# Effects of Ionic Strength, Salt, and pH on Aggregation of Boehmite Nanocrystals: Tumbler Small-Angle Neutron and X-ray Scattering and Imaging Analysis

L. M. Anovitz,<sup>†,</sup>\*<sup>®</sup> X. Zhang,<sup>‡®</sup> J. Soltis,<sup>‡®</sup> E. Nakouzi,<sup>‡</sup> A. J. Krzysko,<sup>§®</sup> J. Chun,<sup>‡®</sup> G. K. Schenter,<sup>‡</sup> T. R. Graham,<sup>§®</sup> K. M. Rosso,<sup>‡®</sup> J. J. De Yoreo,<sup>‡®</sup> A. G. Stack,<sup>†®</sup> <mark>M. Bleuel,<sup>||,⊥</sup> C. Gagnon,<sup>||,⊥</sup> D. F. R. Mildner</mark>,<sup>||</sup> J. Ilavsky,<sup>#</sup> and I. Kuzmenko<sup>#</sup>

<sup>†</sup>Chemical Sciences Division, Oak Ridge National Laboratory, MS 6110, Oak Ridge, Tennessee 37831-6110, United States <sup>‡</sup>Physical Sciences Division. Pacific Northwest National Laboratory, Richland, Washington 99354, United States

<sup>§</sup>The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, Washington 99164, United States

<sup>II</sup>Center for Neutron Research, National Institute of Standards and Technology, Stop 6102, Gaithersburg, Maryland 20889-6102, United States

<sup>1</sup>Department of Materials Science and Eng. J. Clark School of Engineering, University of Maryland, College Park, Maryland 20742, United States

<sup>#</sup>Argonne National Laboratory, 9700 S. Cass Avenue, Bldg. 433A, Argonne, Illinois 60439, United States

ABSTRACT: The US government currently spends significant resources managing the legacies of the Cold War, including 300 million liters of highly radioactive wastes stored in hundreds of tanks at the Hanford (WA) and Savannah River (SC) sites. The materials in these tanks consist of highly radioactive slurries and sludges at very high pH and salt concentrations. The solid particles primarily consist of aluminum hydroxides and oxyhydroxides (gibbsite and boehmite), although many other materials are present. These form complex aggregates that dramatically affect the rheology of the solutions and, therefore, efforts to recover and treat these wastes. In this paper, we have used a combination of transmission and cryo-transmission electron microscopy,



dynamic light scattering, and X-ray and neutron small and ultrasmall-angle scattering to study the aggregation of synthetic nanoboehmite particles at pH 9 (approximately the point of zero charge) and 12, and sodium nitrate and calcium nitrate concentrations up to 1 m. Although the initial particles form individual rhombohedral platelets, once placed in solution they quickly form well-bonded stacks, primary aggregates, up to  $\sim$ 1500 Å long. These are more prevalent at pH = 12. Addition of calcium nitrate or sodium nitrate has a similar effect as lowering pH, but approximately 100 times less calcium than sodium is needed to observe this effect. These aggregates have fractal dimension between 2.5 and 2.6 that are relatively unaffected by salt concentration for calcium nitrate at high pH. Larger aggregates (>~4000 Å) are also formed, but their size distributions are discrete rather than continuous. The fractal dimensions of these aggregates are strongly pH-dependent, but only become dependent on solute at high concentrations.

## INTRODUCTION

Understanding, predicting, and manipulating chemical speciation, interfacial dynamics, and resultant emergent phenomena in complex, heterogeneous environments are central challenges for environmental management and energy technologies. The US government currently spends approximately 6 billion dollars annually managing Cold War legacy contamination, including more than 300 million liters of liquid waste stored in tanks, such as those at Hanford, WA. These contain complex mixtures of saltcakes, sludges, and highly alkaline solutions of concentrated electrolytes aging for decades in the presence of ionizing radiation. The DOE projects that retrieval and processing of the tank materials will require at least 50 years and hundreds of billions of dollars.<sup>1</sup> However, the DOE Report "Basic Research Needs for Environmental Management"<sup>2</sup> identifies fundamental knowledge gaps that limit waste treatment schedules including an inability to anticipate chemical and physical complexity and variability within and

Received: March 15, 2018 **Revised**: September 6, 2018 Published: October 15, 2018



between tanks; unpredictable slurry rheology during sluicing; dissolution rates that are typically much slower than predicted; and controlling subsequent precipitation when desirable.

A key challenge for understanding the rheological responses of these wastes is their complex physicochemical nature.<sup>3-5</sup> They contain high concentrations of caustic dissolved salts (typically, pH > 11-12) and a wide variety of solid particles with broad size distributions  $(0.1-100 \ \mu m)$  and irregular shapes/rough surfaces. The most prevalent solids in the waste are gibbsite Al(OH)<sub>3</sub> and boehmite ( $\gamma$ -AlO(OH)),<sup>6,7</sup> but other salts and Ag, Ni, Pu, Pb, and Sr compounds are present.<sup>8</sup> Rheological responses are, in general, determined by the balance between repulsive and attractive particle interactions from colloidal, hydrodynamic, and frictional forces, influenced by the aforementioned physicochemical characteristics.<sup>9,10</sup> Unfortunately, the unique environments in the waste slurries impose limitations on the use of simple Deryaguin-Landau-Verwey–Overbeek (DLVO) theory<sup>11</sup> to describe the forces between particles, which are expected to be highly dependent on the structures of the crystal surfaces  $^{12-14}$  and the surrounding solution.  $^{12,15-17}$  Examples of such complicated interactions include: (1) coupling between electrostatics and electrodynamics via the effect of ion fluctuation on van der Waals forces<sup>18</sup> and dispersion contributions to electrostatic forces from ion-surface interactions<sup>19</sup> and (2) restabilization of particles at high salt concentrations<sup>20</sup> related to ion hydration. Thus, these forces are dependent not only on ionic strength but also on the type of ions present.<sup>19,21-23</sup> Furthermore, the wide range of particle sizes/shapes would trigger long-range entropic forces<sup>24</sup> closely associated with distributions of ions and solvent molecules near interfaces.

Particle-particle interactions have a significant effect on the rheological properties of the slurry, which reflect the mechanical resistance of those slurries to an external flow field. Thus, the microstructures resulting from particle interactions via aggregation, fusion, or coarsening $^{25-29}$  are *directly* responsible for the rheological response.<sup>10,30</sup> For example, the yield stress of a slurry corresponds to the maximum force per unit area its microstructure can withstand before rupturing at low shear rates. The yield stress is, therefore, dependent on the spatial configuration and strength of interparticle interactions. Consequently, physical insights into the correlation between the physicochemical parameters (e.g., pH and salt concentrations) and the spatial configuration of the microstructures are critical for understanding rheological responses. However, the irregular shapes/rough surfaces of many solid particles in the waste slurries currently prohibit calculation of particle interactions and the resultant dynamics that are the other critical component in understanding rheological responses. These pose significant challenges for describing colloidal and hydrodynamic interactions, particle size evolution, and development of hierarchical structures.

To understand the correlations between spatial configurations and physicochemical parameters during aggregation of tank waste particles under the conditions described above, we have used small and ultrasmall-angle neutron scattering ((U)SANS), dynamic light scattering (DLS), and transmission and cryogenic transmission electron microscopy (TEM, cryo-TEM) to evaluate the effects of pH, cation charge, and ionic strength on the aggregation of boehmite ( $\gamma$ -AlO(OH)), a critical solid for understanding rheological responses at Hanford.

## PREVIOUS WORK

A number of approaches have been used to study aggregation. Static and/or dynamic light scattering,31-35 often combined with TEM and/or optical microscopy (OM), have been used extensively. Cryo-TEM tomography and small-angle X-ray scattering (SAXS) of ferrihydrite aggregates and a combination of wide-angle X-ray scattering (WAXS), SAXS, and transmission X-ray microscopy (TXM) of clay aggregates have yielded detailed insights into aggregate microstructures and aggregation kinetics.<sup>36,37</sup> TEM<sup>25,38–42</sup> and atomic force microscopy<sup>43–48</sup> have shown that the forces involved can be subdivided into: (1) a short-range regime where atomic structure dictates the structure of the hydration layers and their overlap and (2) a long-range regime where forces are controlled by bulk solution parameters (pH, ionic strength, and electrolyte type) and atomic details are observed only via their impact on continuum properties (e.g., dielectric constant and surface potential). Higher order structures arise via aggregation, fusion, and particle coarsening,<sup>25–29</sup> which then effect slurry rheology.<sup>49,50</sup> TEM results document both random<sup>25,51</sup> and oriented particle attachment,<sup>25,38–42,52–57</sup> competing with Ostwald ripening, in which local curvature controls the competition between formation of hierarchical structures and particle growth.<sup>25,26</sup>

The majority of the above studies, however, focused on spherical and/or near-spherical particles where diffusional and rotational motions are decoupled. Thus, their applicability to boehmite and gibbsite, which tend to form as flat, rhombohedral platelets, is uncertain. There have, however, been a few studies of the aggregation of nonspherical particles. Micron-sized, rodlike colloidal particles (i.e., asbestos fibers and synthetic glass rods) were studied using a custom-made liquid cell with high-magnification inverted OM.<sup>58</sup> Studies on fractal dimensions have been performed for disk-like clay particles (i.e., bentonite and kaolinite) to understand the effects of pH on aggregate microstructure via DLS,<sup>59,60</sup> and an underlying mechanism for the formation of fractal structures from colloidal boehmite rods (whose surface chemistry should be identical to that of the phase of interest here) has been suggested using Monte Carlo simulations.<sup>61</sup> Although these provide some general insights for nonspherical particles, our particles are rhombohedral, exhibiting sharp edges, common characteristics of boehmites at high pH. Beattie et al.<sup>6</sup> investigated the aggregation of boehmite particles, but did not investigate the structures in detail and did not consider the boehmite shape. Thus, although flocculation, solubility, and rates of dissolution and precipitation are essential parameters for safe and efficient waste processing, our current state of knowledge is inadequate to predict particle behavior.

Small-angle scattering has previously been used to investigate aggregation of a number of materials. Teixeira<sup>63</sup> suggested the use of small-angle scattering to characterize aggregate fractal dimensions. Gerber et al.<sup>64</sup> used SAXS to study the aggregation of SiO<sub>2</sub> clusters in sodium water glass. Radlinski et al.<sup>65</sup> used SAXS and SANS to study aggregation of *n*-alkanes in organic solvents, and Chou and Hong<sup>66</sup> used small-angle light scattering to study the nucleation and growth, diffusive aggregation, and late-stage Ostwald ripening of polymer gels. SANS analysis of boehmite and pseudoboehmite powders (not in solution)<sup>67</sup> revealed mass fractal behavior in the pseudoboehmite ( $D_m = 3.02$ ), but boehmite showed a Porod-like (smooth surface) slope near -4 (-3.92). Pseudoboehmite also showed an intensity increase at low-Q, which might represent a larger particle size or the presence of aggregates. A SANS investigation has also been conducted of asphaltine aggregation in crude oil,<sup>68</sup> and numerous other studies have used this approach to study aggregation phenomena, often of organic and/or biological materials.

