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Monitoring polymer flocculation in oil sands tailings: A population balance model approach

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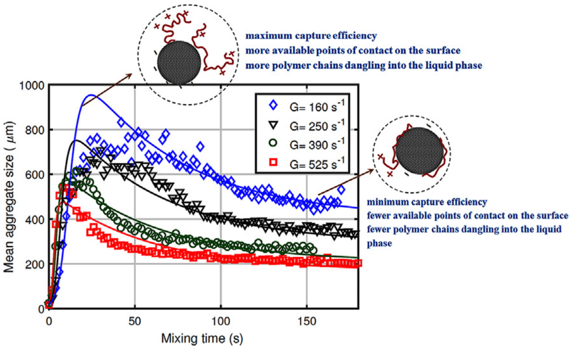
HIGHLIGHTS

- Population balances were used to model polymer-induced flocculation of MFT.
- A new capture efficiency was introduced to account for polymer chain relaxation.
- FBRM was used to validate aggregate size obtained by the model for MFT flocculation.
- The model predicted MFT flocculation with shear rate, time and flocculant dosage.

GRAPHICAL ABSTRACT



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ABSTRACT

Oil sands mature fine tailings are stable suspensions of clay particles and residual bitumen in an alkaline aqueous medium. They are formed when bitumen is extracted from oil sands using the Clark hot water process. Polymer flocculants are widely used to flocculate and subsequently dewater these tailings, but our knowledge is limited to empirical observations on how they work. A fundamental mathematical model would help monitor and design flocculation and dewatering processes more efficiently. In this study, we used a population balance model to describe the flocculation of mature fine tailings (MFT) with poly(vinylbenzyl trimethylammonium chloride). A time varying function was defined to account for the aggregate size evolution during MFT flocculation induced by polymer chains relaxation and rearrangement on the particle surfaces. The validity of the model was tested by varying the shear rate, mixing time and flocculant dosage using focused beam reflectance measurements (FBRM). The proposed model is a first step towards a more rational and quantitative approach to monitor and control treatment processes for oil sands tailings.

1. Introduction

Population balances are used to describe how the size and distribution of particles in a population change as a function of time [1]. Marian von Smoluchowski, the godfather of stochastic physics, was the first to describe the aggregation of monodisperse colloidal particles using population balances approximately 100 years ago [2–4]. Since then, population balances have been used to describe processes such as crystallization [5,6], polymerization [7,8], granulation [9,10], coagulation and flocculation [11,12].

Flocculation is a process in which large aggregates are formed from fine particles with the help of long polymer chains (flocculant). Light weight fine particles (in the range of micrometers) in wastewaters or mineral processing (waste streams) usually carry surface charges that

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significantly delay (or even prevent) the aggregation and settling of the particles. Polymer chains adsorb to particle surfaces and accelerate the aggregation process, forming aggregates up to a few millimeters in size, through bridging, induced by van der Waals forces or by charge neutralization. Mixing promotes the flocculation by enhancing the flocculant dispersion, adsorption, and not the least, the collision rates between particles and polymer molecules. Therefore, flocculation is governed by two events: 1) aggregation due to contact of particles and 2) fragmentation (breakage) due to fluid shear forces. To model the flocculation, population balances must account for aggregation and fragmentation events during flocculation processes. No general explicit solution exists for these population balance equations, although some analytical solutions have been proposed under simplifying assumptions [1]. The two numerical methods widely used to solve population balances involve discretization (Hounslow et al. [13] Kumar and Ramkrishna [14], Spicer and Pratsinis [15]), and the method of moments (McGraw [16] and Fox et al. [17]).

Several researchers have used population balances to describe the flocculation of real or synthetic colloidal systems. For instance, Ding et al. used population balances to describe activated sludge flocculation [18], Ahmad et al. modeled the flocculation of palm oil mil effluents [19], and Heath et al. adapted population balances to describe calcite flocculation in turbulent pipe flow [20]. Our work is the first attempt to model the flocculation of oil sands tailings.

Canada's oil sand deposits are the third largest oil reserves in the world. The heavy crude oil (bitumen) they contain is extracted using large volumes of warm water. The net water consumption (after subtracting the water recycled back to the process) varies depending on the method of extraction. For instance, every barrel of bitumen produced by surface mining consumes about 3 barrels of fresh water [21]. Since the first commercial production of bitumen by surface mining in a Suncor mine in 1967, close to 600 km^2 of land have been affected by oil sands mining, 180 km^2 of which are currently occupied by tailing ponds. This area, more than 1.5 times the size of city of Vancouver, continues to grow, posing considerable environmental concerns [22].

Tailings are pumped to ponds, where sand settles quickly and is used to build containment dikes. The solids suspended in fluid fine tailings (containing mineral particles with characteristic dimensions below 44 μm) remain in slurry for as long as five years of gradual sedimentation, and eventually form a mud-like slurry (30–40% solids by weight) called mature fine tailings (MFT). The volume of MFT generated in this process is approximately 1.5 times larger than the volume of bitumen extracted from oil sands [22].

