



## Research paper

## pH dependence of bentonite aggregate size and morphology on polymer-clay flocculation



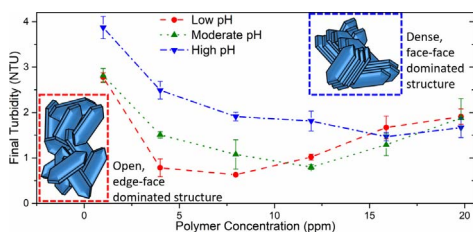
Nikolas Wilkinson<sup>a</sup>, Athena Metaxas<sup>a</sup>, Chase Quinney<sup>b</sup>, Susith Wickramaratne<sup>c</sup>,  
Theresa M. Reineke<sup>c</sup>, Cari S. Dutcher<sup>b,\*</sup>

<sup>a</sup> Department of Chemical Engineering and Materials Science, University of Minnesota - Twin Cities, 421 Washington Avenue SE, Minneapolis, MN 55455, USA

<sup>b</sup> Department of Mechanical Engineering, University of Minnesota - Twin Cities, 111 Church Street SE, Minneapolis, MN 55455, USA

<sup>c</sup> Department of Chemistry, University of Minnesota - Twin Cities, 207 Pleasant Street SE, Minneapolis, MN 55455, USA

## GRAPHICAL ABSTRACT



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## ABSTRACT

Polymer-driven flocculation of suspended particulate is a commonly used technique in applications ranging from water treatment to composite material synthesis. When complex particulate is present, such as anisotropic clays, solution physiochemical effects on flocculation become nontrivial. Properties such as ionic strength and pH affect both the individual particulate aggregates themselves, as well as the polymer – particle flocculation event. Using bentonite, a common inorganic clay, and cationic polyacrylamide, we show here that the clay's aggregate morphology is a more direct control parameter of optimal polymer dose and final turbidity than zeta potential for aqueous bentonite systems. Solutions were studied over a pH range from 3 to 11, resulting in zeta potentials from  $-73$  to  $-106$  mV and bentonite area averaged particle sizes ranging from 2 to 4.5  $\mu\text{m}$ . Flocculation performance is the same when bentonite aggregate morphology is the same, regardless of a change in zeta potential. Likewise, when bentonite aggregate morphology changes, flocculation performance also changes, regardless of the identical zeta potential. The optimal polymer dosing for flocculation also depends on aggregate structure. Aggregates formed by edge-face dominated structures formed at low pH require less polymeric dosing, whereas aggregates formed by face-face dominated structures formed at high pH require more polymer dosing. Finally, using laser scanning confocal microscopy, it was observed that when the aggregate size remains relatively constant, the internal floc structure also remains constant, regardless of pH or bentonite aggregate morphology. Therefore, it appears that initial clay aggregate morphology controls the extent of polymer adsorption, determining optimal polymer dose, while aggregate size controls the internal floc structure. This work sheds light on the complexities of polymer flocculation towards improving reagent polymer dosing and optimization for applications such as water purification.

\* Corresponding Author.

E-mail address: [cdutcher@umn.edu](mailto:cdutcher@umn.edu) (C.S. Dutcher).

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## 1. Introduction

Flocculation of particulate with polymers in aqueous solution is a widespread practice, with applications ranging from water treatment to composite material synthesis [1–5]. These varied applications occur in a range of chemical environments, from acidic, to neutral, to basic conditions. Additionally, surface waters, often a source of many drinking water supplies, have time variant solution chemistry, resulting in conditions that change throughout treatment operations. Bentonite, the inorganic clay used here, is a ubiquitous inorganic smectite clay mineral commonly found in surface waters. Bentonite has a high water absorption capacity and, as a result, more than 10 million tons per year [6–8] are used in drilling fluids, paints, pharmaceuticals, adhesives, and in wastewater treatment as an absorbent [9].

Recent work has explored the effect of ionic strength and ionic strength history on the flocculation of bentonite using cationic polyacrylamide, examining both flocculation performance and internal floc structure using confocal microscopy [10,11]. It was observed that increasing NaCl concentration drastically reduced optimal polymer dosing levels, and changed the internal floc structure from a highly interconnected, bridged structure at low ionic strength to a patchy, less connected structure at high ionic strength. Increasing ionic strength was also observed to increase bentonite average aggregate size by more than 2 orders of magnitude. However, if the bentonite was first dissolved in distilled water prior to the addition of salt, the initial bentonite average aggregate size remained relatively small. Flocculation of these sterically stabilized small aggregates, even at high ionic strengths, resulted in the highly interconnected, bridged floc structure observed previously only at low ionic strengths. The results indicated that the initial bentonite aggregate size, rather than ionic strength, controls internal floc structure for clay systems [11].

In addition to aggregate size, the morphology of aggregates certainly influences the way the polymer interacts with the aggregate. Aggregate surface area has been shown to greatly affect cationic polyacrylamide adsorption [12]. For inorganic clay particles such as bentonite, the morphology varies nonlinearly in solution with pH. Individual bentonite particles have been described as thin sheets, or flakes, that can self-interact in three different ways: edge-edge, face-face, and edge-face. The different interactions lead to bentonite aggregates with different surface structures and surface areas. Edge-edge interactions lead to chain-like morphologies, whereas face-face interactions lead to dense stacks. Edge-face interactions lead to very open and random morphologies. While all three of these interactions generally occur within a bentonite aggregate, morphology is often dominated by one type of interaction.