#### **EXPERIMENTAL METHODS**

In this paper, we analyze the correlation between aggregation of synthetic nanoboehmite and fluid composition by comparing aggregation in solutions at pH 9 and 12, which contain sodium nitrate (NaNO<sub>3</sub>) and calcium nitrate  $(Ca(NO_3)_2)$  at concentrations ranging from 0 to 1 m. The pH range was selected because available data suggest that the point of zero charge for boehmite (or pseudoboehmite) lies somewhere between pH 7.3 and 9.2, although values as high as 11.6 have been reported for various boehmite nanostructures.<sup>74</sup> Thus, we can evaluate the effects of the high pH values in the Hanford tanks on the formation and stability of boehmite aggregates. The typical supernate (i.e., the aqueous liquid phase) in the nuclear wastes is a concentrated aqueous solution of primarily sodium salts, including sodium nitrate. Sodium nitrate is also the most common solid phase in saltcake wastes, although the mineralogy varies significantly among Hanford tank wastes. Thus, it was selected as one of the salts for this study. Furthermore, we added calcium nitrate to our test suite to provide additional physical insights as to the effects of cationic valence on aggregation, as calcium ions are also present in the nuclear wastes.<sup>5</sup> Therefore, we believe that the salts selected for our study are directly relevant for understanding the physicochemical conditions of the waste slurries. Experiments were run at room temperature, and boehmite concentrations were fixed at 20 wt % boehmite.

Boehmite Synthesis and Characterization. Boehmite was prepared using a hydrothermal approach. An aqueous solution of Al(NO<sub>3</sub>)<sub>3</sub> was prepared by dissolving 60 g of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (≥98%, Sigma-Aldrich) in 600 mL of deionized water at room temperature. The pH of this solution was adjusted to 10 by addition of 3 M NaOH (≥98%, Sigma-Aldrich) in deionized water. After stirring for 1 h, the gel-like precipitates were collected by centrifugation (8000 rpm) and washed three times with deionized water. The gels were then placed in Teflon lined 125 mL Parr Vessels and suspended in 0.1 M NaOH (pH 13) at a ratio of 0.4 g of gel to 1 mL of 0.1 M NaOH solution. The total volume of the gel-NaOH solution was 100 mL. The Parr vessel was then placed in an oven equipped with a rotating element operating at 10 Hz for 3 days at 120 °C. Afterward, the produced boehmite was collected by centrifugation and washed three times with deionized water. Finally, the resulting sample was dried in an oven at 80 °C overnight.

X-ray Diffraction (XRD) and Brunauer–Emmett–Teller (BET) Measurements. XRD patterns of all samples were recorded on a Philips X'pert Multi-Purpose Diffractometer (MPD) (PANAlytical, Almelo, The Netherlands) equipped with a fixed Cu anode operating at 50 kV and 40 mA. XRD patterns were collected from 5 to 80° 2 $\theta$ . Phase identification was performed using JADE 9.5.1 from Materials Data Inc. and the 2012 PDF4+ database from the International Center for Diffraction Data (ICDD). Surface areas were measured using the BET method<sup>75</sup> using a Quatachrome Autosorb BET instrument. The sample (0.0858 g) was analyzed using nitrogen as the absorbate and was outgassed at 100 °C for 16 h.

**Fluid Preparation.** Fluids were prepared in a glovebox. An aqueous solution at pH 14 was prepared from Ar-sparged, 18 M $\Omega$ ·cm water (Milli-Q Advantage A10) and a 50 wt % NaOH solution (Sigma-Aldrich). This was then diluted to either pH 9 or 12. NaNO<sub>3</sub> (Sigma-Aldrich) or Ca(NO<sub>3</sub>)<sub>2</sub> (Sigma-Aldrich) was then added as necessary to appropriate concentrations (see Table 1 below). Additional NaOH was then added to return the samples to the required pH values. All pH values were checked using an Orion Products glass electrode with a Denver Instruments model 250 meter.

Table 1. Sample Analyzed

cell	boehmite (wt %)	pH (NaOH)	salt	salt concentration $(m)$	scattering contrast (×10 <sup>20</sup> cm <sup>-4</sup> )
2	20	12	none		16.0961
3	20	9	none		16.0961
4	20	9	NaNO <sub>3</sub>	1	14.5725
5	20	12	$NaNO_3$	1	14.5725
6	20	9	$Ca(NO_3)_2$	1	13.3167
7	20	12	$Ca(NO_3)_2$	sat	13.3167
8	20	9	$NaNO_3$	0.1	15.9404
9	20	9	$NaNO_3$	0.01	16.0805
10	20	9	$Ca(NO_3)_2$	0.1	15.8063
11	20	9	$Ca(NO_3)_2$	0.01	16.0670
12	20	12	$NaNO_3$	0.1	15.9404
13	20	12	NaNO <sub>3</sub>	0.01	16.0805
14	20	12	$Ca(NO_3)_2$	0.1	15.8063
15	1	11.01	none		16.0961
16	20	12	$Ca(NO_3)_2$	0.01	16.0670

Unfortunately, it is not possible to make a 1 m (molal, mol/kg solvent) Ca(NO<sub>3</sub>)<sub>2</sub> solution at pH = 12 at room temperature. The log K value for the reaction

$$Ca(OH)_2 + 2H^+ = Ca^{2+} + H_2O$$
 (1)

is 22.8.<sup>76</sup> Thus, at pH 12,  $Ca(OH)_2$  is expected to precipitate, leaving a  $Ca^{2+}$  concentration of  $log[Ca^{2+}] = -1.2$ . This was observed for the nominally 1 *m* solution, and all pH = 12 calcium nitrate solutions were centrifuged to assure that no  $Ca(OH)_2$  particles remained. In this paper, therefore, this solution will be referred to as saturated.

Prior to use, fluid samples were sealed in bottles with septa in the lids. These were transferred when needed for SANS to the experimental vessels by syringe to minimize air exposure and possible  $Na_2CO_3$  formation.

**Transmission and Cryo-Transmission Electron Microscopy.** Samples for TEM (FEI Titan TEM) observation were prepared by dispersing the as-synthesized boehmite nanocrystals in nuclease-free, ultrapure water (ThermoFisher Scientific) using an Fisher Scientific probe sonicator (120 W, 20 kHz) operating at 80% amplitude for 5 min. The mass concentration of boehmite was 1 mg/mL. Higher concentrations immediately showed large structures (>1  $\mu$ m) that could not be properly imaged. Drops of this solution were then placed onto a copper grid (Lacey Carbon, 300 mesh, Copper, Ted Pella, Inc.), which was dried for a few minutes under ambient conditions prior to being introduced into the TEM. The samples were imaged using an acceleration voltage of 300 kV.

Cryo-TEM specimens were prepared by placing a 3  $\mu$ L drop of boehmite suspension onto a 200 mesh copper TEM grid coated with lacey carbon film (EMS). All grids were glow discharged under air for 1 min at 15 mA (EasiGlow, Ted Pella) prior to use. The suspension was prepared by sonicating a 1 mg/mL boehmite solution for 30 min with a probe sonicator, then transferring 100  $\mu$ L to a solution of 5 mM sodium nitrate. The grid was loaded into an FEI Vitrobot Mark IV plunge freezing vitrification instrument (FEI, Hilsboro, OR) maintained at room temperature and 70% relative humidity. Blotting parameters were 1 s blot time, 1 s relaxation time, and a blotting force of 1 (a unitless parameter). The grid was then rapidly plunged into liquid ethane to vitrify the specimen and transferred to storage under liquid nitrogen. Once vitrified, specimens were transferred under liquid nitrogen to a Gatan 626 cryo-TEM holder, which maintains cryogenic conditions during imaging  $(-176 \ ^\circ C)$  and inserted into an FEI Titan 80-300 Environmental TEM equipped with a field emission electron gun operated at 300 kV under low-dose conditions. Images were collected with a US 1000  $2k \times 2k$  charge capture device (CCD) camera (Gatan, Inc.) operated via Digital Micrograph (Gatan, Inc.).

**Dynamic Light Scattering.** Dynamic light scattering was used to determine the size of the initial particles prior to aggregation. For this

purpose, 10 mg of the boehmite was dispersed in 10 mL of pure water. The sample was sonicated for 30 min using a Fisher Scientific probe sonicator (120 W, 20 kHz) operating at 80% amplitude. The data were then collected using a Brookhaven Instrument 90Plus Nanoparticle Size Analyzer. Ten measurements of 10 s each were combined to produce a single normalized autocorrelation function (Figure 1) and subsequently analyzed as a monomodal size



Figure 1. Autocorrelation function of boehmite suspension obtained using DLS. The measurements show an average particle diameter of 1360 ( $\pm$ 110) Å.

distribution. No aggregation was observed during acquisition. As this was a dilute solution, the viscosity was assumed to be that of pure water ( $8.90 \times 10^{-4}$  Pa s). The calculated average hydrodynamic diameter was 1360 (±110) Å.

**Small-Angle and Ultrasmall-Angle Neutron Scattering.** Details of the neutron small-angle scattering approaches have been reported elsewhere<sup>77–85</sup> and are, therefore, summarized briefly. SANS and USANS were used to probe aggregate sizes from ~100 Å to ~15  $\mu$ m. Measurements were performed on powdered samples suspended in an aqueous fluid. Standard titanium cells were used with a 1 mm path length and two 1 mm thick quartz glass windows with the beam incident along the surface normal. To keep the sample suspended during the measurement, these cells were placed in the 4R sample tumbler<sup>86,87</sup> and rotated along an axis parallel to the beam at approximately 10 rotations per min.

SANS measurements were conducted on the NGB 30 m SANS instrument at the NIST Center for Neutron Research (NCNR<sup>88</sup>) using a 5/8 in. cadmium mask. Three sample-to-detector distances (1, 4, and 13 m) were used with  $\lambda = 6$  Å at 1, 4 and 13 m, and 8.4 Å at 13 m with MgF<sub>2</sub> lenses to extend the Q range to lower values, the latter providing better overlap with the USANS data at low-Q, while still providing good counting statistics and overlap with the 4 m SANS data without them, with a wavelength resolution  $\Delta \lambda / \lambda = 0.12$ . Measurements were performed with the detector offset to extend the range of the scattering vector Q ( $Q = 2\pi/d$ ) at 1 m. The resultant scattering vector ranged from 0.0009 to 0.43 Å<sup>-1</sup>, which corresponds to sizes from approximately 15 to 7000 Å. Data were corrected for empty-beam scattering, background counts, detector uniformity, sample transmission, and scattering volume and reduced to an absolute scale (differential scattering cross-section per unit volume) by normalization to the intensity of the direct beam. The twodimensional data were always azimuthally symmetric and were circularly averaged to produce one-dimensional intensity profiles (I(O)).