MFT is identified by its suspended minerals and water chemistry, which vary depending on the extraction geological location and process. A typical MFT is a suspension of fine mineral particles (mostly clays, 30–40% by weight), water (60–70%), and residual bitumen (2–5%). MFT clays are mostly kaolinite and interlayered kaolinite-smectite (35% by weight, 10–20 $\text{m}^2\,\text{g}^{-1}$), and illite and interlayered illite-smectite (60–65%, 65–100 $\text{m}^2\,\text{g}^{-1}$), chlorite (3–5%,) and swelling clays (e.g. montmorillonite, 1–2%, 700–840 m^2g^{-1}) [23,24]. MFT water contains inorganic ions, and has a typical pH of about 8. The suspended particles have net negative surface charges that prevent them from aggregating and settling by gravity.

Oil sands producers treat MFT with technologies such as thin lift, rim ditching, consolidated/composite tailings, and centrifugation. Each has their own advantages and disadvantages. For example, thin lift drying, where flocculated tailings are spread and allowed to dewater over an area with shallow slope, is a relatively inexpensive practice but requires large land area, while centrifugation or filtration of flocculated tailings may be effective dewatering methods that do not require much space, but are also more expensive [22].

Regardless of what method is used, polymer flocculants are the basis of most of these treatment technologies. Polymer flocculants destabilize MFT particles via bridging, charge patching, and/or charge neutralization. Current commercial flocculants are designed to treat a variety of wastewater types, and are highly soluble in water. They generally belong to the polyacrylamide (PAM) family and its ionic copolymers. When PAM-based flocculants are used to treat MFT, they produce a loose cake with a gel-like structure that is hard to dewater [25].

Currently, the leading researchers in this field are trying to develop new polymer flocculants designed to work in the challenging MFT environment. Most of their effort, however, has been spent on evaluating potential flocculants through indirect performance indicators such as settling rate, supernatant water clarity, sediment solids content, dewaterability through capillary suction time, shear monitoring, sieve testing, or pressure filtration [26–32].

Several operating conditions, however, influence MFT flocculation: 1) flocculant dosage, 2) flocculant microstructure (molecular weight, charge density, comonomer composition, branching density, grafting frequency, polydispersity), 3) water chemistry (pH, ion strength), 4) mixing time, pattern and intensity, and 5) primary particle size and concentration of the suspended solids [33–37]. All these variables affect the dynamics of aggregate formation, flocculation mode, aggregate size, density, dewaterability, and compressibility. These conditions are key to evaluate the performance of new flocculants, and the subsequent dewatering and consolidation of the sediments. One of the crucial steps in the efficient design of dewatering processes is controlling the flocculation process by polymers. Faced with so many variables, we are convinced that a mathematical model that could quantify the effect of *at least* some of these conditions on tailings flocculation would be extremely useful to develop new flocculants and tailings treatment processes. Population balance models can predict the size of aggregates, which is directly linked to their settling velocities, this information is essential to determine the size and efficiency of a treatment process, such as large scale thickeners. Furthermore, aggregate size is correlated with aggregate density, which directly influences dewatering and filterability of sediments of the flocculated tailings. More importantly, population balances can be integrated with computational fluid dynamics (CFD) models to predict a full spectrum of aggregate size and concentration within a large-scale treatment unit experiencing large variations in fluid mixing conditions [38].

In this article, we propose an approach that may help fill this need: a population balance model to describe MFT aggregate formation using the novel flocculant poly(vinylbenzyl trimethylammonium chloride), poly(VBTMAC). This approach, however, is not limited to poly(VBTMAC), but could be used with other flocculants. We used experimental MFT batch flocculation data obtained by in situ focused beam reflectance measurement (FBRM) to train our model and validate its predictions considering 3 industrially relevant variables: shear rate, mixing time, and flocculant dosage. This is the first step in a long-term research effort to establish quantitative methods to correlate polymer type and treatment conditions to MFT flocculation and dewatering performance.

2. Experimental

2.1. Materials

Monomer, vinylbenzyl trimethylammonium chloride (VBTMAC) and initiator, 2,20-Azobis(2-methylpropionamidine) dihydrochloride (V-50) were purchased from Sigma–Aldrich. Shell Canada supplied the MFT sample.

2.2. Flocculant synthesis and characterization

A partially hydrophobic cationic flocculant, poly(VBTMAC), was synthesized by aqueous free radical solution polymerization at 50 °C in a 0.5 L glass polyclave reactor (büchiglasuster®, Switzerland) equipped with a temperature-controlled jacket, impeller, and a purging line. A 0.5 M VBTMAC solution was introduced into the reactor and purged