus the slurry viscosity decays to an equilibrium value. As a result, most fine solids suspensions become pseudoplastic and exhibit thixotropic behaviour upon agitation.

For a given type of fines slurry, its steady state viscosities at different shear rates and shear yield stress increase with increasing solids concentration. An example is provided by Boger (2009) for red mud. The development in slurry viscosity can be substantially enhanced by introducing certain minerals, as shown by Masliyah, et al. (2011), in which a small quantity (1% w/w) of montmorillonite is shown to significantly thicken the 40% (w/w) kaolinite suspension. As montmorillonite is susceptible to swelling by absorption of water between its unit layers, its presence is expected to reduce the amount of free (unbound) water in the slurry and increase the effective solids volume fraction, both of which directly contribute to the increased slurry viscosity. Amounts of dissolved ions and counter ions (Leong & Boger, 1990; Johnson, et al., 2000; Penner & Lagaly, 2001), pH (Leong & Boger, 1990; Johnson, et al., 2000), and adsorbed surfactants or other macromolecules (Harbour, et al., 2007) are also able to modify the interactions between particles, thus directly affecting their rheological properties.

Generally it is undesirable to have high concentrations of fine solids in a slurry due to the entrapment of large amounts of water within the network of loose aggregates, that subsequently interact to from a 3-dimensional gel. In oil sands ores, clay-sized materials of > 16% w/w, or ultra-fine particles (sized less than 0.3 μm) of > 1.5% w/w, were shown to exceed the gel concentration, causing plant operational issues when present in an extraction slurry (Tu, et al., 2005).

2.2. Enhanced settling and densification

This section provides a general review of the available techniques for accelerating the sedimentation of dispersed fine solids. Fine solids suspension, a by-product of the gravity settling of typical mineral tailings, entraps a significant amount of valuable process water and prevents direct and timely re-use of water and reclamation of disposed fluid fine tailings. From the above discussions, it is clear that the urgency and importance of fine solids separation from liquids cannot be understated. However, due to the highly dispersive nature of the solids, gravity sedimentation is usually ineffective and destabilization of the suspended solids by aggregation is often a necessary first step. Naturally, accelerated settling will occur after particle aggregation, followed by the densification of the settled solid sediments.

Particle aggregation

Aggregation refers to the attachment of two entities via physical and/or chemical mechanisms, and its kinetics is generally determined by collision frequency and efficiency in a given suspension. Perikinetic aggregation occurs in a static suspension through Brownian motion with efficiency directly related to the interaction energy barrier between the solid particles. Upon agitation, the orthokinetic collision frequency becomes dependent on fluid shear and aggregate size for entities larger than 1 μm. The orthokinetic collision is less pronounced for smaller particles and aggregates, where the effect of temperature is still more significant (Masliyah & Bhattacharjee, 2006). Collision efficiency can be improved by applying relatively high rate of shear to overcome the energy barrier in an orthokinetic setting. However hydrodynamic (viscous) interactions between two particles at close approach are known to reduce the probability of attachment (Elimelech, et al., 1995).

Within the scope of this article, it is desirable to form aggregates from suspended solids in the silt and clay size fractions. In such system the apparent particle size can be increased so that both perikinetic and orthokinetic aggregations contribute to destabilizing the suspension. As discussed in section 2.1, particle aggregations occurring at the secondary interaction energy minimum result in aggregates that are porous, easily disrupted, and have large capacities for process water entrainment. Thus aggregates in the primary energy minimum, or strong aggregation, are more favored for their high compactness and integrity. For industrial fine solids suspensions that are typically highly stabilized, it is apparent that either increasing the solids kinetic energy or decreasing the magnitude of the energy barrier is necessary for successful particle attachment. In practice, additional kinetic energy is usually imparted to particles by mechanical mixing, combined with the introduction of coagulating and/or flocculating agents that serve to reduce the interaction energy barrier. The terms "coagulation" and "flocculation" are often used interchangeably in literature. In this article, however, coagulation is defined as particle aggregation brought by the addition of inorganic salts to reduce electrostatic double layer repulsive force, whereas flocculation refers to the same phenomena induced by organic polymers or other macromolecules that bridge the particles. In flocculation, therefore, the interaction of polymer with particles and conformation of polymers play a more decisive role than colloidal forces between the particles in destabilizing colloidal suspensions.

Coagulation

The addition of inorganic salts is well-known for its effectiveness at destabilizing fine solids suspensions (Hogg, 2000). Coagulation and sedimentation of suspended particles have been employed extensively in the water treatment industry, where a variety of chemical agents such as alum, lime, ferric chloride, and pre-hydrolyzed chemicals are used.

It is generally recognized that upon addition to aqueous environments, inorganic salts undergo hydrolysis into the corresponding cations and anions, forming a variety of monomeric and polymeric products that depend on the type, valency and dosage of ions, solution pH, and temperature (Duan & Gregory, 2003). At concentrations below bulk saturation, surfaces of negatively-charged fine particles electrostatically attract hydrolyzed metal cations, screening the surface charge for other particles. Quantitatively, an increase of ionic concentration leads to a reduced thickness of the electric double layer as indicated by Eq. (2), resulting in a more rapid decay of the repulsive double layer interaction with increasing inter-particle distances. Therefore for simple systems, the attractive van der Waals interaction becomes more prevalent at very small separation distances between two particles, reducing the energy barrier and hence increasing the probability of particle aggregation. At a critical coagulation concentration (CCC), the magnitude of the energy barrier reaches zero, where the suspension destabilizes spontaneously. The value of CCC for a given electrolyte depends strongly on its valency, and can be estimated by the Schulze-Hardy rule (Masliyah, et al., 2011). As well, depending on the suspension pH, metallic salts such as alum can precipitate on the dispersed solids and nucleate into amorphous metal hydroxide patches (Duan & Gregory, 2003). These neutral or positively-charged patches are attracted to oppositely charged bare particle surfaces. Further increasing the ionic concentration will cause increased coverage of the adsorbed ions on the solid surfaces and shrinkage of the electric double layer. On the other hand, addition of excess salts gradually results in charge reversal of solid surfaces, which re-stabilizes the suspension.

Although charge screening by ionic species can improve inter-particle collision efficiency, the corresponding rates of aggregation reported by Duan and Gregory (2003) are very slow for dilute (50 mg/L) kaolinite suspensions. They attributed the slow rate of particle aggregation to the low collision frequency due to the low population and small size of the constituent particles, and to the limited particle enlargements offered by the hydroxide precipitates. However, using the same suspension with ferric chloride as the coagulating agent, Ching, et al. (1994) accelerated the rate of particle aggregation at shear rates of 94 s^{-1} and greater. Although frequency of inter-particle collisions can be improved by this manner at low coagulant dosages, in practice the coagulant is overdosed to achieve rapid and widespread precipitation of the amorphous metal hydroxide, which enmeshes and captures most of the suspended fine particles as it moves downward via "sweep flocculation" (Duan & Gregory, 2003). Under such conditions, the mechanisms of particle aggregation are, in principle, thought to be similar to "bridging" of particles with polymeric flocculants, which will be discussed in the next section.

Flocculation

The aggregation of fine particles by polymeric and other macromolecular additives (flocculants) is utilized in many applications both in and outside mineral processing, and has attracted immense academic interest (Smith-Palmer & Pelton, 2012). Common flocculants include polyacrylamide (PAM), poly(diallyldimethyl ammonium chloride) (PDADMAC),

polyethylene oxide (PEO), chitosan-based polymers, etc. The flocculants can be synthesized for a variety of molecular weight (MW), electric charge type and charge density to suit specific requirements. Additional structural modifications can also be incorporated to produce novel flocculants of interesting properties, such as the temperature-sensitive poly(N-isopropyl acrylamide) (poly-NIPAM) (O'Shea, et al., 2010), and impregnation of positively charged colloidal $Al(OH)_3$ particles in PAM, the latter being referred to as the hybrid flocculant Al-PAM (Alamgir, et al., 2012).