Ultrasmall-angle neutron scattering measurements were performed on the BT5 instrument at the NCNR.<sup>89</sup> Samples were mounted on 5/ 8 in. cadmium masks. A pair of triple-bounce channel-cut perfect silicon (220) crystals was used for the monochromator and analyzer. The wavelength was 2.38 Å with a wavelength resolution  $\Delta \lambda / \lambda =$ 0.059. Data were collected over a Q range from 4.2 × 10<sup>-5</sup> to 2.7 ×  $10^{-3}$  Å<sup>-1</sup>, which corresponds to 2400 Å to ~15  $\mu m$ . The horizontal Q resolution (full width at half-maximum) was 2.5  $\times$   $10^{-5}$  Å<sup>-1</sup>. Scattering intensity data were corrected for empty beam and constant background. The corrected data were converted to an absolute scale by measuring the attenuation of the direct beam. Data reduction and desmearing were accomplished using data reduction software provided by NIST/NCNR.<sup>90</sup>

Small-Angle (SAXS) and Ultrasmall-Angle (USAXS) X-ray Scattering. Analysis of the effects of ultrasonic processing on the samples was obtained via ultrasmall and small angle X-ray scattering and wide-angle X-ray scattering (WAXS) (to reveal Bragg peaks of mineral phases) at the Advanced Photon Source at Argonne National Laboratory on beamline 9ID.91,92 A Fisher Scientific model D100 ultrasonic probe operating at 1.6  $\pm$  1 W RMS and 22.7 kHz was placed in a small hole in a 100 mL plastic bottle containing 50 mL of sample, and a peristaltic pump was used to continuously pump the sample (via another small hole) through a 1 mm ID quartz glass tube in the beam and back to the sample vial. A stream of argon was blown over the sample to minimize Na<sub>2</sub>CO<sub>3</sub> formation. The argon flow was kept relatively low, and the holes in the bottle were either entirely or nearly filled by the tubes and probes. Thus, no significant evaporation was expected, and none was observed. The X-ray wavelength was 0.6888(8) Å, and the beam size was 1 mm. USAXS data were acquired for 30 s with a Q range from 0.0001 to 6  $A^{-1}$  and a Q resolution of ~0.00008  $A^{-1}$ . SAXS data were acquired over a Q range from ~0.03 to 1.3 [1/A]. WAXS data were acquired for d-spacings ranging from approximately 6 to 0.8 A. The sample remained boehmite throughout the experiment. Data were reduced and analyzed using the IRENA and NIKA macro packages.<sup>93,94</sup> For a detailed description of the application of scattering to the characterization and analysis of porosity and pore structures, we refer the reader to Anovitz and Cole.<sup>7</sup>

#### RESULTS

**XRD and BET.** XRD indicated the as-prepared sample was pure boehmite (Figure 2); the diffraction pattern is in



Figure 2. XRD pattern of the as-synthesized boehmite nanocrystals. The measured diffraction pattern is compared to PDF 04-012-5050.

agreement with reference data (ICDD PDF # 00-74-1895). The strong diffraction peak at a  $2\theta$  angle of 14.5° was assigned to (010) diffraction. Rietvelt refinement yielded orthorhombic unit cell parameters of a = 2.859, b = 12.240, and c = 3.169 Å. XRD whole pattern fitting was also used to estimate a crystallite domain size of 99 Å. The BET measurement yielded a surface area of 104.7 m<sup>2</sup>/g. Assuming a spherical geometry and a bulk density<sup>95</sup> of 3.04 g/cm<sup>2</sup>, this is equivalent to a particle with a radius of 94 Å, or a cylinder with a radius of 250



**Figure 3.** TEM images of synthetic boehmite. (A, B) Dry material after synthesis, (C, D) cryo-TEM images of boehmite in 10 mg boehmite/10 mL fluid,  $[NaNO_3] = 0.01$  M, pH 9 fluid showing oriented attachment of boehmite nanoplatelets by stacking along the basal plane.

Å and a height of 84 Å, which agrees well with the XRD measurement.

**TEM and Cryo-TEM.** Figure 3 shows micrographs of the synthetic boehmite as dried after synthesis (imaged via TEM) and in a vitrified suspension (imaged via cryo-TEM). The images of dry boehmite show that the initial synthetic material is composed of individual rhombohedral particles, with typical dimensions of length = 293 ( $\pm$ 94) Å, width = 220 ( $\pm$ 73) Å, thickness = 60 ( $\pm$ 13) Å, in reasonable agreement to both the XRD and BET results. Once immersed in an alkaline solution (pH = 7-13), however, these particles quickly aggregate into small stacks (primary aggregates) that are very hard to reseparate. The stacked grains are somewhat staggered, yielding dimensions measured by cryo-TEM at time = 0 of length = 1510 ( $\pm$ 900) Å, width = 870 ( $\pm$ 470) Å, height = 650  $(\pm 420)$  Å, where "t = 0" is the time at which the boehmite particles are placed in the solution of interest and aggregation begins, length is the stacking direction, width is the maximum aggregate length in the plane normal to the stacking direction, and height is the aggregate width in the same plane, but in the direction perpendicular to the width (i.e., height is in the direction of the cross product from length and width, such that length, width, and height define an orthonormal system). The distribution of these dimensions is shown in Figure 4.

It should also be noted that both the XRD and TEM data suggest that our starting material is boehmite and not pseudoboehmite. Pseudoboehmite is essentially a finely crystalline boehmite, which consists of the same or similar octahedral layers in the xz plane but lacks three-dimensional order because the number of unit cells in the y direction is restricted. It consists of a significant number of crystallites,



**Figure 4.** Distribution of primary stack sizes in three dimensions as measured from TEM images at t = 0. The gray boxes show second and third quartile limits and median. The whiskers show quartiles zero and four. The outliers are shown as gray circles. The black box shows the mean.

which contain a single unit cell along y or single octahedral layers. It contains more water than boemite, which is commonly intercalated between octahedral layers, and these layers are normally randomly, but sometimes regularly, arranged. The XRD pattern of pseudoboehmite is similar to that of boehmite, but the relative intensities of the peaks differ, and the peaks are broader.<sup>96,97</sup> As shown in Figure 3, in our assynthesized boehmite, the thicknesses of the plates are larger than 50 Å. There is no evidence to show the boehmite lacks

three-dimensional order in the y direction, and the XRD pattern (Figure 1) matches that of boehmite, not pseudo-boehmite.

Small-Angle Neutron Scattering. Seventeen samples were analyzed by (U)SANS. With one exception (cell 15), all contained 20 wt % solid, calculated in a molal fashion (e.g., grams solid per gram fluid). With that same exception, all were prepared by weighing the solid into the cell, sealing the cell, then adding the fluid. The mixture was then stirred with a needle, shaken by hand, and then left for at least 0.5 h in an ultrasonic bath to distribute the sample in the fluid and break up any remaining clumps. Cell 15 was prepared with only 1 wt % solid to estimate the structure factor for the solid, although the images in Figure 3 suggest that some aggregation likely occurred. To assure as complete disaggregation as possible, this sample was placed in a small vial, a CV17 converter/transducer ultrasonic probe on a model GE375 ultrasonic processor was inserted, and the sample was sonicated for 2 min in 20 s bursts with a 1/4 in. tip at 45% power and a 50% duty cycle. The processor has a listed maximum power of 375 W.

Although it might be assumed that the ultrasonic treatment would break up any aggregates, this is not necessarily the case. Kinetic analyses by small-angle X-ray scattering (Anovitz et al., unpublished data) have shown that, with time, addition of mechanical energy using an ultrasonic probe can drive the formation of large aggregates in the system. However, this requires some time to initiate. Figure 5 shows short time (<10



**Figure 5.** Ultrasmall-angle X-ray scattering data for a sample with 2.5 wt % boehmite in pH 9 (NaOH) solution. Red: starting material. Purple: 9 min of ultrasonic processing. Green: 131 min of ultrasonic processing. Short ultrasonic times merely break up large, weakly bound clumps. Longer ultrasonic times force nucleation of larger aggregates. Intermediate-scale aggregates are not affected.

min) (U)SAXS analyses obtained at the Advanced Photon Source. As can be seen, there is an initial decrease in the intensity at low-Q, showing the break up of the initial clumps in the powder as the sample is dispersed in the liquid. With longer ultrasonic times, however, aggregate formation becomes apparent at larger scales (smaller Q-values). The hump in the data at intermediate scales (near Q = 0.01 Å<sup>-1</sup> or, given  $d = 2\pi/Q$ , ~630 Å, but representing a polydisperse range of sizes) likely represents the primary aggregates observed by cryo-TEM (Figure 3). Thus, the short ultrasonic treatment used to prepare sample 15 likely broke up many of the initial clumps, but did not form larger, more stable aggregates. To calculate the particle size distributions for each of the samples, it was first necessary to calculate the scattering contrast in each. Scattering contrast is the square of the difference in scattering length density (SLD) between the particles and the surrounding fluid. Although the SLD of boehmite is easily calculated based on its composition (AlO(OH)) and density (3.04 g/cm<sup>3</sup>) using IRENA, calculation of the values for the fluids requires taking into account both their composition and density. Since the concentrations of NaOH in pure H<sub>2</sub>O/NaOH solutions at pH 9 ( $1 \times 10^{-5} m$ ) and pH 12 (0.01 m) are relatively small, densities were calculated on the basis of nitrate content alone, although the NaOH content was included in the fluid composition. Fitting available data<sup>98</sup> yielded, for an H<sub>2</sub>O/NaNO<sub>3</sub> solution

density 
$$(g/mL) = -0.0015x^2 + 0.0516x + 0.9990$$
  
 $r^2 = 0.9999$  (2)

where x is the molality of NaNO<sub>3</sub> in the solution. Similarly, the data of Carpio et al.<sup>99</sup> yielded

density 
$$(g/mL) = 0.0002x^3 - 0.0067x^2 + 0.1146x + 0.9991$$
  
 $r^2 = 0.9999$  (3)

where x is the molality of  $Ca(NO_3)_2$ . The resultant SLD's are given in Table 1.

