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Sedimentation of fine particles of kaolinite and polymer-coated kaolinite in cyclohexane: Implications for fines removal from extracted bitumen in non-aqueous processes

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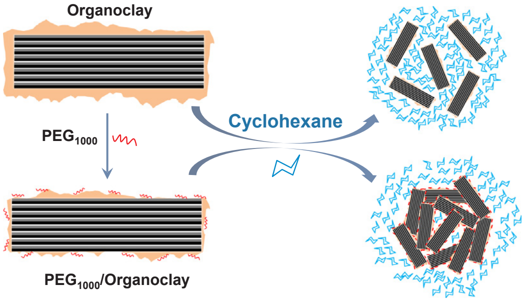
GRAPHICAL ABSTRACT



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ABSTRACT

Sedimentation of kaolinite microparticles (< 1 µm) in cyclohexane was investigated in order to design efficient methods for fine particles removal in bitumen froth from oil sands processing. Kaolinite coated by copolymers (Polyethylene-block-poly(ethylene glycol) (P/P), and poly(4vinylpyridine co-styrene) (V/S)) were used as model particles to mimic the behaviour of fines present in bitumen. The model compounds were prepared by adsorption of the copolymers onto kaolinite. Characterization results (FTIR, TGA, ^{13}C NMR and XRD) confirmed the presence of the organic matter (2.0% for V/S and 3.4% for P/P) exclusively on the external surface of clay platelets. The presence of these copolymers reduced strongly the sedimentation rate of kaolinite in cyclohexane, as a result of the organophilic interactions between modified clay and cyclohexane. Addition of polyethylene glycol (PEG$_{1000}$) in the clay suspension increased the sedimentation rate. A model suggesting the adsorption of this polymer at the surface of modified clay particles with subsequent improvement of the aggregation of particles was proposed to interpret the phenomenon. When dry mature fine tailings (D-MFT) were used for sedimentation experiments, the presence of 0.0125% of PEG$_{1000}$ (w/w) improved the sedimentation rate by a factor of 20. The results obtained in this work are promising for the design of simple and efficient methods for fines removal in the context of non-aqueous bitumen extractions.

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1. Introduction

Oil sands represent a significant oil reserve mostly located in North and South America [1]. They consist of a mixture of minerals (mostly sand and some amounts of clays), water and bitumen. Bitumen is a complex mixture of organic compounds consisting of light hydrocarbons, simple aromatic compounds (named resins) and compounds with high molecular weight called asphaltenes [2]. In recent years, innovations in petroleum extraction from oil sands rendered its large scale exploitation possible. Whatever the process applied for the extraction (aqueous extraction or Steam Assisted Gravity Drainage), the product obtained contains large amount of fine particles that must be removed to improve bitumen quality [3–6]. These particles were found to induce pipelines occlusion by facilitating asphaltenes precipitation. These fines also reduce the activity of catalysts used for bitumen processing into light petroleum by-products. The removal of fine particles from bitumen therefore represents a major issue for the valorization of bitumen extracted from oil sands. For this purpose, two strategies are used to reduce the amount of fines in water extracted bitumen froth: the naphthenic froth treatment and the paraffinic froth treatment. These methods are energy and time consuming [7].

It has been shown that the fine particles present in bitumen consist essentially of clay minerals, the most abundant ones being illite and kaolinite [8–11]. Interestingly, kaolinite was identified as the most important clay mineral in the stability of these fine particles in bitumen [11].

Kaolinite is a 1:1 phyllosilicate with structural formula $Al_2Si_2O_5(OH)_4$. One elemental layer of this clay mineral consists of one silicon based tetrahedral sheet bound to one aluminum based octahedral sheet. The stacking of these individual layers to yield kaolinite platelets is ensured by hydrogen bonding and dipolar interactions existing between the consecutive siloxane and aluminols surfaces [12–14]. This explains why intercalation and mainly grafting reaction in the interlayer surface remain particularly challenging [15–17]. The two basal surfaces of these kaolinite platelets show different chemical properties. The aluminol surface carries an overall positive charge because of the partial positive charges associated to the surface hydrogen atoms. In addition, this surface is hydrophilic while the siloxane surface is organophilic and carries an overall negative charge associated to the partial negative charges of the oxygen atoms. This Janus-character of kaolinite particles was confirmed by some authors during the adsorption of organic compounds in non-polar solvents [18–20]. Other authors have exploited this feature to functionalize the two basal surfaces with different compounds [21–23]. These properties also explain the strong interactions existing between kaolinite and bitumen compounds. Indeed, the characterization of fine particles found in bitumen froth shows that they are covered by a layer of organic material, particularly difficult to remove. This organic layer that surrounds the mineral particles results in the strong stability of the fines in the extracted bitumen. Only few works in the literature are dedicated to the study of the behaviour of kaolinite in organic solvents in presence of other organic compounds [18,19,24], and more specifically the study of kaolinite settlement in organic solvents.

