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Improved Fundamental Understanding of Aluminum Chemistry and Interactions of Aluminate Anion with Co-Anions: Project 277636 Report

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IMPROVED FUNDAMENTAL UNDERSTANDING OF ALUMINUM CHEMISTRY AND INTERACTIONS OF ALUMINATE ANION WITH CO-ANIONS: PROJECT 277636 REPORT

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Abstract

Aluminum (Al) is the second most prevalent component in the sludge phase, after sodium (Na), in Hanford Tank Waste. Al accounts for one third of the total inventory of High-Level Waste (HLW) sludge and amounts to 4,140 metric tons. Al-bearing solids in the sludge phase, being sparingly soluble, present a grand technical challenge for waste volume reduction in HLW vitrification and subsequent disposal. This project aims to understand the fundamental chemistry of aluminum from the *in-situ* determination of the morphology and crystallinity of aluminum-bearing phases to the kinetic and thermodynamic behaviors of sparingly soluble Al-bearing solids under tank waste conditions.

This report summarizes the major results from the tasks performed by Sandia National Laboratories (SNL), Oak Ridge National Laboratory (ORNL), University of Idaho (UI), and Geochemagine LLC, during the budget period of three installments with each installment covering six months.

The SNL Team, UI Team, and Geochemagine LLC focus on the experimental and modeling investigations of Al chemistry in multiple component systems at elevated temperatures relevant to Hanford tank waste, performing Tasks 3 through 6 detailed in the Proposal. The major findings and discoveries are summarized in Chapters 2 through 6 in the report. The experimental and model work targets both of kinetic and equilibrium aspects of Al chemistry. In the kinetic aspect, we have discovered that the dissolution kinetics of gibbsite in nitrite-

dominated media is about one order of magnitude lower than that in nitrate-dominated media. These findings will have important implications/applications to Hanford tank waste. In the equilibrium aspect, based on our solubility measurements, we have established a thermodynamic model to describe the interactions of aluminate ($\text{Al}(\text{OH})_4^-$) with nitrate (NO_3^-) valid to high ionic strengths at temperatures from 25 °C to 100 °C. This model will have applications to Hanford tank waste.

The ORNL team uses *in situ* multimodal analysis strategy to study Al chemistry of simulated tank waste using microfluidic reactors and advanced chemical imaging and mass spectrometry (MS) techniques, performing Tasks 1 and 2 detailed in the Proposal. Because the SALVI device is vacuum compatible and transferrable among different platforms, we can use it in scanning electron microscopy (SEM), vacuum ultraviolet single photon mass spectrometry (VUV SPI-MS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study the chemical speciation and colloid stability in liquids in this project. Additionally, *ex situ* transmission electron microscopy (TEM) and x-ray diffraction (XRD) spectroscopy can be used to verify particle phase to further the understanding of the Al-bearing phases. The results are summarized in Chapters 7 through 10 in this report.

Chapters 5 and 7 through 10 in the report may contain unpublished information.

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1. Introduction

A diverse set of Al phases have been identified in Hanford waste sludge, including gibbsite [α -Al(OH)₃], boehmite [γ -AlOOH], amorphous aluminum hydroxide, dawsonite [NaAl(OH)₂CO₃], nitrate-cancrinite [Na₈(AlSiO₄)₆(NO₃)₂·*n*H₂O], aluminosilicates, and soluble aluminate [NaAl(OH)₄] (e.g., Buck and McNamara, 2004; Krupka et al., 2006; Reynolds et al., 2012; Allred et al., 2020). The three predominant Al-bearing solid phases are sodium aluminate [NaAl(OH)₄], gibbsite [α -Al(OH)₃], and boehmite [γ -AlOOH], followed by unknown aluminosilicate phases, zeolite and an unknown Cr phase (Westesen and Peterson, 2021). The variation in particle size is several orders of magnitude. While many particles are in the nanometer (nm) to micrometer (μ m) range, the largest gibbsite agglomerates observed are up to 7 μ m (e.g., Peterson et al., 2018; Page et al., 2020). The particle size distribution and the morphological variability of Al-bearing solid phases directly control the rheological behavior of waste sludge. Limited studies have been carried out on the solubility and dissolution/precipitation kinetics of gibbsite and boehmite after the adsorption of Cr(III) species (e.g., Cui et al., 2020). However, no such studies have been conducted Al-silicates and dawsonite.

In this project, we aim to address the following issues: (1) Why are the measured Al solubilities in the waste highly variable and generally higher than those predicted from simple chemical systems? (2) How can we improve the existing thermodynamic model (e.g., using machine learning) to account for the complex interactions of chemical species in waste sludge? (3) What are the effects of the coexisting chemical components on Al phase dissolution and transformation? (4) Specifically, what controls gibbsite to boehmite transformation or vice versa? (5) What controls the large variabilities observed in the efficiency of aluminum removal among different tanks? (6) How does the stratification of waste sludge (e.g., the formation of saltcake) affect Al dissolution and removal? And (7) how can we formulate new washing and leaching solution recipes to accelerate Al dissolution and removal? Our preliminary work indicates that chemical species such as borate and CO₂ may increase Al solubility and enhance boehmite to gibbsite transformation, respectively (see the next section for details). The issue of whether these species can promote Al dissolution and removal in waste pretreatment will also be addressed.

The teams at Sandia National Laboratories, University of Idaho, and Geochemagine LLC are in charge of performing Tasks 3 through 6, covering the Research Theme B—Experimental insights into solubility and kinetic behaviors of Al-bearing phases in multiple component solutions, and Research Theme C—Mechanistic understanding of Al chemistry in Hanford tank waste solutions on multiple scales and a predictive model based on such an understanding. The Research Theme B aims at acquiring the experimental parameters that will be fed into the models to clarify the optimal conditions for the pretreatment of HLW sludge, and Research Theme C primarily targets the fundamental understanding of Al chemistry in high ionic strength and complex solutions at elevated temperatures and establishing a predictive model for pretreatment sludge waste. The ORNL Team is responsible Tasks 1 and 2, covering Research

Theme A—Insight into *In-Situ* Formation of Al-bearing Phases in Simulated Tank Waste Solutions. Each section authored by the respective teams is followed by the relevant references and appendices, if applicable.