Perhaps the sole constraint to the seemingly endless types of modifications is the adsorption behaviour of the polymer product on fine solids upon introduction into a given suspension, which is well-described by Smith-Palmer and Pelton (2012). In essence, segment(s) of the polymer flocculant is (are) convectively and/or diffusively transported to the solid-water interface where irreversible solid-polymer attachment can occur non-specifically (e.g., van der Waals or electrostatic attraction) or specifically (e.g., hydrogen bonding), followed by polymer re-orientation. In some cases polymer-solid adsorption does not occur at all due to, for example, electrostatic repulsion between hydrolyzed PAM and negatively charged silica or bitumen-coated solid surface at their experimental conditions, as shown by Klein, et al. (2013). The rate of polymer adsorption is generally faster for lower molecular weight flocculants, setting up the barrier governed by the surface coverage that prevents further polymer adsorption. Once adsorbed, the polymer conformation depends on a number of factors, some of which are discussed next. Several possible conformations are shown by Alagha, et al. (2013) in Figure 4.
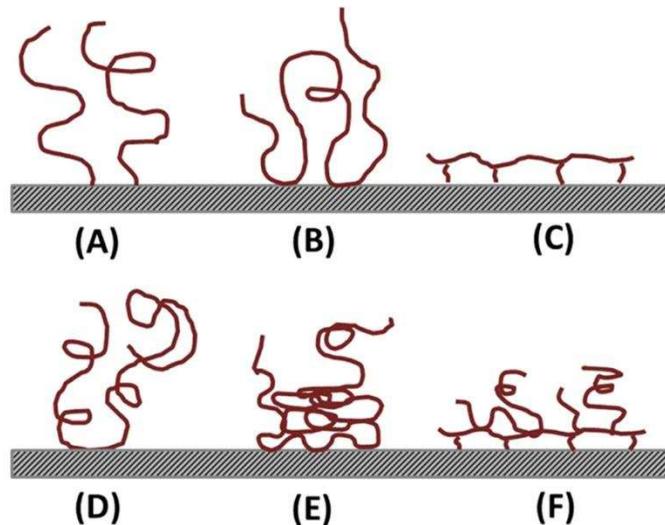

Figure 4: Possible polymeric flocculant conformations following adsorption (adopted from Alagha, et al., 2013. Permission pending.)

- Polymer-solids interaction: strong attraction will result in the polymer collapsing onto the solid surface (Fig. 2 cases C and F), and weak attraction leads to the polymer extending away from its anchor points (cases A, B, and D).
- Polymer-water interaction: strong affinity to water will encourage the polymer chain to maximize its contact area with water, resulting in conformations of polymer

brushes (e.g. case A, B, D); relatively hydrophobic polymers, on the other hand, will minimize their contact area in water resulting in mushroom-like conformations.

- Polymer self-interaction: excessive attraction between functional groups on the polymer chain will favor self-collapse and the formation of loops and coils (e.g. case E).
- Polymer chain stiffness: stiffer polymers, such as highly charged polymers, will have increased resistance to changes in their conformation.

Since the selection criterion for optimum removal of fine solids from aqueous suspensions is to quickly capture fines, the following conditions would have to be satisfied based on the above qualitative observations. Interactions between polymer and solids should be weakly attractive, since electrosteric or steric stabilization can occur (for charged and neutral polymers, respectively) if the polymers are strongly attracted to and hence fully cover the solids. Strong repulsion between the polymer and solids, on the other hand, can drastically reduce the collision efficiency between solids and polymers, as previously mentioned. When present in aqueous environments, the flocculant should have some degree of hydrophilic nature such that it is soluble in water and its extension into the aqueous phase in the form of loops is favourable. The extent of self-interaction should be minimized in order to promote greater contact points for solids capture, and levels of chain stiffness should be balanced between the preservation of chain integrity under fluid shear and sufficient mobility for chain re-orientation.

Once a properly-chosen polymer is attached to a solid particle, polymer brushes and loops extend from its anchor points into the aqueous phase and serve as connectors for the aggregation of additional solids via bridging, charge neutralization, and charged patch flocculation. Complex flocculation utilizing compounds such as cofactors (co-additives) for PEO-induced flocculation are common in the paper industry (Gaudreault, et al., 2005), and can involve sophisticated reaction and aggregation pathways in combination with the aforementioned mechanisms. As more solids accumulate on the polymer chain, the particle-polymer aggregate attains a much larger apparent particle size that readily settles under gravity.

Particle bridging is generally considered an attractive interaction in addition to the van der Waals attraction, with interaction energy formulated by Ji, et al. (2013) in terms of inter-particle distance for two spherical particles that depends strongly on the adsorbed polymer conformations (in terms of their contour length) and adsorption-specific parameters. Connecting particles in electrostatically-stabilized fine suspensions requires that the length of the extending polymer chains or loops meets or exceeds the combined electric double layer thickness of two particles, which precludes the use of short-chain polymers as flocculant unless electrolytes are present in significant quantities. Generally this mechanism is prevalent for polymers of low charge density (usually identified by "anionicity" or "cationicity"). This phenomenon also takes place in "sweep flocculation". Due to an excess of metal salts, waterborne metal hydroxide complexes are able to grow into large fractal structures that essentially act as an inorganic polymer. As a result, in addition to charge neutralization and electric double layer compression that usually accompanies coagulation, bridging of suspended particles and their subsequent flocculation are therefore possible.

At higher (> 30%) charge densities, polymers strongly adhere to oppositely charged solids neutralizing the surface charge (Smith-Palmer & Pelton, 2012). This leads to the polymers collapsing on the solid surface, which is especially detrimental at high flocculant dosages. However, incomplete surface coverage occurs at low dosages, where the attached polymer

"patches" are able to attract and flocculate other oppositely charged particles. Thus in practice it is critically important to determine the optimum dosage for a given type of flocculant to maximize solids attachment, while exercising due diligence in flocculant distribution to avoid local overdose (Masliyah, et al., 2011). The charged patch flocculation mechanism bears similarities to the precipitation of amorphous metal hydroxides on solid surfaces in coagulation. Additionally, when present in large concentrations, water-soluble flocculants that do not interact with solid surfaces can also induce aggregation via depletion flocculation. Since regions sandwiched between adjacent solid particles are energetically unfavorable for the presence of non-adsorbing flocculants, concentration gradients would exist between these regions and bulk solution, which produces an osmotic flow that drains water out of the flocculant-depleted regions and slowly propels particles closer to each other. At close inter-particle distances, the osmotic driving force is counteracted by the electric double layers on each particle, thus resulting in weak and reversible aggregation. Often for industrial applications it is only necessary to consider flocculation by bridging, charge neutralization, and charged patch mechanisms as they operate much more effective and faster than depletion flocculation. As an example for negatively charged particles flocculated by cationic polymers, Smith-Palmer and Pelton (2012) provided a summary of important factors that can affect the performance of these mechanisms as shown in Table 4.