In this work, we present new developments of a strategy that can be used to facilitate the sedimentation of fines present in bitumen. It consists of adding a compound (PEG_{1000} in this case) to a kaolinite suspension that can interact with clay particles and facilitate their sedimentation. Such an approach was explored by some authors in water, using cationic polymers or amines and alkylammonium as kaolinite settlement promoter [25,26]. We first worked with model clay materials based on kaolinite modified by two copolymers. These model clay materials were designed to present chemical properties similar to that of fines present in bitumen. The copolymers used for the preparation of model clay materials were selected based on their chemical properties close to those of chemical compounds found in bitumen, and that absorbs onto clay minerals. These chemical compounds present both organophilic groups and heteroatoms that ensure their hydrophilic character. Sedimentation of these particles was then studied in cyclohexane as solvent. The choice of cyclohexane is explained by recent works which showed that this solvent represents an excellent candidate for non-aqueous extraction of bitumen [6,27]. Subsequently, dry Mature Fine Tailings (D-MFT), were used to perform sedimentation experiments in order to operate with systems displaying properties closer to those obtained during bitumen recovery from oil sands. These model kaolinite fine particles and D-MFT were characterized by FTIR, NMR, XRD and TGA. Sedimentation experiments were monitored by mean of turbidity measurements. The second order kinetic model was used to fit the experimental data for efficient comparison of the results obtained.

2. Experimental section

2.1. Materials and chemicals

Polyethylene-block-poly(ethylene glycol) (P/P), and poly(4vinylpyridine co-styrene) (V/S) were purchased from Aldrich. Cyclohexane, chloroform and toluene were of analytical grade. Well-crystallized kaolinite (KGa-1b) was obtained from the Source Clay Repository of the Clay Minerals Society, Purdue University, West Lafayette, IN, USA. Fraction under 1 μm was collected by sedimentation and used for the preparation of composite materials. MFT suspension obtained from Syncrude Canada Ltd. (Fort McMurray, AB, Canada) was oven-dried at 60 °C, crushed in a mortar and sieved (100 μm mesh) to obtain the dry mature fine tailings (D-MFT) used in this work.

2.2. Kaolinite preparation and modification

For the preparation of the composite materials, 50 mg of copolymer (P/P or V/S) was dissolved in a round bottom flask containing 15 mL of chloroform. 300 mg of fine fraction of kaolinite (< 1 μm) was then added to the copolymer solution and the resulting mixture stirred for 15 h at room temperature (~23 °C). The solid was recovered by centrifugation and washed with chloroform (3×10 mL) and dried in oven at 60 °C for 15 h. The resulting materials were named K-P/P or K-V/S when P/P or V/S was used respectively for adsorption experiments.

2.3. Characterization

Solid-state ^{13}C NMR CP/MAS spectra of model compounds (K-P/P and K-V/S) and D-MFT were collected on a Bruker AVANCE 200 spectrometer, operating at a spinning rate of 4.5 kHz.

Powder XRD patterns of Kaolinite, K-P/P, K-V/S and D-MFT samples were recorded using a Rigaku Ultima IV diffractometer operating with Cu-Kα radiation ($\lambda = 1.54056$ Å) using a generator operating at a voltage of 45 kV and a current of 40 mA.

KBr pellets of Kaolinite, K-P/P, K-V/S and D-MFT samples were prepared for the FTIR analysis and the spectra recorded on a Thermoscientific Nicolet 6700 FT-IR apparatus.

Thermal gravimetric analyses (TGA) of Kaolinite, K-P/P, K-V/S and D-MFT samples were recorded using a TA instrument Q5000 under house air flow (25 mL min^{-1}) at a heating rate of 10 °C min^{-1}.

2.4. Sample preparation for turbidity measurements.

Since PEG_{1000} was poorly soluble in cyclohexane, a minimal amount of toluene was used as a co-solvent to improve its solubility in cyclohexane. A PEG_{1000} solution in toluene was thus prepared by solubilizing 100 mg of the polymer in 2 mL of toluene to yield a final concentration of 50 g L^{-1}.

For turbidity experiments using copolymer covered kaolinite composites, 10 mg of clay material was introduced in a vial containing 10 mL of cyclohexane. The mixture was first sonicated in an ultrasound bath for 1 min and stirred on a shaker for additional 60 min. The vial