This report summarizes major technical updates accomplished by the above teams, in the performance period funded by the project. The budget period had three installments with each installment covering six months.

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2. Kinetic Aspects of Al Chemistry—Kinetics of Gibbsite Dissolution in Concentrated NaOH + NaNO₃ and NaOH + NaNO₂ Solutions at Elevated Temperatures: A Tale of Two Legends

2.1. Summary

The kinetics of gibbsite dissolution and precipitation in alkaline solutions is important to many industrial processes. The kinetics in pure NaOH solutions have been relatively well known, especially in the Bayer process to extract aluminum from bauxite ores. However, in tank waste such as those at Hanford and Savannah River Sites in the USA, the kinetics can be greatly complicated by the presence of high concentrations of nitrate and nitrite in addition to NaOH. Understanding the effects of nitrate and nitrite on gibbsite dissolution and precipitation is important for the optimization of a pretreatment process of the tank waste sludges and associated supernatants. In this study, we investigated the dissolution kinetics of gibbsite in concentrated NaOH + NaNO₃ and NaOH + NaNO₂ solutions. In our experiments, NaOH concentration ranges from 1.0 mol·dm⁻³ to 3.0 mol·dm⁻³, while NaNO₃ and NaNO₂ concentrations range from 1.0 mol·dm⁻³ to 5.0 mol·dm⁻³, covering typical chemical conditions observed in Hanford Tank Waste. A kinetic model was formulated and fitted to the experimental data to extract key thermodynamic and kinetic parameters for gibbsite dissolution. Our experimental results reveal that the dissolution rate constants of gibbsite in nitrite media are about one order of magnitude lower than those in corresponding nitrate media, indicating an inhibitory effect of nitrite on mineral dissolution. This inhibitory effect can possibly be attributed to the formation of a passivating layer of >Al-NO₂⁻ on the mineral surface (“>” denoting surface complexes”). In solution, nitrite—a Lewis base—forms an aqueous complex of Al(OH)₃NO₂⁻ and thus increases the apparent solubility of gibbsite, which pushes the dissolution towards a far-from-equilibrium state, leading to etch pit development on the mineral surface. The results presented here have important implications for the pretreatment of tank waste sludge.

2.2. Background

Gibbsite has many important applications, including manufacturing high-temperature refractory materials, specialty glass, ceramics, abrasives, micro-abrasives, catalysts, adsorbents, and flame retardants (Geology Science, 2025). Gibbsite-derived materials are used as flocculants to remove suspended particles and impurities in water. Gibbsite is also used as a filler in paper, plastic and rubber, and a substrate and insulation material for electronic components. In cosmetics, gibbsite-derived materials are used in products like toothpaste, where they serve as mild abrasives for tooth cleaning. They may also be used in skincare products as thickening agents or as fillers in powders and creams.

Aluminum is primarily extracted from bauxite ores via the Bayer process (e.g., Pereira et al., 2009). The Bayer process consists of four steps. The first step is to digest bauxite (mainly gibbsite or boehmite, or their mixture) in concentrated NaOH or caustic Na₂CO₃ solutions at elevated temperatures. The second step is to separate the insoluble residues. The third step is to precipitate the dissolved aluminum mainly as gibbsite. The fourth step is to calcinate the precipitate to produce alumina. As gibbsite is involved in the first and the third steps in the Bayer process, the dissolution/precipitation kinetics of gibbsite in NaOH and Na₂CO₃ solutions has been extensively investigated (e.g., Glastonbury, 1967; Brontrger et al., 1974; Pereira et al.,

2009; Yang et al., 2017, 2018; Wu et al., 2020, 2022; Ma et al., 2023). In geoscience, the dissolution and precipitation kinetics of gibbsite has generally been investigated for pH below 7 to assess the Al(III) from geological environments at ambient temperatures (e.g., Nagy and Lasaga, 1992, 1993; Dietzel and Bohme, 2005).

In Hanford Tank Waste, aluminum is the second most dominant element, only after sodium, and accounts for one third of the total inventory of high-level nuclear waste (HLW) sludge. At the same time, there are high concentrations of sodium nitrate and nitrite in addition to high NaOH concentrations. The tank waste at the Savannah River site has similar chemical compositions (e.g., Martino et al., 2023; Martino, 2024). The effects of nitrate and nitrite on the dissolution/precipitation kinetics of aluminum-bearing phases including gibbsite are poorly known. Understanding such effects is important for the pretreatment of waste sludge. This study investigates the dissolution kinetics of gibbsite in concentrated NaOH + NaNO₃ and NaOH + NaNO₂ solutions at 60 °C.

2.3. Experimental Procedure

2.3.1 Gibbsite Agglomerate Preparation

Before dissolution experiments, large gibbsite agglomerates were synthesized. Gibbsite agglomerates were prepared by using a method similar to that of Zeng et al. (2007) by first rinsing aluminum hydroxide from Thermo Scientific with DI water (18.2 MΩ). Then, the dried product was sieved to less than 45 μm. This fine powder was used as the primary seed. To activate the primary seed, it was boiled in DI water for 90 minutes then dried for 24 hours at 65 °C. Then a supersaturated sodium aluminate solution was prepared by dissolving 73.75 grams of sodium aluminate from Sigma Aldrich in 250 mL of DI water at 80 °C, assisted by manual mixing until all salts were completely dissolved.

Once the prepared sodium aluminate solution was ready, the mass was recorded, and it was transferred to an Erlenmeyer flask on a hot plate and heated to 75 °C. The activated seed was then added to equal a 0.33 seed:mass ratio. The sodium aluminate solution and activated seed were allowed to heat and stir on a hot plate at 75°C for both overnight and over 1 week. The agglomeration on each time scale will result in different particle size. After incubation the material was filtered and rinsed with hot DI water. The final product was allowed to dry at 70°C for 24 hours.