Morphological changes of the bentonite particles are attributable to the bentonite interaction strength, which varies with ionic strength, and the inhomogeneous charge distribution on bentonite sheets, which varies with pH. It has been observed that an increase of ionic strength changes the structure of bentonite particles from a porous, edge-face arrangement to an edge-edge dominated structure, to ultimately a much denser, face-face structure [13–16]. Likewise, Tombácz and Szekeres [17] found that as the pH of bentonite solutions increased from 4 to 8.5, a change of the structure was observed. At pH 4, the bentonite aggregates exhibited an open, edge-face and edge-edge dominated structure and at pH 8.5, the bentonite aggregates exhibited a dense, face-face dominated structure. Additionally, they found that the stability of bentonite solutions to salt-induced aggregation increased as pH increased from pH 4 to 8.5 [17].

There are several previous studies exploring the effect of pH on equilibrium adsorption of cationic polymer to clay surfaces [18–20]. In general, these studies have found that the adsorption capacity of clay minerals for cationic polymers increases as pH increases, due to the increased interaction strength of the positive cation on the polymer with negative charges on the clays at high pH. However, these adsorption capacity measurements are not performed in the often complex

and turbulent hydrodynamic mixing conditions used in flocculation processes. Studies of flocculation performance with pH show that flocculation performance decreases with increasing pH [21,22]. Decreasing polymer charge has been used to explain the observed decreased flocculation performance [21]. There was limited consideration of initial aggregate size or aggregate structure in these prior studies however, and there have been no studies exploring the internal polymer-particle floc structure with variations of pH.

In this work, we aim to explore the relative importance of pH and zeta potential and bentonite aggregate morphology on flocculation performance and internal floc structure. The effect of initial, pre-flocculation bentonite aggregate morphology on flocculation performance is explored by examining final turbidity curves and the optimal polymer dose. Internal floc structure is examined using a fluorescent analogue of the cationic polyacrylamide and laser scanning confocal microscopy. These results exploring pH effects build on prior work exploring the effect of ionic strength, and shed new light on the complexity of solution condition effects on flocculation of anisotropic, natural clays.

## 2. Materials and methods

### 2.1. Materials

The materials used here are identical to those described elsewhere [10,11]. Water used in experiments is distilled water from Premium Waters, Inc. Powdered Na-bentonite and NaCl, as well as aqueous solutions of NaOH and HCl are ACS grade from Fisher Scientific and used as received. The Na-bentonite from Alfa Aesar was mined in Great Britain, with a supplied chemical composition mass analysis of 57.1% SiO<sub>2</sub>, 17.79% Al<sub>2</sub>O<sub>3</sub>, 4.64% Fe<sub>2</sub>O<sub>3</sub>, 3.98% CaO, 3.68% MgO, 3.27% Na<sub>2</sub>O, 0.9% K<sub>2</sub>O, 0.77% TiO<sub>2</sub>, 0.06% Mn<sub>2</sub>O<sub>3</sub>, and 7.85% components lost during chemical analysis.

The commercial polymer used in this study is cationic polyacrylamide (FLOPAM FO 4190 SH, SNF Polydyne) with 10% quaternary amine monomer charge groups and molecular weight of  $6 \times 10^6$  g/mol. A 0.2 wt% stock solution was made by mixing 0.8 g of the polymer into 400 mL of distilled water using a Jiffy LM model mixer in a 500 mL container, as instructed by the manufacturer. Generally, solution pH can also change the charge state of cationic polymers. However, the cationic polyacrylamide used here contains a quaternary ammonium, which is largely unaffected by pH. The polymer interaction with pH is discussed in more detail in Section 3.1.

For internal structure visualization, fluorescent Cyanine5-labeled PAEMAM-*s*-PMAAPTA (polyN-(2-aminoethyl)methacrylamide -*s*- poly[3-(methacryloylamino)propyl] trimethylammonium chloride) ( $M_n = 3.3$  MDa,  $dn/dc$  (experimental) = 0.1081,  $M_w/M_n = 1.247$ ) was used and was synthesized in the same manner as described previously [10,11]. The fluorescent polymer has the same quaternary amine cationic charge group as the commercial polymer, with the same charge percent of approximately 10 mol%.

### 2.2. Procedure

The procedures used here have been described previously [10,11], with the addition of measurement of pH, and is summarized below. For all experiments, 30 mg of bentonite was added into 1 L of water in 2 L Pyrex jars. The bentonite was then dispersed at 300 RPM for 30 min in a VELS Scientifica JTL4 Flocculator. A 10 mL sample was then withdrawn to take an initial turbidity measurement using a LaMotte turbidity meter and a pH measurement using a Mettler Toledo SevenExcellence pH meter. All measurements were taken in triplicate and averaged. Once the pH was measured, the speed of the flocculator was then decreased to 200 RPM and the desired amount of polymer was injected into each jar. The polymer was mixed into the solution at 200 RPM for 3 min, then slow mixed for 30 min at 30 RPM. At the end of the slow mix, the solution would sit undisturbed for 5 min. Turbidity and pH

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