High-salt stabilization of Laponite clay particles

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Abstract

Colloidal radioactive transuranic wastes are currently buried in large tanks in the form of dense colloids in high salt, high pH aqueous media. These facilities are beginning to fail, so it is necessary to transport and "package" them for more permanent disposal, processes requiring understanding of the microstructure that develops under such conditions. Laponite RD clay is believed to be a good simulant for the colloids in the waste tanks, and the present study addresses their behavior under high salt conditions, where previous studies have frequently observed the phenomenon of "restabilization," i.e., the attainment of aggregation *stability* at high electrolyte conditions. Specifically, the aggregation kinetics and the resulting cluster structure (fractal dimension) of Laponite RD clay colloids at high concentrations of $BaCl_2$ (an electrolyte previously shown to lead to restabilization) are investigated. At low-to-intermediate electrolyte concentrations, the clay is found to behave in accord with DLVO theory, i.e., low salt conditions yield slow aggregation into densely-packed aggregates, whereas intermediate salt concentrations, sufficient to cause double layer collapse, produce rapid aggregation into open aggregates. High salt concentrations, however, show slow rates of aggregation. The aggregate structure under these conditions is found to mimic that found for very low electrolyte concentrations, i.e., high fractal dimension. Further experiments show that a sudden increase in salt concentration in a system containing young open aggregates produced under intermediate salt concentrations causes them to reform into more compact structures.
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1. Introduction

The understanding of the interaction between colloids as described by the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory coupled with the knowledge of the growth process and the resulting cluster structure have long been applied to describe aggregation of electrostatically-stabilized particles [1]. Full destabilization achieved by the displacement of the charged surface groups or a reduction in the Debye–Hückel screening length leads to Smoluchowski kinetics for diffusion limited cluster-cluster aggregation. When the aggregation rate is limited only by the time between collisions, the formation of open aggregate structures, with fractal dimensions, D_f, ranging between 1.7 and 1.8, results. While this scenario describing the aggregation of electrostatically-stabilized colloids has been well established, certain cases exist where the aggregation behavior does not follow traditional DLVO theory. For instance, several studies of colloidal systems (clay particles [2], metal colloids [3], oxide particles [4,5], amphoteric latex particles [6], Pluronics [7] and protein coated latex particles [8], and a globular protein (apoferritin) [9]) have observed an *increase* in stability or a decrease in aggregation rate at relatively high salt concentrations. This is in contrast to that predicted by DLVO theory, i.e., once electrostatic repulsion is screened, further addition of salt should not slow down the expected rapid aggregation. However, non-DLVO forces, i.e., hydration forces, are believed to dominate at high salt concentrations, and a reduction in aggregation rate is observed. While some empirical observations (Schulze–Hardy rule and Hofmeister series) may provide guidance in determining the critical coagulation concentration (CCC) for aggregation, it is usually not possible to determine whether or not high-salt stabilization will occur. The

interactions between the ions and the surface are quite irregular and do not follow any obvious ionic parameter in high salt media [7,10–12]. A recent theory proposed by Manciu and Ruckenstein attempts to address these irregularities [13]. In this theory, high-salt stabilization is attributed to the ability of acidic and basic sites on the surface to associate with the abundance of counterions that exist at high salt concentrations creating ion pairs or surface dipoles. These surface dipoles then polarize the water molecules, ordered as ice-like structures, which propagate generating a repulsive force upon overlap of these hydration shells. The aggregate structure (fractal dimension) under conditions where high-salt stabilization of electrostatically-stabilized colloids occurs has not yet been investigated. Under ordinary conditions, high fractal dimensions (2.0–2.1) or compact aggregates have been observed for the slow "reaction-limited" cluster–cluster aggregation (RLCA) occurring in aqueous systems with low electrolyte concentration, while low fractal dimensions (1.7–1.8) are observed for aggregates formed by rapid diffusion-limited cluster–cluster aggregation (DLCA) occurring at high salt concentrations [1]. A recent study has shown that for intermediate conditions, the aggregate fractal dimension is in direct proportion to the logarithm of the stability ratio, i.e., $\log W$, where the stability ratio is defined as the ratio of the rate constant for rapid aggregation to that for the aggregation observed [14].