Specific surface areas of the initial gibbsite material and the materials reacted with NaOH + NaNO₂ solutions were determined with Brunauer-Emmett-Teller (BET) measurements and range from 0.93 to 3.77 m²/g (Fig. 2.1). In our BET surface area analysis on gibbsite samples, the samples were weighed out to ~3 g aliquots. The samples were degassed with nitrogen gas at 60 °C for 24 hours. The BET analysis was performed using a Tristar II Plus micromeritics instrument. The absorbent was nitrogen gas with helium as the carrier gas. The measured BET surface area ranged from < 1 m²/g to ~3.8 m²/g. Most of the samples had good correlation coefficient values and positive c-values >10, indicating a good interaction between the N₂ gas and the gibbsite powder thus making the BET equation suitable. The surface area values were lower compared to what was found in the literature: 5 – 15 m²/g for boehmite and gibbsite (Mercury et al. 2020, Alex et al. 2011). In Alex et al. (2011), boehmite was synthesized by

thermal decomposition of gibbsite at 350 °C for 2 hours, and boehmite was subject to activation via mechanical milling. In Mercury et al. (2020), gibbsite generated by the Bayer process was mechanically activated via attrition milling with varying grinding ball-to-powder ratios for 24 hours. Therefore, as the samples in the literature experienced mechanical activation, the differences in the surface areas determined in this study from the literature values are expected.

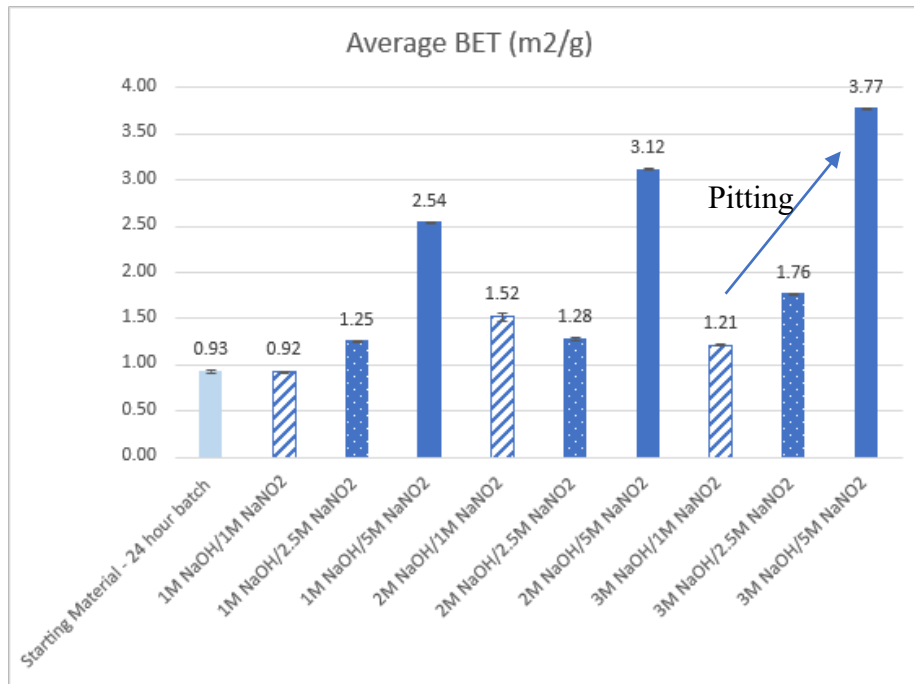


Figure 2.1. Specific surface areas of gibbsite materials used in the dissolution experiments

2.3.2 Dissolution Experiments

Dissolution experiments were prepared by adding 3 grams of the above agglomerated gibbsite to Nalgene bottles with 50 mL of supporting solution. The supporting solutions were a series of mixtures of NaOH + NaNO₃ and of NaOH + NaNO₂ with NaOH concentrations ranging from 1.0 M to 3.0 M, NaNO₃ concentrations from 1.0 M to 5.0 M, and NaNO₂ concentrations from 1.0 M to 5.0 M (Table 2.1). These supporting solutions were prepared from reagent grade NaOH from Fisher Scientific (LOT# 126910), NaNO₃ from Sigma-Aldrich (LOT# MKCT1005), and NaNO₂ from ACROS (LOT# B0137005). Supporting solutions were allowed to react with the agglomerated gibbsite in an oven at 60 °C until designated sampling times, which occurred every hour from 1 hour to 35 hours. During this period, the solutions were not agitated. Sampling was done by removing 1 mL of liquid from each experiment, which resulted in the slight change in the ratios of solid to solution, and solution samples were filtered using 0.22 µm pore-size, 25 mm disc syringe nylon filters from VWR, and the sample mass was determined with a Mettler balance precise to the fourth decimal place of a gram and transferred to a 10 mL volumetric flask stabilized with 0.5 mL 1.0 M NaOH and filling the remaining volume with DI water. Before analysis they were further diluted to 1:10 and then analyzed using a Perkin Elmer

dual-view inductively coupled plasma-atomic emission spectrometer (Perkin Elmer DV 8300) for Al concentration at the 396.153 nm wavelength against Al standards (SPEX CertiPrep).

Table 2.1. Supporting solution matrices for dissolution kinetics experiments of gibbsite at 60 °C

1.0 M NaOH with	2.0 M NaOH with	3.0 M NaOH with
1.0 M NaNO ₃ or 1.0 M NaNO ₂	1.0 M NaNO ₃ or 1.0 M NaNO ₂	1.0 M NaNO ₃ or 1.0 M NaNO ₂
2.5 M NaNO ₃ or 2.5 M NaNO ₂	2.5 M NaNO ₃ or 2.5 M NaNO ₂	2.5 M NaNO ₃ or 2.5 M NaNO ₂
5.0 M NaNO ₃ or 5.0 M NaNO ₂	5.0 M NaNO ₃ or 5.0 M NaNO ₂	5.0 M NaNO ₃ or 5.0 M NaNO ₂

2.4. Results and Discussion

2.4.1. Experimental Results

Total molality of aluminum ($\Sigma m_{\text{Al(III)}}$, mol·kg⁻¹) for the dissolution of gibbsite in NaOH + NaNO₃ mixtures is presented in Figures 2.2 through 2.4. The gibbsite materials used for the kinetic experiments include (1) the seeds recrystallized overnight and (2) the seeds recrystallized for a week. Total molalities of aluminum are computed based on aluminum concentrations determined by ICP-AES along with experimentally determined densities of gibbsite-saturated NaOH + NaNO₃ and NaOH + NaNO₂ solutions (Tables 2.A1 and 2.A2).