Table 4: Impact of selected flocculant and solution properties on major flocculation mechanisms (adopted from Smith-Palmer and Pelton, 2012)

Condition of Increasing	Mechanism		
	Charge Neutralization	Charge Patch Flocculation	Bridging
Polymer Concentration	Destabilization	Destabilization then restabilization	Destabilization then restabilization
Polymer MW	Negligible	Small increase	Increase
Polymer Charge Density	Increase	Increase	Increase then decrease
Electrolyte Concentration	Increase	Decrease	Increase

Though the application of polymers for fine particle flocculation has proven largely successful, the anisotropic and irregular nature of the dispersed particles often necessitates additional measures to complement and improve the efficacy of single-polymer systems. Introduction of additional coagulant and/or flocculant that specifically binds to particle surfaces of different nature (Figure 5), offers the opportunity to increase the compactness and size of the solids-polymer aggregates, both of which further improve the rate of slurry clarification (Yuan & Shaw, 2007; Alagha, et al., 2013). Changes in adsorption conformations via external inputs are also possible for "smart" flocculants such as poly-NIPAM, whose hydrophobicity is found to be heavily influenced by slurry temperature (Franks, et al., 2009; Li, et al., 2007). Thus below the hydrophobic transition temperature, poly-NIPAM is hydrophilic and can be deployed similarly as a PAM. Increasing the system

temperature past transition will cause the adsorbed poly-NIPAM to minimize its contact area with water and therefore shrink in size, which reduces the solids-polymer aggregate size but increases the density of the aggregates. This switchable feature has been demonstrated to form sediments of lower moisture content than PAM. Application of such novel polymers for tailings management (among a variety of purposes) in the mining industry is an exciting field of work and has gained traction over the last 10 years.
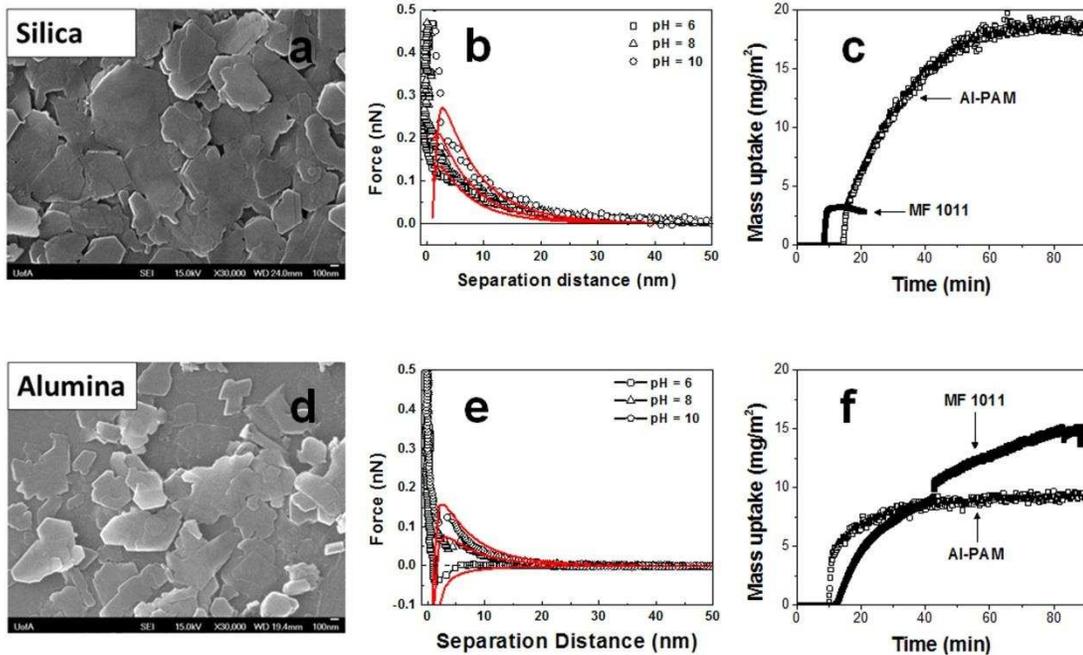

Figure 5: The added benefit of dual polymer addition is demonstrated when measuring polymer adsorption on anisotropic basal planes of kaolinite. Adopted from Alagha, et al. (2013). Permission pending. SEM micrographs of deposited kaolinite nanoparticles on silica and alumina piezo-electric sensors show a near uniform coverage with basal planes mostly exposed (a and d). To determine the preferential arrangement of the kaolinite nanoparticles on the sensor surface AFM force curves between a silicon nitride probe and the deposited particle layer were measured in Milli-Q® water at pH's 6, 8 and 10. A purely repulsive interaction on the silica sensor confirms exposure of the tetrahedral silica basal plane, while the pH dependent charge (repulsion pH 8 and 10, attraction pH 6) confirms the predominant exposure of the octahedral alumina basal plane (b and e). Measuring the adsorption properties of anionic (MF 1011) and cationic-hybrid (Al-PAM) flocculants on the two basal planes of kaolinite by quartz crystal microbalance – dissipation monitoring, preferential uptake of Al-PAM and MF 1011 is measured on the tetrahedral silica and octahedral alumina basal plane, respectively (c and f). From the adsorption properties it is anticipated that large compact flocs formed by electrostatic interaction with Al-PAM will bridge smaller flocs through the hydrogen bonding of the octahedral basal plane by MF 1011 (Alagha, et al., 2013). Dual polymer studies have been shown to form larger more compact flocs of the highest settling rate and lowest supernatant turbidity (data unpublished).

Other methods

Although suspension destabilization by aggregation via coagulation or flocculation is currently of industrial prevalence, many studies on alternative methods for enhanced particle settling have been published up to date. Some examples are presented here.

In 1955, Whitmore demonstrated that settling of a dispersed suspension can be enhanced by introducing neutrally buoyant particles (Whitmore, 1955). Among other researchers, experiments by Venkataraman and Weiland (1985) confirmed this phenomenon and suggested thickening of settled phases. The underlying physics and associated dynamic models were reviewed by Kulkarni, et al. (1993). In summary, the buoyant particles flow against gravity and produce "convection fingers" that generate a downward velocity, which propels the suspending solids to the bottom, subject to restrictions on buoyant and dispersed particle concentrations (as well as feed flow rate) that discouraged its potential for industrial applications. Interestingly, insights gained from these studies have led to the development of the inclined plate settler, which has been commercially deployed in, for example, particle size classification in the oil sands industry (Davis, et al., 1989; Nasr-El-Din, et al., 1990).

As fine solids generally have pH-dependent surface charges in a suspension, formation of aggregates can also be promoted by the addition of acids or bases to reduce the surface charge, thereby lowering the extent of mutual repulsion and promote destabilization. Instead of using large (and often costly) amounts of acids and bases, treatments with alternative acidifying or alkalising agents, many of them being waste materials, have shown promise. For example, Zhu, et al. (2011) investigated the injection of CO_2 into combined oil sand tailings (sand and fines), and determined conditions that significantly improved solids settling and sediment compaction without segregation of fines and sand. They have demonstrated a pH reduction from 8.2-8.4 to 5.9-6.2 in two samples that was attributed to the dissolution of CO_2 and subsequent formation of carbonic acid. Similarly, effective red mud neutralization was demonstrated by Jones and Haynes (2011) whom also noted its benefit on the quality of recycled process water. This type of approach appears beneficial and environmentally sound. Sequestration of other industrial flue gases (SO_x, NO_x, etc.) on suspension destabilization could also be investigated.

2.3. Consolidation and dewatering

After initially destabilizing the dispersed fine solids from a slurry, the settled solids form a water-saturated sludge of variable strength. It is often necessary to expel additional water from the sediment for further volume reduction and increase in mechanical strength of the sediment to meet the regulatory specifications for safe deposition. Historically, the mining industry has taken several key steps towards sustainable waste management practices on a broad scale (Jones & Boger, 2012). Subsequently, established guidelines and best practices (without universal geotechnical targets) became readily available for the dewatering and deposition of fine mineral tailings. As the most stringent extension to status quo regulations, the ERCB specifies minimum trafficable shear strengths of 5 kPa for consolidated oil sands tailings that has been deposited for one year, and 10 kPa after five years (ERCB, 2009). We urge other mining industries to establish similar standards suitable for respective types of tailings. Since the residual process water is physically contained inside the pores of the settled sediment, external energy is usually required to counteract the capillary pressure and further desiccate the solids. Energy demand increases further if it is desired to remove water that has been chemically bound to particle surfaces (Morey, 2013). Other processes utilize the

difference of physical or chemical properties between water and the bulk solids to achieve their separation. This section reviews the general principles associated with each of these approaches.