The present work seeks to characterize the aggregation behavior (both aggregation kinetics and aggregate structure) of an electrostatically-stabilized colloid, Laponite clay particles, over a wide range of $BaCl_2$ concentrations. Barium chloride is selected as the electrolyte because of its ability, observed earlier in the authors' laboratory, to cause colloidal stabilization at high concentrations [7]. In the present study, clay particles are used as a simulant for stored transuranic waste at the Hanford site, Richland, WA [15]. The desire to remove liquid-like nuclear waste stored in carbon–steel tanks and its conversion to solid waste suitable for permanent disposal provides the motivation for such a study. The wastes are high in salt content, extremely alkaline, and contain particulates, organics, and inorganics. Attempts at waste removal would require an understanding of the microstructure that could form under such conditions. This study thus seeks to determine the relationship between aggregation rate and aggregate fractal dimension under conditions where high-salt stabilization may occur. Aggregation kinetics in terms of stability ratios are followed to observe if in fact restabilization occurs in high salt concentrations for Laponite RD suspensions and if so, what is the resulting cluster structure. Aggregate structure arising from the nature of the aggregation process is determined using fractal scaling of clusters in light scattering. If a reduction in aggregation rate, i.e., reduction in sticking probability, is observed in concentrated $BaCl_2$ solutions, restructuring experiments are conducted to follow any changes in aggregate structure upon transferring fresh aggregates grown under intermediate salt conditions (CCC) to high salt media. Additional electrophoretic mobility measurements were performed to indicate any changes to the synthetic clay surface upon change in salt concentration.

2. Materials and methods

2.1. Materials

The clay particles used were Laponite RD (Laporte Industries, Cheshire, UK) obtained as dry powder with a density of 2.57 g/cm^3 and a chemical composition: SiO_2 66.2, MgO 30.2, Na_2O 2.9, and Li_2O 0.7 wt% [16]. When dispersed, Laponite particles exist as colloidal discs, approximately 30 nm in diameter and 1 nm thick, in aqueous solutions when concentrations are below 3 wt%. The face of the colloid has a net negative charge while the edge of the disk is less negative or even positive, depending on the pH. If Laponite is dispersed into deionized water at pH below 8.5, dissolution or degradation of clay particles occurs [2,16,17]. This is accompanied by an increase in the pH of the suspension. As a result, the aggregation kinetics of clay in $BaCl_2$ solutions were examined in this study for two cases:

Case 1: Suspension in deionized water at pH 6.5–7.5.
Case 2: Suspension in deionized water at pH 10.

In this study, an equilibrium pH value of 10 results for both cases. For the following experiments, particle suspensions were made daily in order to prevent a gradual decrease in pH due to the CO_2 absorption from air.

All water used was deionized (conductivity of 0.5 μS/cm) with a pH of 6.5–7.5 while additional filtering (0.20 μm Nylon) occurred for all water, salt solutions, and Laponite suspensions. The pH of the suspensions was adjusted using 0.1 M NaOH and HCl solution. The salt used was barium chloride (J.T. Baker Inc., Phillipsburg, NJ).

2.2. Methods

Suspensions were prepared by dispersing approximately 0.1 g Laponite in 20 ml of deionized water using rapid agitation for 5 min with a Genie Vortex Mixer (Scientific Industries, Bohemia, NY). During this time, the mixer speed should be sufficiently high to produce a vortex. The suspension was mixed with a stir bar for additional 2 h (without creating a vortex) and then was passed through a 0.20 μm Nylon syringe filter. For aggregation and restructuring experiments, it was subsequently diluted to the desired particle number concentration of 1×10^{11} particles/ml and was again passed through the syringe filter. Dynamic light scattering was used to detect the presence of any aggregates and returned a hydrodynamic diameter of 33.6 ± 3.2 nm.

Aggregation kinetics were monitored at 25 °C using dynamic light scattering. Measurements began immediately after the particle suspension was added to the desired salt concentration. Dynamic light scattering was performed using the Brookhaven Instruments (Holtsville, NY) ZetaPALS system consisting of a BI-APD avalanche photodiode, and 522-channel Model BI-9000AT digital correlator, together with a LaserMax, Inc. (Rochester, NY) diode laser operating at 658 nm and