Figure 2.2 shows that Al(III) concentrations in the experiments in the matrices with 1.0 mol·dm⁻³ NaOH reach a plateau after about 25 hours in experimental duration. The starting materials with one week recrystallization have consistently higher dissolved Al(III) concentrations than those with overnight recrystallization. This may be due to adsorption of some sodium aluminate from the oversaturated solution on the surface of the starting materials with one week recrystallization. The concentration of nitrate positively influences the dissolution of gibbsite, but the effect is not pronounced for the experiments with seeds recrystallized overnight. With increasing NaOH concentration, as shown in Figures 3 and 4, the effect of nitrate becomes more pronounced. Figures 2.2 through 2.4 suggest that Al(III) concentrations in all experiments reach a plateau at around 25 hours. If we take this plateau concentration as gibbsite solubility at a given chemical condition, Figures 2.2-2.4 show that gibbsite solubility increases with both NaOH and NaNO₃ concentrations.

Error bars are included in Figures 2.2 through 2.4 for experiments with seeds recrystallized overnight. The symbol size is similar to error bars. This is also true with the experimental results in mixtures of NaOH + NaNO₂, i.e., the symbol size is also similar to error bars.

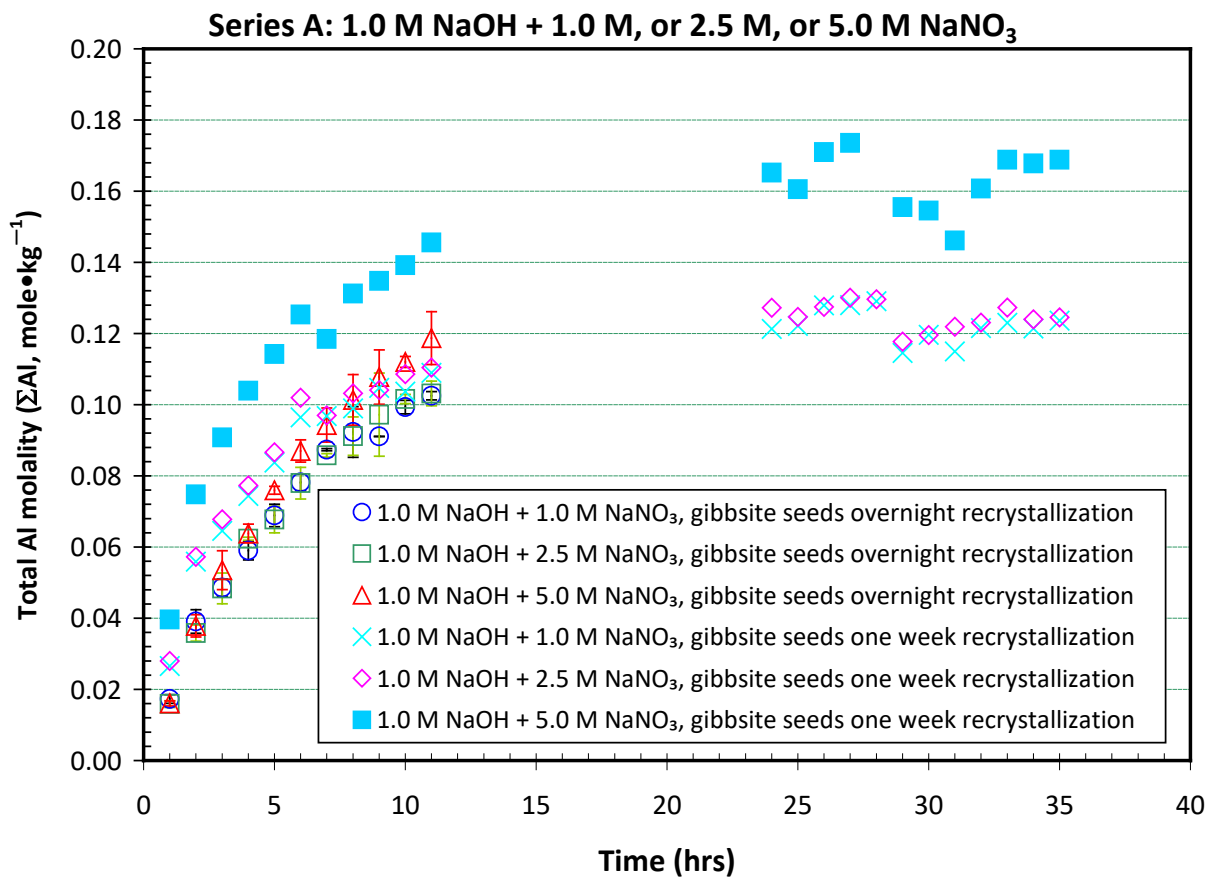


Figure 2.2. Total dissolved total aluminum concentrations as a function of experimental time for gibbsite in mixtures of 1.0 mol $\cdot\text{dm}^{-3}$ NaOH + 1.0 mol $\cdot\text{dm}^{-3}$ NaNO₃, 1.0 mol $\cdot\text{dm}^{-3}$ NaOH + 2.5 mol $\cdot\text{dm}^{-3}$ NaNO₃, and 1.0 mol $\cdot\text{dm}^{-3}$ NaOH + 5.0 mol $\cdot\text{dm}^{-3}$ NaNO₃ at 60 °C.