Figure 6 shows the scattering data for a cell 15, the sample with 1 wt % boehmite at pH 11.1. Although the USANS



**Figure 6.** (U)SANS scattering data for cell 15 fitted to a Gunier– Porod model.<sup>100</sup> The data are flat in the USANS range ( $Q < 8.9 \times 10^{-4}$ ) suggesting only minimal formation of large aggregates.

counts were rather low, leading to somewhat noisy data, it is clear that this is a relatively simple curve, with a flat top at low-Q and a flat background at high-Q. These data were, therefore, fitted to a single level Guinier–Porod model<sup>100</sup> assuming a cylindrical particle shape (Table 2). This model has three regions described as

$$I(Q) = \frac{G_2}{Q^{S_2}} \exp\left(\frac{-Q^2 R_{g^2}^2}{3 - S_2}\right) \text{ for } Q \le Q_2$$
(4)

$$I(Q) = \frac{G_1}{Q^{S_1}} \exp\left(\frac{-Q^2 R_{g_1}^2}{3 - S_1}\right) \text{ for } Q_2 \le Q \le Q_1$$
(5)

	$R_{\rm g}$ (Å)	cut off	5000	500	500	100	500	500	500	500	500	500	3000	3000	750	500		
level 2	$D_{s3}$		2.478	2.264	2.314	2.008	2.506	2.441	2.338	2.419	2.376	2.388	2.512	2.525	2.525	2.482		
	Ρ		3.522	3.736	3.686	3.992	3.494	3.559	3.662	3.581	3.624	3.612	3.488	3.475	3.478	3.518	back	1.1
	$R_{\rm g1}$ (Å)		$6.64 \times 10^{4}$	$5.38 \times 10^{4}$	$5.90 \times 10^{4}$	$6.80 \times 10^{4}$	$5.90 \times 10^{4}$	$6.31 \times 10^{4}$	$5.85 \times 10^{4}$	$5.45 \times 10^{4}$	$5.62 \times 10^{4}$	$5.18 \times 10^{4}$	$6.01 \times 10^{4}$	$7.51 \times 10^{4}$	$7.06 \times 10^{4}$	$5.21 \times 10^{4}$	$R_{ m g}$ cut $({ m \AA})$	20
	в		$1.060 \times 10^{10}$	$8.851 \times 10^{9}$	$1.066 \times 10^{10}$	$2.283 \times 10^{10}$	$1.002 \times 10^{10}$	$1.623 \times 10^{10}$	$9.589 \times 10^{9}$	$8.059 \times 10^{9}$	$1.062 \times 10^{10}$	$9.546 \times 10^{9}$	$1.111 \times 10^{10}$	$1.539 \times 10$	$2.500 \times 10^{10}$	$7.296 \times 10^{10}$	$D_{S2}$	3.253
	back $(cm^{-1})$		0.01	1.026	1.024	1.238	1.117	1.057	1.25	1.233	1.115	1.064	1.083	1.087	1.145	26.47	Ρ	2.747
level 1	$R_{\rm g}$ (Å)	cut off	13	1	1	1	1	1	1	1	1	1	1	1	1	1	$R_{ m cyl}$ (Å)	133.83
	$D_{s2}$		2.553	2.521	2.469	2.428	2.483	2.723	2.480	2.483	2.509	2.499	2.591	2.485	2.493	2.298	$R_{ m g1}$ (Å)	94.63
	Ρ		3.447	3.479	3.531	3.572	3.517	3.277	3.520	3.517	3.491	3.501	3.409	3.515	3.507	3.702	G	0.03001
	$R_{ m cyl}$ (Å)		48.4	66.7	6.99	74.7	63.5	84.4	68.6	66.5	74.8	71.2	40.7	58.1	69.5	71.9	$3-S_1$	1.419
	$R_{\mathrm{gl}}$ (Å)		34.2	47.2	47.3	52.8	44.9	59.7	48.5	47.1	52.9	50.4	28.8	41.1	49.1	50.8	$S_1$	1.581
	Ŀ		0.0237	0.7978	0.8666	1.632	0.4074	3.334	0.7506	0.7195	1.677	1.457	0.0388	0.1943	1.009	2.141	$L_{ m cyl}$ (Å)	2156.9
	3-S <sub>1</sub>		0.908	1.741	1.711	2.000	1.564	2.000	1.696	1.588	1.928	1.794	1.023	1.327	1.769	2.000	$R_{ m g2}$ (Å)	629.8
	$S_1$		2.092	1.259	1.289	1.000	1.436	1.000	1.304	1.412	1.072	1.206	1.977	1.673	1.231	1.000	$S_2$	0
	cell		2	з	4	s	6	7	8	6	10	11	12	13	14	16		15

Table 2. Fitting Parameters, Gunier-Porod Model

$$I(Q) = \frac{D}{Q^d} \text{ for } Q \ge Q_1 \tag{6}$$

$$Q_{1} = \frac{1}{R_{g1}} \left[ \frac{(d-s1)(3-s1)}{2} \right]^{1/2}$$
(7)

$$Q_{2} = \left[ (s_{1} - s_{2}) / \left( \frac{2}{3 - s2} R_{g2}^{2} - \frac{2}{3 - s1} R_{g1}^{2} \right) \right]^{1/2}$$
(8)

$$G_{2} = G_{1} \exp \left[-Q_{2}^{2} \left(\frac{R_{g1}^{2}}{3-s1} - \frac{R_{g2}^{2}}{3-s2}\right)\right] Q_{2}^{(s2-s1)}$$
(9)

$$D = \frac{G_1}{R_{g1}^{(d-s1)}} \exp\left[-\frac{(d-s1)}{2}\right] \left[\frac{(d-s1)(3-s1)}{2}\right]^{(d-s1)/2}$$
(10)

where *Q* is the inverse space distance, I(Q) is the intensity at *Q*,  $Q_1$  and  $Q_2$  mark the boundaries between the three segments of the equation, *d* is the Porod exponent, *G* and *D* are the Guinier and Porod scale factors, respectively,  $3-s_1$  and  $3-s_2$  are dimensionality parameters, such that for spheres s = 0, for rods s = 1, and for lamellae or platelets s = 2, and  $R_{g1}$  and  $R_{g2}$  are the radii of gyration for the short and overall sizes of the scattering object. For a cylinder of radius *R* and length *L* 

$$R_{g2} = (L^2/12 + R^2/2)^{1/2}$$
(11)

and

$$R_{\rm g1} = R/(2)^{1/2} \tag{12}$$

The calculated scatterer radius,  $\sim 134$  Å, is reasonably consistent with the results from the imaging, surface area, and XRD data for individual particles. The fitted length (2157 Å), however, is somewhat longer than observed in cryo-TEM, suggesting the stacks grow with time, at least initially, as the (U)SANS data were acquired up to several hours after initial mixing. Twice the calculated radius of gyration (1260 Å), however, is very close to the hydrodynamic diameter calculated from the DLS measurements.<sup>101</sup>

The size distributions (Figure 7) were calculated using the total non-negative least squares approach (IRENA<sup>94</sup>) assuming cylindrical scatterers with a 1:1 diameter-to-length ratio. As can be seen in Figure 3, the axial ratios of the primary aggregate stacks are all relatively small, approximately between one and two. Thus, there should be little difference between assuming the particles are spheres or cylinders. The scattering data were, therefore, fitted as cylinders with an axial ratio of 1, as the TEM imagery showed this was closer to the shape of the actual particles. Tests of larger ratios made little difference. Particle sizes begin at approximately 107 Å, again approximately the primary particle radius, and there is a power-law distribution of decreasing particle concentration with increasing particle size up to approximately 1600 Å. The calculation also suggests a limited number of larger aggregates around 5  $\mu$ m in size. Because of their very low suggested concentrations, however, it is unclear if these are real or an artifact of the calculation.

Figure 8 shows the scattering data and fitted curve for cell 2, 20 wt % boehmite in a pH 12 solution with no added salt. In addition to the expected increase in scattering intensity, these data show a second level of larger scatterers at low-Q. This obscures the position of  $R_{g2}$  for the high-Q distribution and



**Figure 7.** Particle volume distribution for 1% boehmite in pH 11.1 solution. Results are shown on two scales because of the low concentration of the larger-scale aggregates. The filled circles (left axis), open circles, (right axis). The sizes of the more common smaller particles fall along a power-law distribution, with the larger particles (aggregates?) being about 67 times less common than the smallest in this region.



**Figure 8.** (U)SANS scattering data for 20 wt % boehmite in pH 12  $H_2O/NaOH$ . Intensity has increased relative to Figure 5 as expected. Sloping data at low-Q imply the presence of larger features (aggregates) in the sample. Data have been fitted to a two level Gunier–Porod model.<sup>100</sup>

was fitted using a second level of the Guinier–Porod model. The larger radius of gyration fitted to this curve (Table 2) is also poorly defined, as it is near the low-Q limit of the data. Although the intensities and fitted details of the curves varied, each of the 20 wt % boehmite sample scattering curves was qualitatively similar to that shown in Figure 8 for cell 2. These data are also quite similar to SANS patterns for pseudoboehmite,<sup>67</sup> described as "a voluminous gel-like aggregate of nanoparticles of irregular shapes".

Nominally, the integrated intensities of each of the 20 wt % samples should be the same, as each contained the same solid concentration. However, in the tumbler experiment, the Cd mask only allowed the neutron beam access to part of the cell (to define the beam and limit scattering from the cell edges). Thus, part of the material was hidden from the beam at any given time, and there is no guarantee that the integrated values will be identical. In fact, this was the case, although the values were close. To compare results for the various experiments, therefore, the scatterer volume distributions were normalized to a total volume of 1.

Figure 9 shows the normalized particle volume distributions for 20 wt % boehmite in pH = 9 and 12  $H_2O/NaOH$  solutions



Figure 9. Normalized particle volume distribution for 20 wt % boehmite in pH 9 (gray circles) and pH 12 (filled circles)  $H_2O/NaOH$  solution.

with no salt. Both curves consist of three sections: the highest concentration of scatterers between 70 and 240 Å probably represents the primary particles, volumes from 240 to ~4000 Å probably describe the primary aggregates and may be composed of a series of discrete peaks, and a third region from approximately 1 to 18  $\mu$ m at much lower concentration probably reflects larger aggregates that generate the increase in scattering intensity at low-Q illustrated for cell 2 (Figures 8 and 9). The primary difference between the two curves is that at pH 9, there are fewer primary aggregates, with better defined size distributions, and more primary particles. This suggests that the surface potential increase associated with pH (i.e., adsorption of OH- as a potential determining ion), which should decrease aggregation, is less significant than the Debye length (electrical double layer thickness) decrease due to increased sodium concentration associated with increased pH through addition of sodium as NaOH.