Dewatering and material strength

Mechanical strength of a fine solids suspension can be characterized in terms of its shear yield stress (resistance against flow) and compressive yield stress (resistance against compression), both of which grow exponentially with increasing solid content. Depending on the mineralogy, exact size distribution, and interactions between particles, a red mud sample that is typically fluid-like at less than 40% (w/w) solids can develop hundreds to thousands of Pascals in shear yield stress, and more than 18 kPa of compressive yield stress when dewatered to 60% (w/w) solids (Nguyen & Boger, 1998). Likewise, a sample of 10% (w/w) phosphate tailings with shear yield stress of 2.6 Pa consolidates, with external efforts, to a sludge of about 700 Pa at 48% (w/w) solids, although the accompanied increase in its compressive yield stress was unknown (Tao, et al., 2008). However, permeability of the congregated fine material decreases rapidly as the material consolidates and blocks paths of least resistance for entrained water, which significantly slows down the rate of further water removal. Additional strategies to counteract the decrease of material permeability and water release are usually incorporated as part of any commonly encountered dewatering process.

2.3.1. <u>Application of external energy</u>

Fine solids sludge formed from sedimentation and densification processes contains, in most cases, water trapped between randomly-oriented, thin-layered amorphous particles in the silt and clay size ranges. The small size and high surface area-to-volume ratios of fine particles suggest the existence of a myriad of internal nano-scale capillaries capable of storing large quantities of water. Consequently, sludge desaturation would require input of energy to work against the enormous capillary pressure as well as time-dependent compressive yield stress of the solid structure. Typical external energy sources are thermal, mechanical, electric, and their combinations or variants.

Evaporative and thermal treatments

Water removal by natural desiccation of fine mineral tailings has always been a key component of any land-based tailings management program. Initially, the fine solids sludge is deposited over a large area and exposed to natural elements that can assist (heat, wind, freeze-thaw cycles – see Exclusion of water) or hinder (rain and snow) drying. Clearly, this method is best suited for arid or semi-arid regions. Desiccation of the topmost fraction occurs relatively quickly and induces the formation of surface cracks due to shrinkage from water evaporation. This results in changes to the material permeability and exposes additional material for drying, though some clay minerals are able to self-repair desiccation cracks when subjected to moisture (Rayhani, et al., 2007). However, material fractions at depths of more than ~0.5 m do not experience significant natural drying even after a prolonged period of time, as demonstrated by Masala and Dhadli (2012). Mechanical means are often required to break or remove the top layers for additional exposure. Dedicated tailings drying by, e.g. calcination, is seldom applied unless the products are of economic value. Review of alternate red mud applications in

China and India by Liu, et al. (2009) and Samal, et al. (2013), respectively, provided good examples where the waste material is thermally treated to produce quality construction materials such as cement and fired bricks. Similarly, the kaolinite-rich oil sand fine tailings can also be processed in this manner into a cementing material for concrete (Wong, et al., 2004), although to the best of our knowledge, no large-scale production efforts are proposed at this time.

Centrifugation

When placed in a rotating body of rotation radius r at an angular velocity ω, fine solid sludge is subjected to an enhanced gravitational field that further compresses the sediment layer and releases pore water. The magnitude of such effect is termed relative centrifugal force (RCF) given in Eq. (3) in terms of the gravitational acceleration constant g.

$$RCF = \frac{r\omega^2}{g}$$ (3)

As the solid sediment gradually loses its entrained water, the compressive yield stress of the sediment increases exponentially that counteracts the applied compression force. Thus at a constant RCF value, a given sludge will, in time, consolidate to a corresponding equilibrium solids concentration. Centrifugation is sometimes used also for densification purposes. A comprehensive description of relevant particle sedimentation processes for industrial centrifuges is provided by Leung (1998). The consolidation process is irreversible as the bulk mass generally will not spontaneously re-disperse upon termination of rotation. Theriault et al. (1995) reported insignificant modifications of the equilibrium concentration by a variety of chemical, physical, and enzymatic treatments on MFT. Continuous centrifugation is currently applied in oil sands industry to remove fine solids from diluted bitumen in froth treatment. It is also used for enhanced moisture removal from fine and ultrafine coal in coal preparation plants. Use of centrifugation in the Utah oil sands pilot projects to treat extraction tailings was shown to successfully produce stackable solid deposits and drastically reduce the requirement for fresh water (Mikula, et al., 2008). The construction of a large-scale centrifugal tailings dewatering plant is currently underway in Syncrude Canada (COSIA, 2013). Commercial applications of centrifuges for treating wet mineral tailings are limited elsewhere in the industry.

Filtration and electrofiltration

Filtration is a widely practiced solid-liquid separation technique. In dead-end filtration, the feed material is placed on a porous filter medium (paper, cloth, or membrane), followed by introduction of a pressure gradient across the filter via vacuum, a hyperbaric gas, or mechanical press, that would drain out the entrained liquid while leaving behind a solid cake on the filter media. In this case the flow of filtrate is once-through and orthogonal to the filtration area. For cross-flow filtration the pressurized feed is directed parallel to the filter media, thus requiring recycle of feed flows to effectively treat the same volume of material. Mechanisms of water removal involved in filtration and compression stages are discussed by Mahmoud et al. (2010) and in detail by Dick et al.

(1980) and Lockhart and Veal (1996). At a given pressure gradient and filtration area, the rate of dewatering, or filtrate flux, is a complex function of the suspension and solids properties, such as solids concentration, size distribution, surface charge, hydrophobicity, etc.. These effects are reviewed by many researchers (Lockhart & Veal, 1996; Sung & Turian, 1994; Besra, et al., 2000; Wakeman, 2007).

Filtration of materials that are predominately fine solids is extremely difficult, as demonstrated by Sung and Turian (1994) with -400 mesh (< 37 μm) coal particles, due to their high specific resistance (low permeability) and compressive yield stress in a consolidated filter cake. The authors concluded that the amount of fine particles is a determining factor on the moisture of the solid cake. Indeed, Wakeman (2007) showed that the specific resistance of the filter cake is inversely related to the second power of particle size. To effectively filter fines-rich feed, either: a) cake thickness must be controlled and minimized (Lockhart & Veal, 1996), or b) particles will need to be coagulated and/or flocculated to promote their effective size and reduce resistance to filtration. The latter approach has seen an increasing number of experimental work and applications in treating fine coal tailings (Alam, et al., 2011), red mud (Power, et al., 2011), and oil sand tailings (Xu, et al., 2008; Alamgir, et al., 2012; Wang, et al., 2010), although polymer dosage control is critical for final cake moisture when flocculants are used (Lockhart & Veal, 1996). Surfactants can also be applied at proper dosages to render the particles hydrophobic and hence increase the recession rate of water from the filter cake (Stroh & Stahl, 1990; Morey, 2013).

Reduction of water viscosity also leads to improved filtrate flux, usually achieved by application of hyperbaric steam. Many authors (Peuker & Stahl, 1999; Bott & Langeloh, 2001; Morey, 2013) advocate the advantages of using hyperbaric steam that include: a) its rather unique and stable dewatering front – that is a gradual movement of a sharp interface between steam-saturated, heated filter cake and remaining water-saturated section, allowing for predictive modeling and better process control; b) a very dry cake that can be obtained even at continuous operations, as shown by Bott and Langeloh (2001); c) ability to extract solubilized species into the filtrate, and d) thermal disintegration or vaporization of adsorbed contaminants. A serious drawback with this method is its dependence on the material permeability (Morey, 2013), therefore the movement of the dewatering front is anticipated to be very slow for unconditioned fine tailings, limiting its potential treatment capacity.