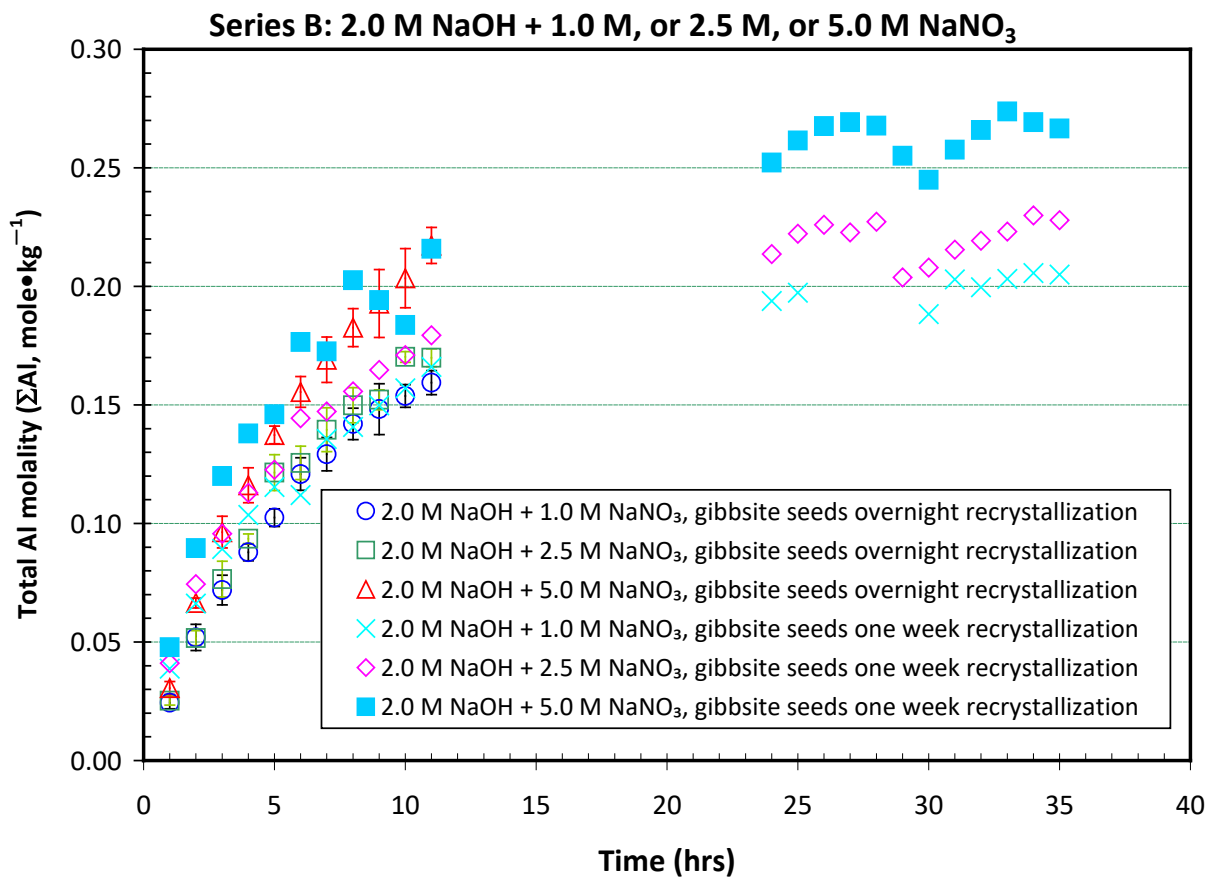


Figure 2.3. Total dissolved aluminum concentrations as a function of experimental time for gibbsite in mixtures of 2.0 mol·dm⁻³ NaOH + 1.0 mol·dm⁻³ NaNO₃, 2.0 mol·dm⁻³ NaOH + 2.5 mol·dm⁻³ NaNO₃, and 2.0 mol·dm⁻³ NaOH + 5.0 mol·dm⁻³ NaNO₃ at 60 °C.