Figure 10 shows the effect of adding salts by comparing the normalized boehmite particle volume distributions at pH 12



**Figure 10.** Normalized boehmite particle volume, pH 12. The open circles (no salt), filled circles (saturated  $Ca(NO_3)_2$ ), gray triangles (1 *m* NaNO<sub>3</sub>).

for solutions with no salt, saturated  $Ca(NO_3)_{2}$ , and 1 *m* NaNO<sub>3</sub>. Both sodium nitrate and calcium nitrate have the same effect as reducing the pH, reducing the number of intermediate-scale aggregates and increasing the scattering from the primary particles. However, the effects of adding sodium nitrate appear to be slightly greater than calcium nitrate, possibly due to its higher concentration. Perhaps not

surprisingly, given the results in Figures 9 and 10, adding salt has little effect on the particle size distributions at pH 9 (Figure 11).



**Figure 11.** Normalized boehmite particle volume, pH 9. The open circles (no salt), filled circles (saturated  $Ca(NO_3)_2$ ), gray triangles (1 *m* NaNO<sub>3</sub>).

Figures 12 and 13 show the normalized boehmite particle volume distributions at pH = 12 as a function of NaNO<sub>3</sub> and



**Figure 12.** Normalized boehmite particle volume, pH 12 as a function of NaNO<sub>3</sub> concentration. The open circles (no salt), filled circles (0.01 m NaNO<sub>3</sub>), gray triangles (0.1 m NaNO<sub>3</sub>), and gray circles (1 m NaNO<sub>3</sub>).

 $Ca(NO_3)_2$  concentrations, respectively. As noted above, both salts decrease the concentration of the intermediate aggregates. However, with sodium nitrate most of this effect occurs at a concentration between 0.1 and 1 *m*, whereas for calcium nitrate the maximum reduction appears to have already occurred by 0.01 *m*. In both cases, however, this is consistent with the change in intermediate-scale aggregate formation observed from pH = 9 to 12 (Figure 9). No restabilization-related reversals are observed. In both cases, the distributions of the larger aggregates become more discrete. Although Anovitz et al.<sup>84</sup> pointed out that the width of such distributions is a function of the fitting approach and parameters, each was fitted using identical parameters and the TNNLS approach, and the results should, therefore, be comparable.

The relative effects of calcium and sodium suggest that calcium is more effective at destabilizing the dispersion by reducing the Debye length than sodium. This is consistent with the expression  $^{102}$ 



**Figure 13.** Normalized boehmite particle volume distributions at pH 12 as a function of  $Ca(NO_3)_2$  concentration. The open circles (no salt), filled circles (0.01 *m*  $Ca(NO_3)_2$ ), gray triangles (0.1 *m*  $Ca(NO_3)_2$ ), gray circles (saturated  $Ca(NO_3)_2$ ).

$$\kappa^{-1} = \left(\frac{\varepsilon \varepsilon_0 kT}{2\varepsilon^2 z^2 n_{\rm b}}\right)^{1/2} \tag{13}$$

where  $\kappa^{-1}$  is the Debye length,  $\varepsilon$  is the dielectric constant,  $\varepsilon_0$  is the vacuum dielectric permittivity, e is the charge of an electron  $(1.6 \times 10^{-19} \text{ J})$ , z is the valence,  $n_b$  is the bulk concentration of electrolytes, T is temperature, and k is the Boltzmann constant. Thus, the effect of adding a cation to the solution is expected to go as the square of its charge, qualitatively explaining the differences observed between calcium and sodium in this experiment.

## DISCUSSION

The fitting model described above provides four variables whose variation as a function of pH and/or salt concentration can be analyzed: the surface fractal dimension of the primary aggregates ( $D_{S2}$ ), the fractal dimension of the large aggregates ( $D_{S3}$ ), the Guinier dimension between the two distributions (3- $S_1$ ), and the radius of the primary aggregate cylinders ( $R_{cyl}$ ). These data are shown in Figures 14 and 15 and listed in Table 2.

The first of these variables,  $D_{s2}$ , from the Porod section of the Guinier–Porod model, describes the surface fractal



**Figure 14.** (Left) Particle surface fractal dimension ( $D_{S2}$ ) and (right) aggregate fractal dimension ( $D_{S3}$ ) as a function of salt molality. Salt-free samples are plotted at 0.001 *m* to allow a logarithmic *x* axis. The highest concentration pH = 12 calcium nitrate data are plotted at 1 *m*, but are actually lower (see text). The curves are for clarity only.



**Figure 15.** Left) Primary aggregate Guinier dimension  $(3-S_1)$  and (right) Primary aggregate cylinder radius  $(R_{cyl})$  as a function of salt molality. Salt-free samples are plotted at 0.001 *m* to allow a logarithmic *x* axis. The highest concentration pH = 12 calcium nitrate data are plotted at 1 *m*, but are actually lower (see text). The curves are for clarity only.

dimension of the smaller particles. It describes scattering at Q-values greater than (sizes smaller than)  $Q_1$ , which is about 0.03  $\text{\AA}^{-1}$  (about 190–270 Å) for most samples. This is about the size of the primary particles, and thus  $D_{s2}$  probably describes primary particle roughness. At pH = 9 (Figure 14), there is little change in  $D_{s2}$  with salt content. The same is true for pH = 12 with sodium nitrate, although there is greater variability. For pH = 12 with calcium nitrate, however, addition of salt first smooths, then significantly roughens the stacking with increased concentration. However, background for the 0.01 m Ca(NO<sub>3</sub>)<sub>2</sub> sample was significantly higher than for the other materials, suggesting this may be an artifact. Thus, except at high calcium nitrate concentration, neither pH nor salt concentration has any effect on primary aggregate roughness. Similarly,  $^{102}$  addition of 1–100 mM NaCl had little effect on the agglomeration of  $nC_{60}$ , but addition of the same concentrations of CaCl<sub>2</sub> increased agglomerate size seven fold, which the authors attributed to a net attractive force between the particles and suppression of the electrical double layer. A reduction was also found in the critical coagulation concentration of  $CeO_2$  nanoparticles at pH = 5.6 from approximately 34 mM for KCl to 9.5 mM for CaCl<sub>2</sub>.<sup>103</sup>

In the case of the secondary aggregate fractal dimension,  $D_{S3}$ , however, both pH and salt concentration affect the aggregate structure. At no or low salt concentration, the fractal dimension of the aggregates at pH 9 is distinctly lower than that at pH 12. As the slopes from which these are derived are between 3 and 4, these are surface, not mass fractals and therefore describe the dependence of the perimeter of the aggregate on ruler length, the roughness, and not the space filling capacity of the structure. Thus, aggregates formed at higher pH are rougher at low salt concentration. As salt concentration increases, however, this appears to become the dominant factor, and aggregates formed in 1 m sodium nitrate have lower fractal dimensions than those formed in calcium nitrate. The secondary aggregates described here are not, however, necessarily identical to those described in Figure 5 after energy has been added to the system during sonication (green curve in Figure 5), but those observed initially (red curve in Figure 5).

The third dimension whose evolution can be characterized as a function of pH and salt content is the Guinier dimension of the smaller aggregates  $(3-S_1)$ . This characterizes the overall shape of the primary aggregates, with values from 0-1 (2 <  $S_1$  $\leq$  3) being lamellar or platelike ( $S_1 = 2$  for smooth infinite lamellae), values from 1 to 2 ( $1 < S_1 \le 2$ ) being rodlike ( $S_1 = 1$ for long smooth cylinders), and values from 2 to 3 ( $0 \le S_1 \le$ 1) being globular ( $S_1 = 0$  for spheres). The values of  $3-S_1$  for these samples all fall approximately between 1 and 2. However, both pH and, at higher pH, salt content, have a significant effect on primary aggregate shape. At pH = 9, salt content has little effect on the Guinier dimension, which varies from about 1.6 to 1.9, essentially constant within the uncertainties of the fits. At pH = 12, however, the Guinier dimension is approximately 1 (rodlike) when no salt is added, but 2 (lamellar) at 1 m for NaNO<sub>3</sub> and saturated  $Ca(NO_3)_2$ . However, as with the decrease in the intermediate-sized aggregate concentrations shown in Figures 12 and 13, the change in the Guinier dimension occurs at very different salt concentrations. For calcium nitrate, the Guinier dimension increases to values near 2 at 0.01 m, but it requires concentrations of 1 m for this change to occur for sodium nitrate.

The final variable whose evolution can be characterized as a function of pH and salt content is the cylinder radius  $(R_{cyl})$  calculated from the radius of gyration of the high-Q distribution. The changes observed here are similar to those observed for the Guinier dimension. At pH 9, there is little change in  $R_{cyl}$  which ranges from 64 Å to 75 Å. For pH = 12, however,  $R_{cyl}$  increases from 48 Å with no salt added to 75 Å at 1 *m* NaNO<sub>3</sub> and 84 Å at saturated Ca(NO<sub>3</sub>)<sub>2</sub>. As with the Guinier dimension, this again occurs at lower salt concentrations for Ca(NO<sub>3</sub>)<sub>2</sub> than for NaNO<sub>3</sub>.

Because it is based on a fitted model, the above discussion only considers two scales: smaller primary aggregates and larger secondary aggregates. However, the calculated particle volume distributions suggest that the sample is actually composed of a series of distributions that show up as peaks in Figures 9-13. Although the widths of such distributions depend on details of the calculation,<sup>84</sup> their presence does not. In fact, in many of the samples analyzed above these peaks occur at, or nearly at, the same sizes in different samples, suggesting that they are a real feature of the aggregate size distribution. This suggests that, for this system, the larger aggregates are built from smaller aggregate distributions of reasonably specific sizes. As the aggregate distributions get larger, however, the assembly process becomes more variable as a function of fluid composition. This result is similar to the multimodal aggregates observed for titania.<sup>104</sup>