Augmentation to conventional filtration operations that must process fine and ultrafine materials can be realized by the application of magnetic, acoustic, electrical, and electro-acoustic energy sources. An excellent review on electric field-assisted mechanical filtration (electrofiltration) was given by Mahmoud, et al. (2010). The electrofiltration method takes advantage of the electrical nature of the solid surfaces and induces electrophoresis of solids, electro-osmosis of water, as well as migration of dissolved ionic species towards the electrodes. In electrofiltration the cathode and anode are immersed in the feed material in such a way that the particle electrophoresis is directed away from the filter media. In such a configuration, according to Yukawa, et al. (1976), the resultant motion of particles would fully oppose the hydraulic transport of particles towards the filter media when a critical electric field is established. This phenomenon would certainly be beneficial to treating negatively-charged fine solids suspensions as the electroosmotic flow of cation-rich water is countercurrent to the electrophoresis of solids, as presented by Mahmoud, et al. (2010) in Figure 6. Thus, formation of low-permeability fine solids cake can be resisted while filtration progresses. Such approach was demonstrated to

accelerate the initial rate of dewatering on a quartz sand suspension with D_{50} of 2 μm and electric field parallel to filtrate flow, though limited improvement was found in the final cake moisture content (Weber & Stahl, 2002). Theoretical modelling by Raats, et al. (2002) showed an increased effectiveness of electrofiltration relative to conventional filtration of treating a concentrated sludge primarily consisted of micron and sub-micron sized particles. Indeed, a recent study by Loginov, et al. (2013) with 23.4% (w/w) sodium bentonite ($D_{50} = 3$ μm) in orthogonal electric field showed similar results as Weber & Stahl (2002). Further enhancements in filtration rate were demonstrated by the optimized addition of lime. Utilization of rotating electrodes, low frequency alternating current (AC), and interrupted input instead of direct current (DC) has shown promise to further improve dewatering rate and performance (Chen & Mujumdar, 2002).
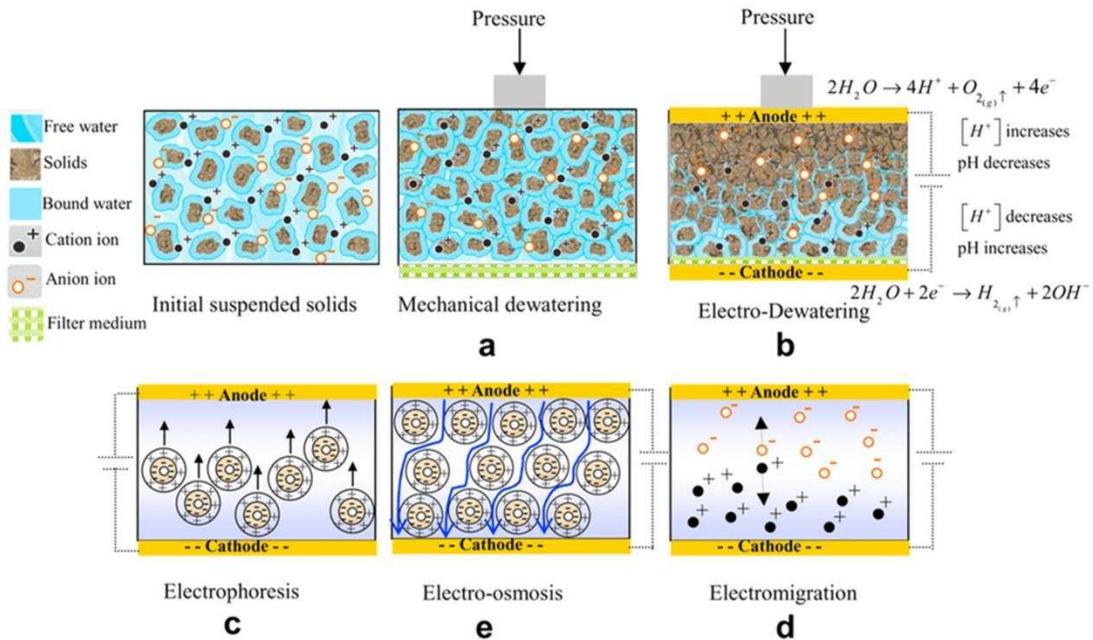

Figure 6: Mechanisms of electrofiltration (adopted from Mahmoud, et al., 2010. Permission pending.)

Other studies have been carried out for similar systems and investigated several beneficial and detrimental side-effects of electrofiltration, which are summarized by Mahmoud, et al. (2010). Electrochemical reactions at the cathode and anode increases and decreases local pH, respectively, which directly affects surface properties of the fine solids. It is foreseeable that, for example, a kaolinite slurry undergoing electrofiltration will gradually coagulate as they migrate toward the anode, and kaolinite particles would still be mobile at the filter media (cathode). In terms of preventing filter cake formation (and thus accelerated dewatering), this trait would be a valuable asset. However, as the operational electric voltages are typically much higher than that required for the electrolysis of water, gas formation will take place at both electrodes. Hydrogen and oxygen gas bubbles are potentially an explosive mixture, and they can also increase the void fraction and electrical resistance of the feed material. As a result, the rate of electrokinetic processes diminishes, contributing to an increased local heating at the electrodes. The resistance heating, on the other hand, reduces the water viscosity and surface tension, both playing a positive (although limited) role in improving the rate of solid-liquid separation. For electrofiltration, periodic cathode cleaning is necessary for

saline suspensions due to ion reduction and deposition of potentially insoluble hydroxides. Finally, the anode material is subject to oxidative corrosion, thus it is imperative to have relatively inert materials, such as those used by Raats, et al. (2002), to ensure the longevity of the process and trouble-free operations. These complications may have hindered the progress on systematic studies using pilot and full-scale equipment, and created difficulties in fully assessing its performance (Mahmoud, et al., 2010).

2.3.2. Exclusion of water

Water retained by a non-soluble porous medium generally has quite different physical and chemical properties from the containment material, which can theoretically be utilized to achieve dewatering. In cold regions for example, volume enlargement of ice and the exclusion of impurities from ice crystal growth have been successfully applied to treat pulp mill and oil sands wastewaters (Gao, et al., 2004). Though not yet applied on an industrial scale, developments in gelation materials that can nucleate or attach to suspended solids (but not water), and absorbents that specifically accept water into their molecular structure also offer new possibilities to effective dewatering.

Freeze-thaw

The basis of the freeze-thaw as a method to treat mineral tailings, and especially fine tailings, is briefly considered as follows. Solidification of pore water physically rejects interstitial mineral and ionic impurities from the ice crystal network towards spaces already occupied by mineral solids, which forces their aggregation. As the network grows, the corresponding volumetric expansion further compresses these aggregates and over-consolidates them, while increasing the average pore size (Proskin, et al., 2010). Therefore upon subsequent thawing, the entrained water experiences increased permeability and seepage can occur under gravity that leads to an overall reduction in sludge volume. Although beneficial from a dewatering viewpoint, freeze-thaw also leads to reduced material compressibility, which may necessitate further treatments for safe deposition (Beier & Sego, 2009). However, the undrained shear strength is observed to improve drastically for coal tailings and MFT due to the compressive stress exerted by the ice phase. Although an extensive study of freeze-thaw on Florida phosphate tailings was reported (Stancyzyk, et al., 1971), no published work could be found on the freeze-thaw treatment of other types of mineral tailings. Since this treatment method is seasonal and strongly depends on actual weather conditions in winter times, the benefits of freeze-thaw may be realized better if it is incorporated to other complementary dewatering technologies.

Gelation and water absorbents

Utilization of gelation agents to selectively bind and remove suspended solids is also an interesting area of research. Chaiko, et al. (1998) applied a combination of alkali silicate and an organic gelling agent to extract nearly all colloidal particles from a suspension. Upon aging at 70-90 $^{\circ}$C, synersis of gel components initiates rapid and spontaneous exclusion of water along with the dissolved salts from the rest of the slurry components. Iwata (2003) deposited sodium alginate on surfaces of the colloidal particles and added the mixture drop-wise to calcium chloride solution that led to the formation of calcium

alginate gel. Gravitational drainage and mechanical press are subsequently applied to expel water while effectively retaining the solids inside the gel. Since both studies used slurries of unspecified solids concentration, the effectiveness of these gelation agents on dewatering of concentrated sludge remains to be investigated.