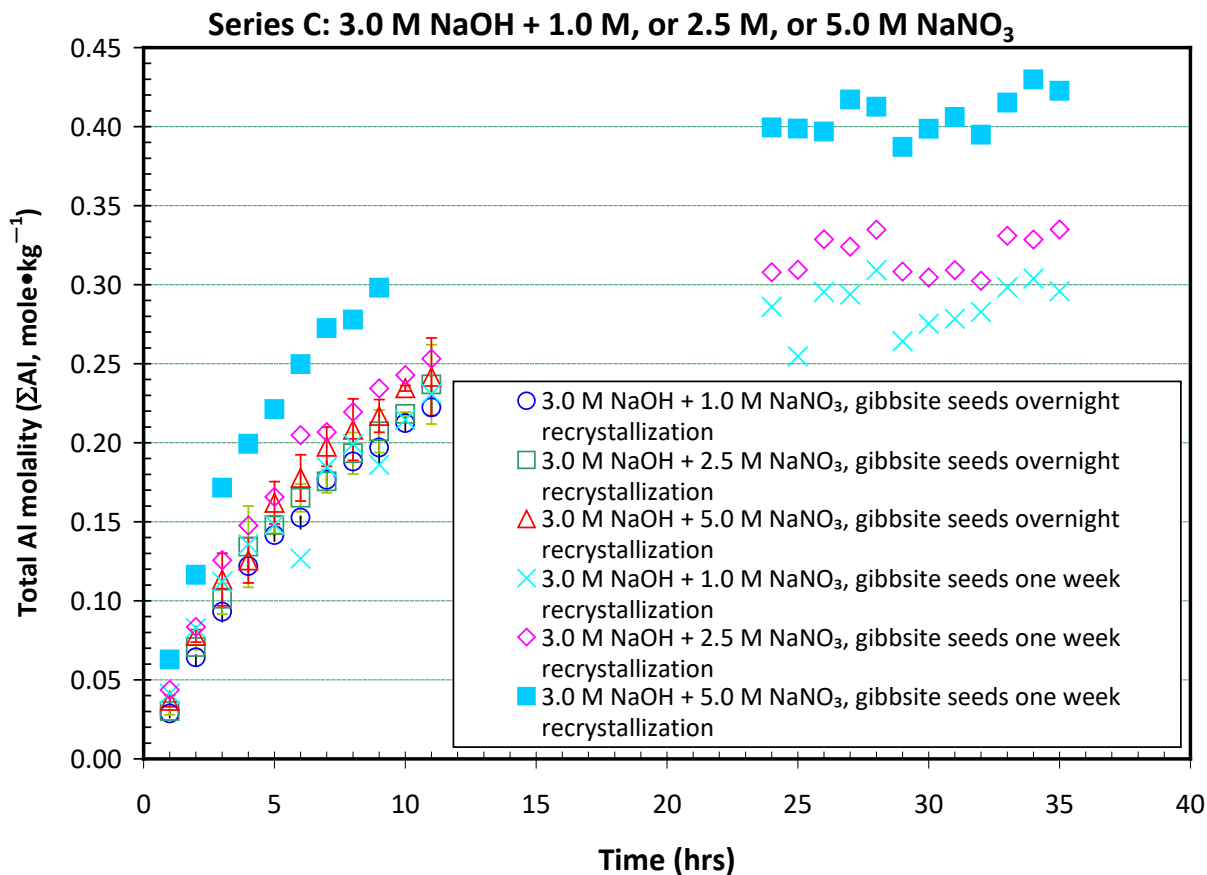


Figure 2.4. Total dissolved total aluminum concentrations as a function of experimental time for gibbsite in mixtures of 3.0 mol $\cdot\text{dm}^{-3}$ NaOH + 1.0 mol $\cdot\text{dm}^{-3}$ NaNO₃, 3.0 mol $\cdot\text{dm}^{-3}$ NaOH + 2.5 mol $\cdot\text{dm}^{-3}$ NaNO₃, and 3.0 mol $\cdot\text{dm}^{-3}$ NaOH + 5.0 mol $\cdot\text{dm}^{-3}$ NaNO₃ at 60 °C.

Interestingly, gibbsite exhibits a very different dissolution behavior in NaOH + NaNO₂ solutions. Figure 2.5 presents the total dissolved Al(III) concentrations as a function of experimental duration in mixtures of NaOH + NaNO₂ with a constant concentration of NaOH at 1.0 mol·dm⁻³ and varying NaNO₂ concentrations ranging from 1.0 to 5.0 mol·dm⁻³. The figure shows that at a constant concentration of NaOH, the amounts of gibbsite dissolved increase with NaNO₂ concentration. Unlike the NaOH + NaNO₃ case, the total dissolved Al concentration increased nearly linearly with time and did not reach a plateau over the experimental duration. Similar results were observed in the mixtures of NaOH and NaNO₂ with higher NaOH concentrations (Figures 2.6 and 2.7). Also note that at 3.0 M NaOH the trends of concentration data points curve up, indicating an acceleration of dissolution rate, which, as shown below, could be attributed to the roughening (e.g., pitting) of dissolution surface.

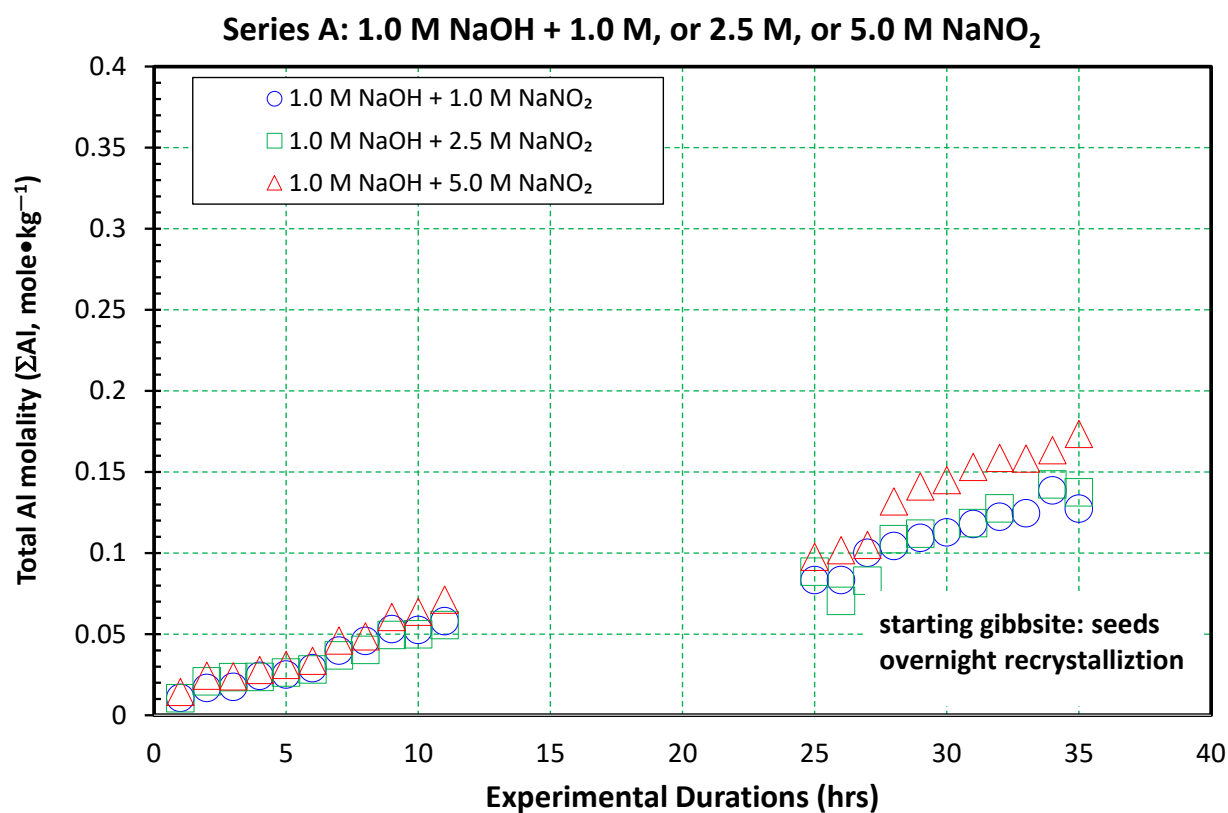


Figure 2.5. Total dissolved aluminum concentrations as a function of experimental time for the dissolution of gibbsite in mixtures of 1.0 mol·dm⁻³ NaOH + 1.0 mol·dm⁻³ NaNO₂, 1.0 mol·dm⁻³ NaOH + 2.5 mol·dm⁻³ NaNO₂, and 1.0 mol·dm⁻³ NaOH + 5.0 mol·dm⁻³ NaNO₂ at 60 °C.