## CONCLUSIONS

The results discussed above provide a description of how changes in the properties of the solutions in the Hanford tanks will affect aggregation of the boehmite particles they contain. At pH values above the point of zero charge, initially isolated boehmite platelets coalesce into what we have described above as primary aggregates: stacks of boehmite platelets up to several hundred nanometers long. It is uncertain, however, whether similar stacking would occur below the point of zero charge, or whether, due to changes in the relative charge of the surfaces and edges of the plates, a "house-of-cards" structure could form. However, because each particle is composed of two crystallographic faces (i.e., (010) basal plane and (101) thin edge), the interfacial chemistry of the boehmite surfaces (e.g., surface oxygen atom densities and reactivity associated to both facets) will influence stacking. These stacks appear to be relatively robustly bonded. Structurally, however, they are somewhat irregular, leading to fractal dimensions between 2.5 and 2.6. Addition of sodium nitrate to the solution has very little effect on this roughness, but at high pH and high concentrations calcium nitrate seems to increase it. Both sodium nitrate and calcium nitrate appear to suppress mediumscale aggregates, although the amount of calcium necessary to do this is approximately 100-fold smaller than that needed for sodium. Near the point of zero charge (pH = 9), however, neither has much effect. Similarly, both the Guinier dimension and the radius of the primary aggregates are relatively unaffected by salt content at pH = 9, but increase with salt content at pH = 12, first for calcium, and only at higher salt concentrations for sodium. This may be due to calcium's higher valence, but may also suggest more specific binding on the boehmite surface, allowing calcium to have a more direct effect on the surface potential of boehmite, as was seen for elements such as zinc, strontium, rubidium, and neodymium in solution on the (011) surface of rutile.<sup>105–108</sup> Analysis of this result awaits X-ray reflectivity studies or molecular dynamics simulations. Larger aggregates appear to form in a series of well-defined sizes, rather than a continuous distribution, which may imply larger-scale clustering of aggregates, rather than individual particle addition. At lower salt concentrations, the higher the pH, the larger the fractal dimension of these aggregates. However, by 1 m, concentrations not unreasonable for the Hanford tanks, salt effects become dominant at higher pH. It is clear, therefore, that under waste tank conditions multiple scales of particle aggregation can be expected, but predicting the nature of these aggregates requires careful analysis of the effects of fluid composition in each tank. Many rheological properties of the slurry result from mechanical responses of the aggregates under flow; the aggregate structure is expected to significantly influence the rheological properties. For example, the yield stress of a slurry, one of the most important rheological properties, is correlated to the number of nearest particles in the aggregate microstructure, coupled with a contact network of particles.<sup>10,109</sup> Therefore, our study of the effects of pH and salts on aggregate structures, such as the fractal dimension, provides useful physical insights to understand slurry rheology as a function of pH and salt effects.

## AUTHOR INFORMATION

#### Corresponding Author

\*E-mail: anovitzlm@ornl.gov.

## ORCID 💿

- L. M. Anovitz: 0000-0002-2609-8750 X. Zhang: 0000-0003-2000-858X J. Soltis: 0000-0002-7442-0193
- A. J. Krzysko: 0000-0002-2438-9730
- J. Chun: 0000-0002-2291-6496
- T. R. Graham: 0000-0001-8907-8004
- K. M. Rosso: 0000-0002-8474-7720
- J. J. De Yoreo: 0000-0002-9194-6699
- A. G. Stack: 0000-0003-4355-3679

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This research was supported by the Interfacial Dynamics in Radioactive Environments and Materials (IDREAM), an Energy Frontier Research Center funded by the US Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES). This research used resources of the Advanced Photon Source, a US Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. (U)SAXS data were collected at on beamline 9IC-D at the Advanced Photon Source, Argonne National Laboratory. We acknowledge the support of the National Institute of Standards and Technology, Center for Neutron Research, US Department of Commerce in providing the research neutron facilities used in this work. Access to both NBG30 SANS and BT5 USANS was provided by the Center for High Resolution Neutron Scattering, a partnership between the National Institute of Standards and Technology and the National Science Foundation under Agreement No. DMR-1508249. Certain commercial equipment, instruments, materials, and software are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology or the Department of Energy nor does it imply that the materials or equipment identified are necessarily the best available for the purpose. The authors have no pertinent commercial of other relationships that are known to them to create a conflict of interest. A portion of this research was performed using EMSL, a national scientific user facility sponsored by the DOE Office of Biological and Environmental Research and located at PNNL. PNNL is a multiprogram national laboratory operated for DOE by Battelle Memorial Institute under Contract No. DE-AC06-76RLO-1830. We would also like to thank Xiaohong Shari Li (PNNL) for the BET measurements.

### REFERENCES

(1) DOE, Secretary of Energy Advisory Board. Report of the Task Force on Technology Development for Environmental Management; US Department of Energy: Washington, DC, 2014.

(2) DOE Basic Research Needs for Environmental Management, 2015.

(3) Poloski, A. P.; Wells, B. E.; Tingey, J. M.; Mahoney, L. A.; Hall, M. N.; Thomson, S. L.; Smith, G. L.; Johnson, M. E.; Meacham, J. E.; Knight, M. A.; Thien, M. G.; Davis, J. J.; Onishi, Y. *Estimate of Hanford Waste Rheology and Settling Behavior*, PNNL-16857 (WTP-RPT-154 Rev. 0); Pacific Northwest National Laboratory: Richland, WA, 2007.

(4) Wells, B. E.; Kurath, D. E.; Mahoney, L. A.; Onishi, Y.; Huckaby, J. L.; Cooley, S. K.; Burns, C. A.; Buck, E. C.; Tingey, J. M.; Daniel, R. C.; Anderson, K. K. *Hanford Waste Physical and Rheological Properties: Data and Gaps*; Pacific Northwest National Laboratory: Richland, Washington, 2011.

(5) Peterson, R. A.; Buck, E. C.; Chun, J.; Daniel, R. C.; Herting, D. L.; Ilton, E. S.; Lumetta, G. J.; Clark, S. B. Review of the scientific understanding of radioactive waste at the U.S. DOE Hanford Site. *Environ. Sci. Technol.* **2018**, *52*, 381–396.

(6) Zhang, X.; Zhang, X. W.; Graham, T. R.; Pearce, C. I.; Mehdi, B. L.; N'Diaye, A. T.; Kerisit, A. N.; Browning, N. D.; Clark, S. B.; Rosso, K. M. Fast synthesis of gibbsite nanoplates and process optimization using Box-Behnken experimental design. *Cryst. Growth Des.* **2017**, *17*, 6801–6808.

(7) Hu, J. Z.; Zhang, X.; Jaegers, N. R.; Wan, C.; Graham, T. R.; Hu, M.; Pearce, C. I.; Felmy, A. R.; Clark, S. B.; Rosso, K. M. Transitions in Al coordination during gibbsite crystallization using high field <sup>27</sup>Al

and <sup>23</sup>Na MAS NMR spectroscopy. J. Phys. Chem. C 2017, 121, 27555–27562.

(8) Herting, D. L.; Reynolds, J. G.; Barton, W. B. Conversion of coarse gibbsite remaining in Hanford nuclear waste tank heels to solid sodium aluminate [NaAl(OH)<sub>4</sub>.1·5H<sub>2</sub>O]. *Ind. Eng. Chem. Res.* **2014**, 53, 13833–13842.

(9) Russel, W. B.; Saville, D. A.; Schowalter, W. R. Colloidal Dispersions; Cambridge University Press: New York, 1989.

(10) Pednekar, S.; Chun, J.; Morris, J. F. Simulation of shear thickening in attractive colloidal suspensions. *Soft Matter* **2017**, *13*, 1773–1779.

(11) Derjaguin, B.; Landau, L. Theory of stability of highly charged liophobic sols and adhesion of highly charged particles in solutions of electrolytes. *Zh. Eksp. Teor. Fiz.* **1945**, *15*, 663–683.

(12) Raju, M.; van Duin, A. C. T.; Fichthorn, K. A. Mechanisms of oriented attachment of  $TiO_2$  nanocrystals in vacuum and humid environments: reactive molecular dynamics. *Nano Lett.* **2014**, *14*, 1836–1842.

(13) Zhang, H.; Banfield, J. F. Energy calculations predict nanoparticle attachment orientations and asymmetric crystal formation. *J. Phys. Chem. Lett.* **2012**, *3*, 2882–2886.

(14) Zhang, H.; De Yoreo, J. J.; Banfield, J. F. A unified description of attachment-based crystal growth. *ACS Nano* **2014**, *8*, 6526–6530. (15) Baimpos, T.; Shrestha, B. R.; Raman, S.; Valtiner, M. Effect of interfacial ion structuring on range and magnitude of electric double layer, hydration, and adhesive interactions between mica surfaces in

addesive interactions between mice surfaces in 0.05-3 M Li<sup>+</sup> and Cs<sup>+</sup> electrolyte solutions. *Langmuir* **2014**, *30*, 4322– 4332.

(16) Pashley, R. M.; Quirk, J. P. The effect of cation valency on DLVO and hydration forces between macroscopic sheets of muscovite mica in relation to clay swelling. *Colloids Surf.* **1984**, *9*, 1-17.

(17) Chun, J.; Mundy, C. J.; Schenter, G. K. The role of solvent heterogeneity in determining the dispersion interaction between nanoassemblies. J. Phys. Chem. B 2015, 119, 5873–5881.

(18) Davies, B.; Ninham, B. W. Van der Waals Forces in electrolytes. *J. Chem. Phys.* **1972**, *56*, 5797–5801.

(19) dos Santos, A. P.; Levin, Y. Ion specificity and the theory of stability of colloidal suspensions. *Phys. Rev. Lett.* 2011, 106, No. 167801.

(20) Manciu, M.; Ruckenstein, E. Role of the hydration force in the stability of colloids at high ionic strengths. *Langmuir* **2001**, *17*, 7061–7070.

(21) Peula-García, J. M.; Ortega-Vinuesa, J. L.; Bastos-González, D. Inversion of Hofmeister series by changing the surface of colloidal particles from hydrophobic to hydrophilic. *J. Phys. Chem. C* **2010**, *114*, 11133–11139.

(22) Das, M. R.; Borah, J. M.; Kunz, W.; Ninham, B. W.; Mahiuddin, S. ion specificity of the zeta potential of  $\alpha$ -alumina, and of the adsorption of p-hydroxybenzoate at the  $\alpha$ -alumina–water interface. J. Colloid Interface Sci. **2010**, 344, 482–491.

(23) Boström, M.; William, D. R.; Ninham, B. W. Specific Ion Effects: Why DLVO Theory Fails for Biology and Colloid Systems. *Phys. Rev. Lett.* **2001**, *87*, No. 168103.

(24) Crocker, J. C.; Matteo, J. A.; Dinsmore, A. D.; Yodh, A. G. Entropic attraction and repulsion in binary colloids probed with a line optical tweezer. *Phys. Rev. Lett.* **1999**, *82*, 4352–4355.

(25) Nielsen, M. H.; Li, D. S.; Zhang, H. Z.; Aloni, S.; Han, T. Y. J.; Frandsen, C.; Seto, J.; Banfield, J. F.; Colfen, H.; De Yoreo, J. J. Investigating processes of nanocrystal formation and transformation via liquid cell TEM. *Microsc. Microanal.* **2014**, *20*, 425–436.

(26) De Yoreo, J. J.; Gilbert, P. U. P. A.; Sommerdijk, N. A. J. M.; Penn, R. L.; Whitelam, S.; Joester, D.; Zhang, H.; Rimer, J. D.; Navrotsky, A.; Banfield, J. F.; Wallace, A. F.; Michel, F. M.; Meldrum, F. C.; Cölfen, H.; Dove, P. M. Crystallization by particle attachment in synthetic, biogenic, and geologic environments. *Science* **2015**, 349, No. aa6760.