Recently, Farkish and Fall (2013) demonstrated the potential of a water absorbent polymer on the consolidation of MFT. At a dosage of 3% (wt. absorbent/wt. MFT) and 7 days of conditioning, the granular cross-linked polyacrylate material is shown to readily absorb water and leave behind a residual with up to ~80% (w/w) solids and close to 9 kPa of undrained shear strength. Further dewatering and structural strength enhancements can be achieved via freeze-thaw cycles and natural drying. Thermal treatment is used to regenerate the material. However the performance of the recycled absorbent was found to gradually deteriorate. As water is ubiquitous in mineral tailings, clearly opportunities exist in the development and application of high-capacity and regenerative water absorbents as a viable dewatering method.

3. Overview of Current Technologies

Improved empirical and semi-empirical understandings on the nature of the fine mineral tailings constituents, their mutual interactions, and role of the conditioning agents have led to a gradual transition of fine tailings handling practices, from outright waste dumping and tailings containment to the development and acceptance of several mature densification and consolidation technologies by mining industries worldwide. Some of these technologies were adopted from historical approaches, such as coagulation by alum and filtration for water purification purposes. Others, such as the paste thickener, were invented as late as the 20th century as a result of advancements in the fundamental scientific knowledge of, for example, colloidal suspensions, flocculants, and fluid mechanics. Descriptions and brief evaluations of these widely established technologies are presented in this section. More detailed technology evaluations are publically available via the Oil Sands Tailings Technology Deployment Roadmap (Consortium of Tailings Management Consultants, 2012). However, substantial performance variations do exist from case to case, which reflect the inadequacy of our current understandings and highlight several key knowledge gaps between theory and practice. Indeed, industrial densification and consolidation equipment is almost exclusively built on the basis of laboratory and pilot plant test data as well as existing operation experience, instead of a fundamental, descriptive theoretical model at this time. Ongoing efforts from the scientific community and the mining industry on the path forward to reduce the environmental footprint of tailings are also discussed.

Concentration of finely dispersed mineral slurries has traditionally been focused on treating the beneficiated value products utilizing equipment such as hydrocyclones, thickeners, filters, and centrifuges to remove excess water for better material handling and reduce costs for transportation (Wu, et al., 2010). The same technologies were adopted, with modifications, by the mining industry as a starting point for fine mineral tailings treatments. Some of these technologies are sufficiently advanced and have been applied commercially, including densification technologies (consolidated and thickened tailings), as well as technologies for dewatering (natural drying and centrifugation). In other sectors of the industry, mechanical, vacuum, or hyperbaric filtration technologies also stood the test of time and became prevalent (Wu, et al., 2010). Much effort has been devoted to evolutionary enhancements on these mature technologies (e.g. electrofiltration) with varying degrees of success. As a result, new and revolutionary technologies (e.g. gelation and absorbents) are relatively scarce and have

seen limited standalone or integrated applications. Current technologies are feasible, but not all of them are economically practical to treat such large volumes of fluid fine tailings on a daily basis, especially in highly variable and extreme climate conditions. However, fundamental research will continue to help the industry identify and improve these technologies to the point where commercialization will eventually become practical due to the need to meet government regulations such as those set by ERCB Directive 074. With continuing effort of industry, for example, technologies such as thin lift drying, flocculation-enhanced centrifugation and/or filtration will mature to become reality. It should be noted that at present there is no 'silver-bullet' to resolve huge fluid fine tailings problems, rather a combination of technologies, such as flocculation-assisted centrifugation and filtration with co-deposition integrated into thin lift drying and/or rim ditching.

3.1. Densification technologies

3.1.1. Traditional technologies

Conventional pond storage

The practice of storage or impoundment of mineral tailings and fine mineral tailings in an engineered structure still remains popular as one of the least expensive treatment options for most mines (Watson, et al., 2010). Gravity sedimentation of solids occurs within the impoundment structure. Due to extremely long residence time to handle solids in the silt and fines size range, large pond sizes are typically required. Self-consolidation of solids forms a sediment layer and separates from the process water, both of which can be withdrawn for further processing and usage. Typical outgoing solids concentrations are in the range of 30-55% (w/w), depending on suspension conditions (Watson, et al., 2010) as discussed in section 2.1. Wu, et al. (2010) noted that the conventional treatment method is of "high capacity, low maintenance, and low operating cost", in agreement with comments made by Watson, et al. (2010), who also indicated the conventional method is the sole reliable technology for plants with high production rates classified by the authors as > 100,000 tonnes/day (tpd).

Hydrocyclones

Traditionally, hydrocyclones are widely used in the mineral processing industry as an inexpensive and compact device for particle classification and concentration purposes. As a high capacity device, hydrocyclone can typically process feed up to 7200 m^3/h and enrich solids up to 50% (w/w) at underflow discharge (Ortega-Rivas, 2012). Operating principles of a hydrocyclone is similar to centrifuges in which a centrifugal force is produced from rotation of slurry, except that hydrocyclones do not have moving parts. As a slurry containing particles of different sizes enters the hydrocyclone, the swirling motion of the fluid flow tends to spin the coarse and dense particles towards the vessel wall while retaining the finer and lighter particles in the center. Wall erosion by solid particles is attributed as the greatest threat to hydrocyclone operations and demands considerable attention in maintenance. Fortunately, advancements in erosion simulation software have led to numerous new equipment designs that significantly reduce vessel wear (Wu, et al., 2010).

Satisfactory separation of dispersed fine solids from water in a hydrocyclone has been difficult due to a lack of generating sufficiently clear overflow (Franks, et al., 2005; Consortium of Tailings Management Consultants, 2012). Recent developments suggest that improvements may be achieved with hydrocyclone units in smaller diameter (Yang, et al., 2013), or operated under modified process conditions, e.g., cyclic flow (Zhao, et al., 2008), and application of an electric field (Nenu, et al., 2010), though care must be taken to avoid underflow blockage for small units. Experimental work on utilizing these performance enhancements in hydrocyclone for treating fine mineral tailings slurry has yet been published at this time.

3.1.2. Assisted fines destabilization

Coagulation-based technologies

Commercial installations of a densification technology utilizing coagulants on fine tailings are best demonstrated by the so called composite or consolidated tailings (CT) process, also known as non-segregating tailings (NST) process, in the oil sands industry. In essence, fresh extraction tailings are classified in a hydrocyclone, and the coarse underflow is mixed with chemical (coagulant) treated MFT (or fresh fluid fine tailings) to create a non-segregating mixture that settles quickly and releases water efficiently (Masliyah, et al., 2011). The CT leaving the process typically has solid concentrations of 57-60% (w/w) which requires further dewatering measures to meet targets set by ERCB Directive 074. In other mining operations, a version of the NST can also be realized if cement or a binder material is added to fine tailings, forming a paste to prevent segregation and improve material strength (Watson, et al., 2010). Capital investments for CT installation can be expensive (Consortium of Tailings Management Consultants, 2012), and major operating cost is by coagulant/binder addition and energy demand from fluid transport. In addition, the process requires high degrees of control over feed properties, which is reflected from the reported poor reliability in actual CT operations with regards to, for example, product quality (Alberta Energy Regulator, 2012; BGC Engineering Inc., 2010).

Flocculation-based technologies

The thickened tailings (TT) and paste thickener processes involve the addition of polymeric flocculants to the feed material, followed by means of proper mixing and, in some cases, clarification inside a thickener. Typical underflow solid concentrations have been reported to be 25-55% (w/w) for oil sand fine tailings (Masliyah, et al., 2011; Consortium of Tailings Management Consultants, 2012), and 50-70% (w/w) for other mineral tailings with conventional and high-rate thickeners at the lower end and above 65% (w/w) for high-density paste thickeners (Watson, et al., 2010). Since its inception in 1973 at Kidd Creek, Canada, commercial applications of TT are gaining popularity. The largest TT project currently in operation is reported to have a capacity of 95,000 tpd, located in northern Chile. Procurement, operation, and maintenance of specialized equipment and flocculants are often required to pursue this option, which can amount to significant costs.