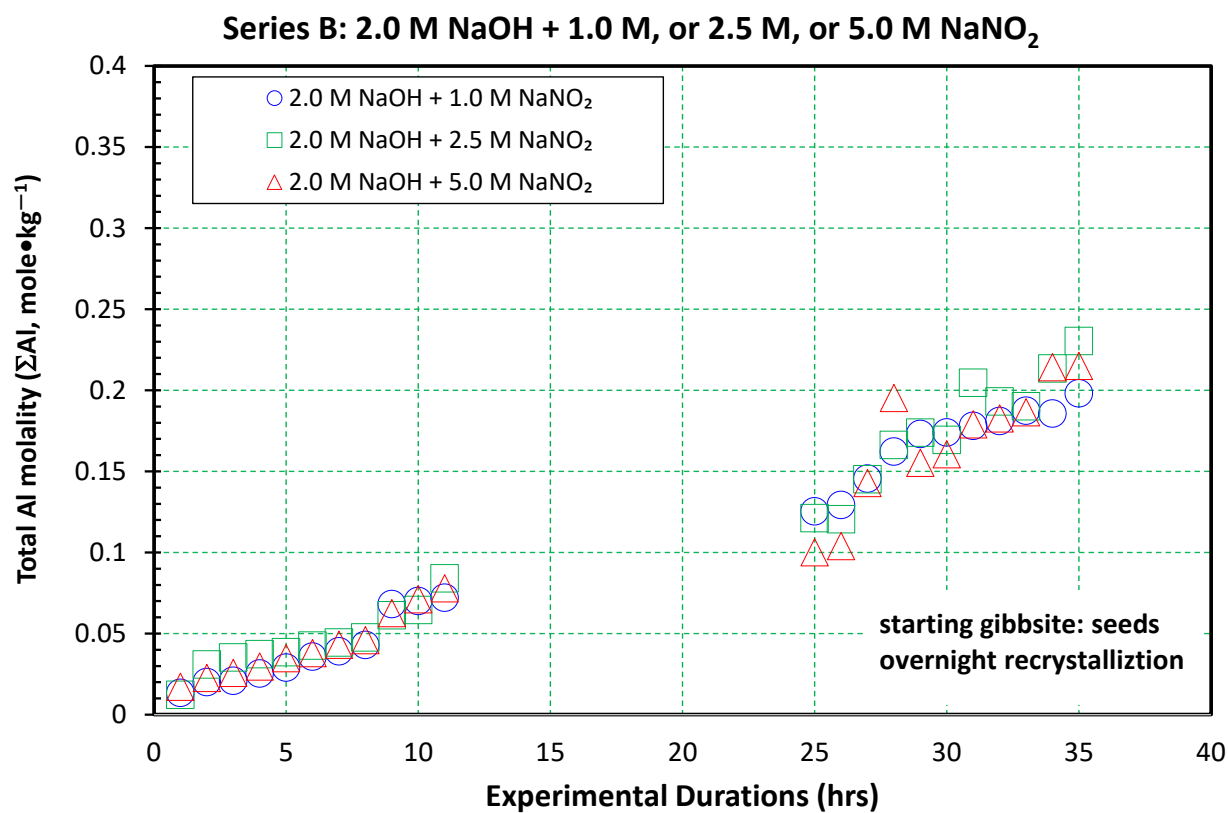


Figure 2.6. Dissolved total aluminum concentrations on a molal scale as a function of experimental time for the dissolution of gibbsite in mixtures of 2.0 mol·dm⁻³ NaOH + 1.0 mol·dm⁻³ NaNO₂, 2.0 mol·dm⁻³ NaOH + 2.5 mol·dm⁻³ NaNO₂, and 2.0 mol·dm⁻³ NaOH + 5.0 mol·dm⁻³ NaNO₂ at 60 °C.