(27) Woehl, T. J.; Evans, J. E.; Arslan, L.; Ristenpart, W. D.; Browning, N. D. Direct in-situ determination of the mechanisms controlling nanoparticle nucleation and growth. ACS Nano 2012, 6, 8599-8610.

(28) Woehl, T. J.; Park, C.; Evans, J. E.; Arslan, I.; Ristenpart, W. D.; Browning, N. D. Observation of aggregative nanoparticle growth: kinetic modeling of the size distribution and growth rate. *Nano Lett.* **2014**, *14*, 373–378.

(29) Zheng, H.; Smith, R. K.; Jun, Y. -W; Kisielowski, C.; Dahmen, U.; Alivisatos, A. P. Observation of single colloidal platinum nanocrystal growth trajectories. *Science* **2009**, *324*, 1309–1312.

(30) Pednekar, S.; Chun, J.; Morris, J. F. Bidisperse and polydisperse suspension rheology at large solid fraction. *J. Rheol.* **2018**, *62*, 513–526.

(31) Lin, M. Y.; Lindsay, H. M.; Weitz, D. A.; Ball, R. C.; Klein, R.; Meakin, P. Universality in colloid aggregation. *Nature* **1989**, *339*, 360–362.

(32) Lin, M. Y.; Lindsay, H. M.; Weitz, D. A.; Ball, R. C.; Klein, R.; Meakin, P. Universal reaction-limited colloid aggregation. *Phys. Rev. A* **1990**, *41*, 2005–2020.

(33) Pusey, P. N.; Rarity, J. G. Measurement of the hydrodynamic fractal dimension of aggregating polystyrene spheres. *Mol. Phys.* **1987**, *62*, 411–418.

(34) Waite, T. D.; Cleaver, J. K.; Beattie, J. K. aggregation kinetics and fractal structure of  $\gamma$  -alumina assemblages. *J. Colloid Interface Sci.* **2001**, 241, 333–339.

(35) Odriozola, G.; Tirado-Miranda, M.; Schmitt, A.; Martinez Lopez, F.; Callejas-Fernandez, J.; Martinez-Garcia, R.; Hidalgo-Alvarez, R. A light scattering study of the transition region between diffusion- and reaction-limited cluster aggregation. *J. Colloid Interface Sci.* **2001**, *240*, 90–96.

(36) Michot, L. J.; Bihannic, I.; Thomas, F.; Lartiges, B. S.; Waldvogel, Y.; Caillet, C.; Thieme, J.; Funari, S. F.; Levitz, P. Coagulation of Na-Montmorillonite by inorganic cations at neutral pH: a combined transmission x-ray microscopy, small angle and wide angle X-ray scattering study. *Langmuir* **2013**, *29*, 3500–3510.

(37) Legg, B. A.; Zhu, M.; Comolli, L. R.; Gilbert, B.; Banfield, J. F. Determination of the three-dimensional structure of ferrihydrite nanoparticle aggregates. *Langmuir* **2014**, *30*, 9931–9940.

(38) Anand, U.; Lu, J.; Loh, D.; Aabdin, Z.; Mirsaidov, U. Hydration layer-mediated pairwise interaction of nanoparticles. *Nano Lett.* **2016**, *16*, 786–790.

(39) Chen, Q.; Cho, H.; Manthiram, K.; Yoshida, M.; Ye, X.; Alivisatos, A. P. Interaction potentials of anisotropic nanocrystals from the trajectory sampling of particle motion using in-situ liquid phase transmission electron microscopy. *ACS Cent. Sci.* **2015**, *1*, 33–39.

(40) Li, D.; Nielsen, M. H.; Lee, J. R. I.; Frandsen, C.; Banfield, J. F.; De Yoreo, J. J. Direction-specific interactions control crystal growth by oriented attachment. *Science* **2012**, *336*, 1014–1018.

(41) Liao, H. G.; Cui, L.; Whitelam, S.; Zheng, H. Real-time imaging of  $Pt_3Fe$  nanorod growth in solution. *Science* **2012**, *336*, 1011–1014.

(42) Welch, D. A.; Woehl, T. J.; Park, C.; Faller, R.; Evans, J. E.; Browning, N. D. Understanding the role of solvation forces on the preferential attachment of nanoparticles in liquid. *ACS Nano* **2016**, *10*, 181–187.

(43) Fukuma, T.; Jarvis, S. P. Development of liquid-environment frequency modulation atomic force microscope with low noise deflection sensor for cantilevers of various dimensions. *Rev. Sci. Instrum.* **2006**, *77*, No. 043701.

(44) Fukuma, T.; Higgins, M. J.; Jarvis, S. P. Direct imaging of individual intrinsic hydration layers on lipid bilayers at angstrom resolution. *Biophys. J.* **2007**, *92*, 3603–3609.

(45) Kilpatrick, J. I.; Loh, S. H.; Jarvis, S. P. Directly probing the effects of ions on hydration forces at interfaces. *J. Am. Chem. Soc.* **2013**, 135, 2628–2634.

(46) Kobayashi, K.; Oyabu, N.; Kimura, K.; Ido, S.; Suzuki, K.; Imai, T.; Tagami, K.; Tsukada, M.; Yamada, H. Visualization of hydration layers on muscovite mica in aqueous solution by frequency-modulation atomic force microscopy. *J. Chem. Phys.* **2013**, *138*, No. 184704.

(47) Zhang, X.; Shen, Z.; Liu, J.; Kerisit, S. N.; Bowden, M. E.; Sushko, M. L.; De Yoreo, J. J.; Rosso, K. M. Direction-specific forces underlying zinc oxide crystal growth by oriented attachment. *Nat. Commun.* **201**7, *8*, No. 835.

(48) Zhang, X.; He, Y.; Sushko, M. L.; Liu, J.; Luo, L.; De Yoreo, J. J.; Mao, S. X.; Wang, C.; Rosso, K. M. Direction-specific van der Waals attraction between rutile  $TiO_2$  nanocrystals. *Science* **2017**, *356*, 434–437.

(49) Mari, R.; Seto, R.; Morris, J. F.; Denn, M. M. Shear thickening, frictionless and frictional rheologies in non-brownian suspensions. *J. Rheol.* **2014**, *58*, 1693–1724.

(50) Seto, R.; Mari, R.; Morris, J. F.; Denn, M. M. Discontinuous shear thickening of frictional hard-sphere suspensions. *Phys. Rev. Lett.* **2013**, *111*, No. 218301.

(51) Kumar, S.; Davis, T. M.; Ramanan, H.; Penn, R. L.; Tsapatsis, M. Aggregative growth of silicalite-1. *J. Phys. Chem. B* 2007, 111, 3398-3403.

(52) Burrows, N. D.; Hale, C. R. H.; Penn, R. L. Effect of pH on the kinetics of crystal growth by oriented aggregation. *Cryst. Growth Des.* **2013**, *13*, 3396–3403.

(53) Burrows, N. D.; Kesselman, E.; Sabyrov, K.; Stemig, A.; Talmon, Y.; Penn, R. L. Crystalline nanoparticle aggregation in non-aqueous solvents. *CrystEngComm* **2014**, *16*, 1472–1481.

(54) Penn, R. L. Kinetics of oriented aggregation. J. Phys. Chem. B 2004, 108, 12707–12712.

(55) Penn, R. L.; Banfield, J. F. Imperfect oriented attachment: dislocation generation in defect-free nanocrystals. *Science* **1998**, *281*, 969–971.

(56) Penn, R. L.; Banfield, J. F. Oriented attachment and growth, twinning, polytypism, and formation of metastable phases; insights from nanocrystalline TiO<sub>2</sub>. *Am. Mineral.* **1998**, *83*, 1077–1082.

(57) Yuwono, V. M.; Burrows, N. D.; Soltis, J. A.; Penn, R. L. Oriented aggregation: formation and transformation of mesocrystal intermediates revealed. *J. Am. Chem. Soc.* **2010**, *132*, 2163–2165.

(58) Wu, L.; Ortiz, C. P.; Jerolmack, D. J. Aggregation of elongated colloids in water. *Langmuir* 2017, 33, 622–629.

(59) Herrington, T. M.; Midmore, B. R. Investigation of scaling effects in the aggregation of dilute kaolinite suspensions by quasielastic light scattering. *Colloids Surf.*, A **1993**, 70, 199–202.

(60) Axford, S. D. T.; Herrington, T. M. Determination of aggregate structures by combined light-scattering and rheological studies. *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 2085–2093.

(61) Mohraz, A.; Moler, D. B.; Ziff, R. M.; Solomon, M. J. Effect of monomer geometry on the fractal structure of colloidal rod aggregates. *Phys. Rev. Lett.* **2004**, *92*, No. 155503.

(62) Beattie, J. K.; Cleaver, J. K.; Waite, T. D. Anomalous aggregation behaviour of aluminium oxyhydroxides. *Colloids Surf., A* **1996**, *111*, 131–138.

(63) Teixeira, J. Small-angle scattering by fractal systems. J. Appl. Crystallogr. 1988, 21, 781–785.

(64) Gerber, T.; Himmel, B.; Hubert, C. WAXS and SAXS investigation of structure formation of gels from sodium-water glass. *J. Non-Cryst. Solids* **1994**, *175*, 160–168.

(65) Radlinski, A. P.; Barre, L.; Espinat, D. Aggregation of n-alkanes in organic solvents. *J. Mol. Struct.* **1996**, 383, 51–56.

(66) Chou, C. -M; Hong, P.-D. Nucleation, Growth, Fractal Aggregation, and Late-Stage Coarsening on Structural Development of Polymer Physical Gels. *Macromolecules* **2004**, *37*, 5596–5606.

(67) Loong, C. K.; Ozawa, M. Mass-fractal-like microstructure and proton disorder in nanostructured pseudoboehmite: a neutron-scattering study. J. Electroanal. Chem. 2005, 584, 5–8.

(68) Headen, T. F.; Boek, E. S.; Stellbrink, J.; Scheven, U. M. Small Angle Neutron Scattering (SANS and V-SANS) Study of asphaltene aggregates in crude oil. *Langmuir* **2009**, *25*, 422–428.

(69) Alwitt, R. S. The point of zero charge of pseudoboehmite. J. Colloid Interface Sci. 1972, 40, 195–198.

(70) Kosmulski, M. pH-dependent surface charging and points of zero charge. IV. Update and new approach. J. Colloid Interface Sci. 2009, 337, 439–448.

(71) Qi, F.; Chen, Z.; Xu, B.; Shen, J.; Ma, J.; Joll, C.; Heitz, A. Influence of surface texture and acid-base properties on ozone decomposition catalyzed by aluminum (hydroxyl) oxides. *Appl. Catal.* B **2008**, *84*, 684–690.