The immediate benefits of using technologies described in section 3.1.2. are near-complete fine solids capture and potential cost savings realized from smaller tailings impoundment structures and water recycle, which offsets, to some extent, increased capital and operating costs from additional equipment, piping, and slurry transportation. Since the extent of water removal in some cases is restricted by available slurry pumping and pipeline transportation technologies (Jones & Boger, 2012), additional dewatering measures are generally necessary. Applications would be favored for mining operations where land or water resources are restricted, and discouraged where exists, for instance, high energy cost, unfavorable project economics, and/or less stringent regulations on mine waste discharge.

3.2. Dewatering technologies

3.2.1. Natural drying

Thin-lift drying

This technology applied to oil sands extraction tailings involves deposition of treated tailings products, such as pond sediments, CT, or TT, in thin layers that are subjected to gravity drainage, natural desiccation, and freeze-thaw cycles. Inclined surface is generally used to enhance water release and collection, and the angle of inclination is highly dependent on the rheological properties of the product, ranging from 0.5-2.0% for pond sediments and 3.0-10.0% for paste tailings (Watson, et al., 2010). Perimeter underdrains are typically in place to control seepage of process water. Successive layers are deposited on the previous layers once sufficient drying is achieved and the material becomes self-supportive. This technology and its variants are also widely applied in the alumina industry to treat red mud, where it is termed as "dry stacking" (Power, et al., 2011). Although inexpensive to operate, this technology requires substantial land area due to long residence time for the deposited layer to reach desirable dryness and strength suitable for subsequent deposition and/or reclamation, which creates limitations to the volume of tailings that can be timely treated.

Deep in-pit deposition (rim ditching)

In comparison with thin-lift drying, deep tailings deposition discharges the treated tailings into deep engineered pits. Natural desiccation and freeze-thaw of topmost layers occur relatively quickly, whereas underdrains, vertical (wick) drains, perimeter rim ditching, and other mud farming operations help to remove water from the deeper sections via exposure, gravity drainage, and self-weight consolidation (BGC Engineering Inc., 2010). Though labour-intensive, successful applications of deep in-pit deposition have been reported for dewatering phosphate tailings in Florida (Carrier, 2001). Geotechnical tests are ongoing to evaluate the strength and trafficability of oil sand tailings deposits over long periods of time. In particular, results from Shell's Tailing Testing Facility appear promising after 5 years in operation (Masala & Dhadli, 2012).

3.2.2. Centrifugation

The continuous solid bowl scroll decanter centrifuge is widely used in mineral processing (Consortium of Tailings Management Consultants, 2012). Pre-treatment of fine tailings is necessary prior to centrifugation for efficient fine solids capture and would eliminate the need for excessively high rate of rotation, which translates to the increase in the treatment throughputs. An application example of a horizontal decanter centrifuge to treat flocculated MFT is given by Masliyah, et al. (2011), in which 270 m^3/h feed is enriched to a solid product of 60% (w/w), while recovering high quality process water of < 1% (w/w) solids. Based on the past experience, adequate process controls will be required to maintain feed solids concentration targets. Capital investments and operation and maintenance costs of centrifugation for oil sands tailings treatment are expected to be significant due to fast-moving mechanical parts.

3.2.3. Filtration

Various mechanical, vacuum, and pressure filtration installations are common for dewatering coal tailings and red mud (Bethell, 2012; Power, et al., 2011), but have rarely been applied in oil sands. Dry disposals of coal tailings are becoming increasingly common and generally performed with belt filter presses and plate-and-frame filters (Bethell, 2012). Belt filter presses require feed pre-treatment, usually by flocculation, and produce solid products that depend on the particle size distribution of the feed. Typical capacities are 3.6-10 tonne per hour per meter of belt width for fine tailings, which produces products of 45-65% (w/w) solids. In belt press filtration, large loss of fine solids (up to 40% w/w of total solids) can occur if feed material is predominately clay-sized (Fenzel, 2012). In 2004, the capital and operating costs are also estimated by Fenzel (2012) to be Australian (AU) $0.49/tonne and AU $1.84/tonne of solids to be treated, respectively. Although cost-effective, the relatively low product solid concentration and product consistency may be unsatisfactory. On the other hand, other filter presses such as plate-and-frame are more expensive but enables near-complete solids capture, which also gives a final product of 18-30% (w/w) surface moisture only (Prat, 2012). Limited data on the filtration rate suggest a flux of 110-140 kg/m^2-h to achieve a surface moisture of 21-23% (w/w) for a South African metallurgical coal tails (Prat, 2012), and similarly for a sample of Pennsylvania anthracite refuse (Verma & Klima, 2010). As a result, large filtration areas are required to accommodate high-rate processing plants. Laboratory investigations on the pressure filtration of oil sands MFT revealed that higher throughputs can be achieved by proper fine solids flocculation and the selection of a two-stage filtration process (Wang, et al., 2010; Alamgir, et al., 2012). Figure 7 compares single stage filtration (plain region) and two-stage filtration (i.e. flocculation and thickening followed by filtration as shown by shaded region) for processing MFT. With appropriate dilution of MFT, the filtration time to achieve 23% (w/w) cake moisture can be reduced from 25 min to 10 min by operating a two-stage filtration process. The two-stage process is favorable since it filters only the thickened sediment. With appropriate choice of flocculant (Al-PAM), large mushroom-like flocs are formed that favor rapid dewatering under applied pressure. Reuse of the clarified supernatant as dilution water ensures that the process produces a net gain of water for recycling, as well as reducing the chemical loading to achieve minimum filtration times. With this configuration it is less critical to have effective flocculation of fines.
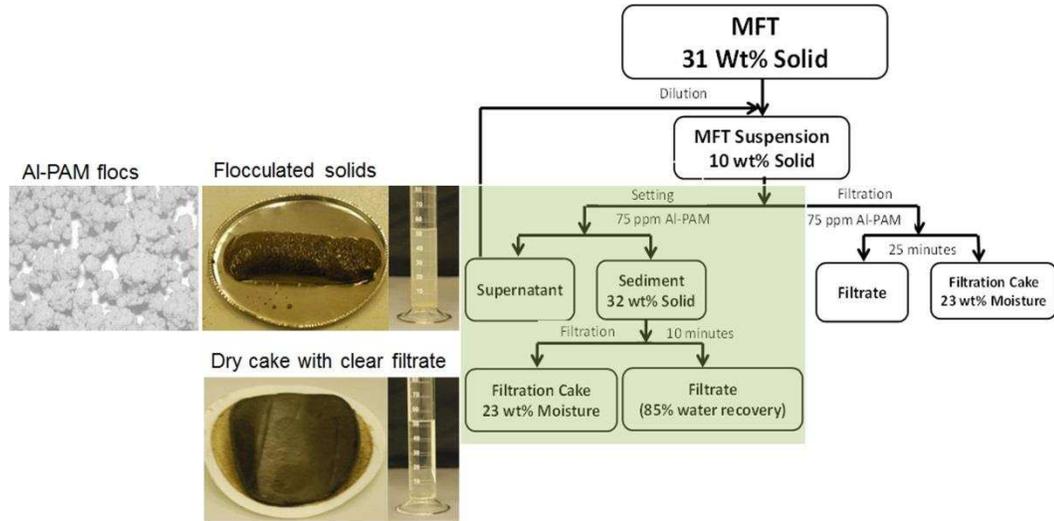
Figure 7: Proposed treatment processes for oil sands MFT using filtration. Shaded rectangle indicates the preferred option. Process as well as product visuals "Flocculated slurry" and "Filtered sediment" are adopted from Alamgir, et al. (2012). Permission pending. Product visual of Al-PAM flocs adopted from Wang, et al. (2010). Permission pending.

To date, few operators have reported commercial applications of pressurized steam filtration, and even fewer for electric field-enhanced filtration. An encouraging prototype setup employing the combined principles of centrifugation and pressure filtration are shown to continuously process 120 L/min of fine coal slurry to products of less than 20% moisture, even when the feed material is dominated by particles of less than 25 μm (Keles, et al., 2010). However its effectiveness on treating fine coal refuse and other fine mineral tailings remains to be investigated.

3.3. Knowledge gaps

There are many proposed short-term and long-term solutions to alleviate or eliminate the accumulation of fine mineral tailings via enhanced solids sedimentation as well as sludge desaturation. Unfortunately over time, only a few have managed to maintain the delicate balance of process efficiency and economics, and not all of these methods are considered commercially robust or reliable at present time. As discussed previously, this is a direct consequence stemming from the generally decreasing ore grade and loss of mineral selectivity with current mechanized mining and hydrometallurgical beneficiation processes, both of which introduce degrees of variability across tailings streams in terms of key physical and chemical properties. Due to their complex nature, current theories on the fundamental properties and conditioning of fine mineral tailings mostly follow empirical or semi-empirical approaches performed with ideal (single solid component) slurries and less commonly, real tailings. Conclusions drawn from existing studies are difficult to extrapolate for a priori industrial equipment selection, design, and operation. For most, if not all industrial applications dealing with fine tailings, sound industry expertise coupled with extensive performance data and evaluations from lab- and pilot-scale tests are mandatory before their full-scale implementation. Unfortunately, even for the most veteran processes and techniques it is still difficult to perform reliable on-line

measurements to determine changes in response to variations in important and relevant feed property parameters. It is a common practice to adjust necessary equipment controls in time by grabbing and analyzing samples at fixed time intervals, which occasionally causes operational problems ranging from off-spec products to equipment blockage. More comprehensive analysis on this aspect can be found in a recent document entitled Oil Sands Tailings Technology Deployment Roadmap (Consortium of Tailings Management Consultants, 2012). This five-part roadmap focused extensively on current and potential technologies/operational guidelines, accumulating information not just from oil sands but from the global minerals and mining sector. The report, compiled through the collaborative efforts of many technical and industrial experts assessed numerous technologies that were categorized based on their current status of deployment and feasibility. We encourage readers of greater interest in this aspect to review the roadmap for more details on individual technologies.

An option available to mine operators is to develop protocols for selective mining to reduce the amount of fine tailings production, however its implementation may be costly and the practice is unnecessary in the long-term. The demand for mineral products continues to grow with no end in sight, even the leanest of ore deposits will become economically attractive to mine. Additionally, it should be noted that although tailings processing and environmental management are generally a minor component of the CAPEX and OPEX profile of a major mining operation, it represents resolving a huge liability issue to mining companies. This potential liability would limit the growth of the industry and further development of the valuable resources due to potential catastrophic disaster of dam structure failures and/or long term land disturbances that present potential risks to wildlife. Resolving such issue is a major step towards responsible development of our valuable natural resources. Thus efforts should be concentrated on facing the tailings problems head-on instead of delaying the inevitable long-term issues. For the foreseeable future, instead of treating fine mineral tailings as a black box, emphasis should be given to advancements in fundamental science for improved comprehension of their macroscopic properties and behaviours. This will certainly serve to better refine current treatment techniques, as well as greatly assisting the development of next-generation techniques that can revolutionize the management of fine mineral tailings.

Since the subject of interest involves a myriad of micron- and nano-sized solid particles, it is essential to address several aforementioned key microscopic properties: e.g. size distribution, mineralogy, and morphology, using standardized characterization methods and procedures, both of which can greatly benefit from improvements to measurement technologies and devices. Also, it is of utmost importance to study the fundamental molecular-scale interactions between solid materials of different mineralogy and morphology across a spectrum of grain sizes in water, and with any chemical additives in the complex solution environments with inevitable soluble species and contaminants. Similarly important is to characterize morphology as well as geotechnical and mechanical properties of the particle aggregates. Foreseeably, the 'silver bullet' to managing fine mineral tailings would involve an array of sub-processes that recognizes these complexities from a fundamental level. There is no single 'silver bullet'. The 'silver bullet' would most likely be an entire process of its own with innovative integration of chemicals and process configurations with the rest of the mining operation.

Current research efforts utilizing ideal and model slurries must continue while special attention should be given to establishing relevant connections to real tailings. In the meantime, available microscopic properties and observations should be carefully

leveraged to achieve quantitative conversion between microscopic behaviours from/to essential macroscopic parameters to fundamentally address and model commonly encountered phenomena such as:

- In enhanced settling: a unified sedimentation-consolidation model addressing fluid-solid state transitions (BGC Engineering Inc., 2010).
- In dewatering: fluid transport through immiscible, compressive, porous media.
- In slurry transport and disposal: rheological and depositional behaviour of thickened tailings, pastes, and dried solids; optimizing transportation equipment and strategies of tailings feed and products.
- Slurry conditioning: molecular interactions between suspended solids, additives, and contaminants; impact of these molecular interactions on enhanced settling, dewatering, and modification of slurry bulk properties; design and synthesis of novel chemical additives; optimized addition and mixing guidelines/strategies.
- Process control and reliability: real-time monitoring of important slurry properties.

Additionally it may be of interest for mine operators to explore alternate uses for unfinished/finished tailings products.

4. Conclusions

In the mining industry, accumulation of large amounts of fine mineral tailings is still an ongoing issue due to increasing demand of mineral products and insufficient means to consume the associated tailings that are generated by mega-scale mining operations. In many cases the tailings are conventionally stored in engineered ponds that are susceptible to accidental discharges and a host of environmental issues that pose significant risk to the public and surrounding areas.

Much effort has been devoted to fundamentally investigate the two key technical issues (slow settling and water capture) involved with fine tailings by addressing their sedimentation, consolidation, stability, and rheological behaviours. Coagulation and flocculation are effective at destabilizing fine solid suspensions, both of which can greatly accelerate solid-liquid separation under the correct conditions. More energy will be needed to further consolidate the solid sediment and release additional water. Specialty reagents that specifically remove water or solids also show some promises. Performance of actual densification and dewatering technologies varies by application. At this time, extensive laboratory and field tests are mandatory before implementation. This is a consequence of our limited understandings on the actual feed material, as difficulties exist when extending the current fundamental understandings to predictively describe actual tailings samples. It is highly desirable to establish links between their microscopic characterization parameters and observable bulk behaviour. Opportunities exist in further refinements and extensions of current scientific models to better describe actual fine mineral tailings. Evidently, better theoretical models improve and assist industrial efforts when processing fine tailings, or solid slurries in general with similar nature, positively affecting a wide range of activities such as equipment design and scale-up, modification and retrofitting, operation and process control, product quality assurance, and ultimately reliability of the process. All of these serve to reduce technical and financial risks of brownfield and greenfield fine tailings treatment technologies, by improving the robustness for existing applications, and the performance certainty for emerging projects.

Compared with the status quo scenario (interpreting fine tailings as a black box), where over-production and under-utilization of tailings have created a vicious cycle of waste accumulation that is prone to environmental damage, the fundamental approach – although difficult at first – helps to drive a virtuous cycle that gradually reduces and eliminates fresh and legacy fine mineral tailings. As noted by Jones and Boger (2012), in the past 30 years or so, growing mutual cooperation between mine operators, global research teams and forums, as well as equipment suppliers to address the challenging issues brought by fine mineral tailings is very encouraging and extremely valuable. These efforts are indispensable for significant contributions to our understandings of the tailings problem while further improving the sustainability of the entire mining industry. Insights gained from such multi-disciplinary exchanges of knowledge offer great potential to the advancements in other related research areas.

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