(72) Qi, F.; Xu, B.; Chen, Z.; Ma, J.; Sun, D.; Zhang, L. Influence of aluminum oxides surface properties on catalyzed ozonation of 2,4,6-trichloroanisole. *Sep. Purif. Technol.* **2009**, *66*, 405–410.

(73) Zhang, T.; Li, C.; Ma, J.; Tian, H.; Qiang, Z. Surface hydroxyl groups of synthetic  $\alpha$ -FeOOH in promoting  $\bullet$ OH generation from aqueous ozone: Property and activity relationship. *Appl. Catal. B: Environ.* **2008**, *82*, 131–137.

(74) Kaledin, L. A.; Tepper, F.; Kaledin, T. G. Pristine point of zero charge (p.p.z.c.) and zeta potentials of boehmite's nanolayer and nanofiber surfaces. *Int. J. Smart Nano Mater.* **2016**, *7*, 1-21.

(75) Brunauer, S.; Emmett, P. H.; Teller, E. Adsorption of Gases in Multimolecular Layers. J. Am. Chem. Soc. **1938**, 60, 309–319.

(76) Stumm, W.; Morgan, J. J. Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters, 2nd ed.; Wiley-Interscience: New York, 1981.

(77) Anovitz, L. M.; Cole, D. R. Characterization and analysis of porosity and pore structures. *Rev. Mineral. Geochem.* **2015**, *80*, 61–164.

(78) Anovitz, L. M.; Lynn, G. W.; Cole, D. R.; Rother, G.; Allard, L. F.; Hamilton, W. A.; Porcar, L.; Kim, M.-H. A new approach to quantification of metamorphism using ultra-small and small angle neutron scattering. *Geochim. Cosmochim. Acta* 2009, 73, 7303–7324.

(79) Anovitz, L. M.; Rother, G.; Cole, D. R. In *Characterization of Rock Pore Features in Geothermal Systems Using Small Angle Neutron Scattering* (SANS). Proceedings of 36th Workshop on Geothermal Reservoir Engineering Sgp-Tr-191; Stanford University: Stanford, CA, 2011; pp 571–582.

(80) Anovitz, L. M.; Cole, D. R.; Rother, G.; Allard, L. F., Jr.; Jackson, A.; Littrell, K. C. Diagenetic changes in macro- to nano-scale porosity in the St. Peter Sandstone: an (ultra) small angle neutron scattering and backscattered electron imaging analysis. *Geochim. Cosmochim. Acta* 2013, *102*, 280–305.

(81) Anovitz, L. M.; Wang, H.-W; Cole, D. R.; Sheets, J.; Rother, G.; Faulder, D. D.; Walters, M. In *Analysis of Multiscale Porosity at the Coso Geothermal Field*. Proceedings of 38th Workshop on Geothermal Reservoir Engineering SPG-TR-198; Stanford University: Stanford, CA, 2013.

(82) Anovitz, L. M.; Cole, D. R.; Jackson, A. J.; Rother, G.; Littrell, K. C.; Allard, L. F.; Pollington, A. D.; Wesolowski, D. J. Effect of quartz overgrowth precipitation on the multiscale porosity of sandstone: a (U)SANS and imaging analysis. *Geochim. Cosmochim.* Acta 2015, 158, 199–222.

(83) Anovitz, L. M.; Cole, D. R.; Sheets, J.; Swift, A.; Elston, H.; Welch, S.; Chipera, S. J.; Littrell, K. C.; Mildner, D. F. R.; Wasbrough, M. J. Effects of maturation on multiscale (nm to mm) porosity in the Eagle Ford Shale. *Interpretations* **2015**, *3*, 1–11.

(84) Anovitz, L. M.; Freiburg, J. T.; Wasbrough, M.; Mildner, D.; Littrell, K. C.; Pipich, V.; et al. The Effects of Burial Diagenesis on Multiscale Porosity in the St. Peter Sandstone: An Imaging SANS and USANS analysis. *Mar. Pet. Geol.* **2018**, *92*, 352–371.

(85) Wang, H.-W.; Anovitz, L. M.; Burg, A.; Cole, D. R.; Allard, L. F.; Jackson, A. J.; Stack, A. G.; Rother, G. Multi-scale characterization of pore evolution in a combustion metamorphic complex, Hatrurim basin, Israel: combining (ultra) small-angle neutron scattering image analysis. *Geochim. Cosmochim. Acta* **2013**, *121*, 339–362.

(86) Olsson, A.; Hellsing, M. S.; Rennie, A. R. A holder to rotate sample cells to avoid sedimentation in small-angle neutron scattering and ultra small-angle neutron scattering experiments. *Meas. Sci. Technol.* **2013**, *24*, No. 105901.

(87) Leão, J. B.; Murphy, R. P.; Wagner, N. J.; Bleuel, M. Dynamic infrared sample controlled (DISCO) temperature for the tumbler cells for ultra small angle neutron scattering (USANS). *J. Neutron Res.* **2017**, *19*, 23–26.

(88) Glinka, C. J.; Barker, J. G.; Hammouda, B.; Krueger, S.; Moyer, J. J.; Orts, W. J. The 30 m small-angle neutron scattering instruments

at the National Institute of Standards and Technology. J. Appl. Crystallogr. 1998, 31, 430-445.

(89) Barker, J. G.; Glinka, C. J.; Moyer, J. J.; Kim, M. H.; Drews, A. R.; Agamalian, M. Design and performance of a thermal-neutron double-crystal diffractometer for USANS at NIST. *J Appl. Crystallogr.* **2005**, *38*, 1004–1011.

(90) Kline, S. R. Reduction and analysis of SANS and USANS data using Igor Pro. J. Appl. Crystallogr. 2006, 39, 895–900.

(91) Ilavsky, J.; Jemian, P. R.; Allen, A. J.; Zhang, F.; Levine, L. E.; Long, G. G. Ultra-small-angle X-ray scattering at the Advanced Photon Source. J. Appl. Crystallogr. 2009, 42, 469–479.

(92) Ilavsky, J.; Zhang, F.; Allen, A. J.; Levine, L. E.; Jemian, P. R.; Long, G. G. Ultra-Small-Angle X-ray Scattering Instrument at the Advanced Photon Source: History, Recent Development, and Current Status. *Metall. Mater. Trans. A* 2013, 44, 68–76.

(93) Ilavsky, J. Nika: software for two-dimensional data reduction. J. Appl. Crystallogr. 2012, 45, 324–328.

(94) Ilavsky, J.; Jemian, P. R. Irena: tool suite for modeling and analysis of small-angle scattering. *J. Appl. Crystallogr.* **2009**, *42*, 347–353.

(95) Zaman, A. C.; Üstündağ, C. B.; Çelik, A.; Kara, A.; Kaya, F.; Kaya, C. Carbon nanotube/boehmite-derived alumina ceramics obtained by hydrothermal synthesis and spark plasma sintering (SPS). *J. Eur. Ceram. Soc.* **2010**, *30*, 3351–3356.

(96) Tettenhorst, R.; Hofmann, D. A. Crystal chemistry of boehmite. *Clays Clay Miner.* **1980**, *28*, 373.

(97) Iijima, S.; Yumura, T.; Liu, Z. One-dimensional nanowires of pseudoboehmite (aluminum oxyhydroxide γ-AlOOH). *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 11759–11764.

(98) Kartzmark, E. M. Conductances, Densities, and Viscosities of Solutions of Sodium Nitrate in Water and in Dioxane–Water, at 25 °C. *Can. J. Chem.* **1972**, *50*, 2845–2850.

(99) Carpio, R.; Mehicic, M.; Borsay, F.; Petrovc, C.; Yeager, E. Investigation of aqueous calcium nitrate, zinc nitrate, and zinc chloride solutions using acoustic velocity measurements. *J. Phys. Chem.* **1982**, *86*, 4980–4987.

(100) Hammouda, B. A new Guinier–Porod model. J. Appl. Crystallogr. 2010, 43, 716–719.

(101) Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge University Press, Cambridge, 1989.

(102) Wang, Y.; Li, Y.; Pennell, K. D. Influence of electrolyte species and concentration on the aggregation and transport of fullerene nanoparticles in quartz sands. *Environ. Toxicol. Chem.* **2008**, *27*, 1860–1867.

(103) Li, K.; Zhang, W.; Huang, Y.; Chen, Y. Aggregation kinetics of CeO<sub>2</sub> nanoparticles in KCl and CaCl<sub>2</sub> solutions: measurements and modeling. *J. Nanopart. Res.* **2011**, *13*, 6483–6491.

(104) Dunphy Guzman, K. A.; Finnegan, M. P.; Banfield, J. F. Influence of surface potential on aggregation and transport of titania nanoparticles. *Environ. Sci. Technol.* **2006**, *40*, 7688–7693.

(105) Zhang, Z.; Fenter, P.; Cheng, L.; Sturchio, N. C.; Bedzyk, M. J.; Předota, M.; Bandura, M. A.; Kubicki, J. D.; Lvov, S. N.; Cummings, P. T.; Chialvo, A. A.; Ridley, M. K.; Bénézeth, P.; Anovitz, L. M.; Palmer, D. A.; Machesky, M. L.; Wesolowski, D. J. Ion Adsorption at the Rutile–Water Interface: Linking Molecular and Macroscopic Properties. *Langmuir* **2004**, *20*, 4954–4969.

(106) Zhang, Z.; Fenter, P.; Cheng, L.; Sturchio, N.; Bedzyk, M.; Machesky, M.; Anovitz, L.; Wesolowski, D.  $Zn^{2+}$  and  $Sr^{2+}$  adsorption at the TiO<sub>2</sub> (110)-electrolyte interface: influence of ionic strength, coverage, and anions. *J. Colloid Interface Sci.* **2006**, 295, 50–64.

(107) Zhang, Z.; Fenter, P.; Sturchio, N. C.; Bedzyk, M. J.; Machesky, M. L.; Wesolowski, D. J. Structure of rutile  $TiO_2$  (110) in water and 1molal Rb<sup>+</sup> at pH 12: Inter-relationship among surface charge, interfacial hydration structure, and substrate structural displacements. *Surf. Sci.* **2007**, *601*, 1129–1143.

(108) Ridley, M. K.; Machesky, M. L.; Wesolowski, D. J.; Palmer, D. A. Surface complexation of neodymium at the rutile-water interface: A potentiometric and modeling study in NaCl media to 250 °C. *Geochim. Cosmochim. Acta* **2005**, *69*, 63–81.

(109) Chun, J.; Oh, T.; Luna, M.; Schweiger, M. J. Effect of Particle Size Distribution on Slurry Rheology: Nuclear Simulant Slurries. *Colloids Surf.*, A **2011**, 384, 304–310.