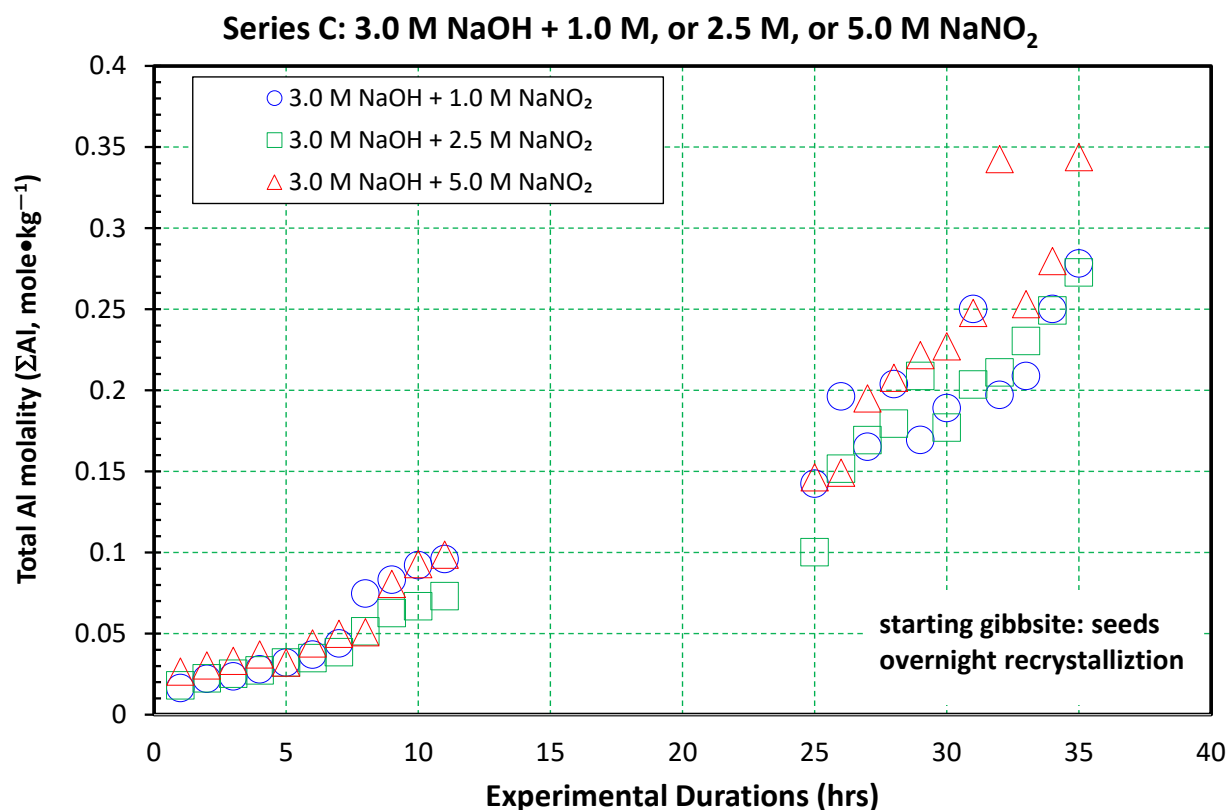


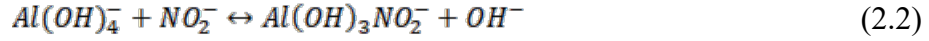
Figure 2.7. Dissolved total aluminum concentrations on a molal scale as a function of experimental time for the dissolution of gibbsite in mixtures of 3.0 mol·dm⁻³ NaOH + 1.0 mol·dm⁻³ NaNO₂, 3.0 mol·dm⁻³ NaOH + 2.5 mol·dm⁻³ NaNO₂, and 3.0 mol·dm⁻³ NaOH + 5.0 mol·dm⁻³ NaNO₂ at 60 °C.

2.4.2. Kinetic Modeling

There have been numerous kinetic modeling studies of gibbsite in NaOH solutions (e.g., Pereira et al., 2009; Bao and Nguyen, 2010; Bao et al., 2010a, 2010b; Greman et al., 2010; Xie et al., 2016; Shen et al., 2018; Guo et al., 2021, 2024; Riechers et al., 2023; Kandas et al., 2024; Zhu et al., 2024). However, to our best knowledge, there are no prior kinetic models regarding dissolution of gibbsite in NaOH + NaNO₃ and NaOH + NaNO₂ solutions. In the following, we describe our efforts in this aspect.

A kinetic model has been developed to extract the relevant apparent thermodynamic and kinetic parameters for gibbsite dissolution from the experimental data summarized above. The model system is illustrated in Figure 8. The system includes dissolving gibbsite solid Al(OH)₃(s) and dissolved species $Al(OH)_4^-$, $Al(OH)_3NO_2^-$, NO_3^- , NO_2^- , and OH^- (Figure 2.8). As shown below, NO_2^- has a significant effect on gibbsite dissolution, and it is assumed that NO_2^- can form

a surface species and thus may impact gibbsite dissolution kinetics. Gibbsite dissolution in a NaOH-NaNO₃/NaOH-NaNO₂ solution can be described by the following reactions:



Here we assume that NaNO₃ acts only as a background electrolyte and thus does not directly participate in aqueous speciation. In contrast, NO_2^- is a Lewis acid with one lone electron pair and known to form complexes with various cations (Hitchman, and Rowbottom, 1982). We therefore assume that NO_2^- tends to form the complex $Al(OH)_3NO_2^-$ or attach to a solid surface, thus altering gibbsite dissolution kinetics in the system of interest.

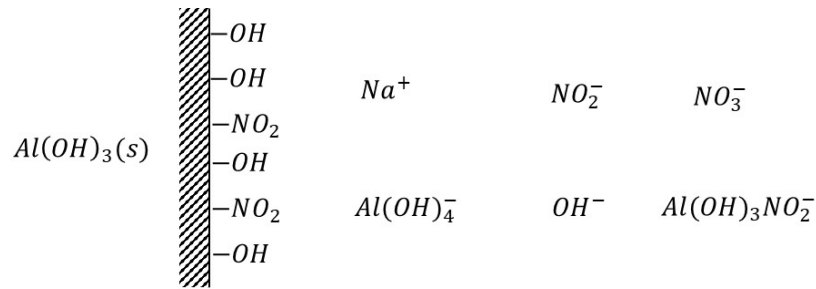


Figure 2.8. Model system of gibbsite dissolution in concentrated NaOH-NaNO₃-NaNO₂ solutions

With these assumptions, as shown in Appendix B, the evolution of the concentration of total dissolved Al (m_{Al}) in the system can be described by:

$$\frac{dm_{Al}}{dt} = k'(1 + \alpha t^2) \left(1 - \frac{m_{Al}}{\bar{m}_{Al}} \right) \quad (2.3)$$

with

$$k' = kS_0Q \quad (2.4)$$

where $\bar{m}_{Al}$ is the solubility of gibbsite; α is a pitting parameter; k is the rate constant for reaction (2.1); k' is the apparent rate constant; S_0 is the initial specific surface area of gibbsite; Q is the solid/water ratio; and t is the dissolution time. Equation (2.3) is used to extract kinetic parameters for gibbsite dissolution by fitting the equation to experimental data.

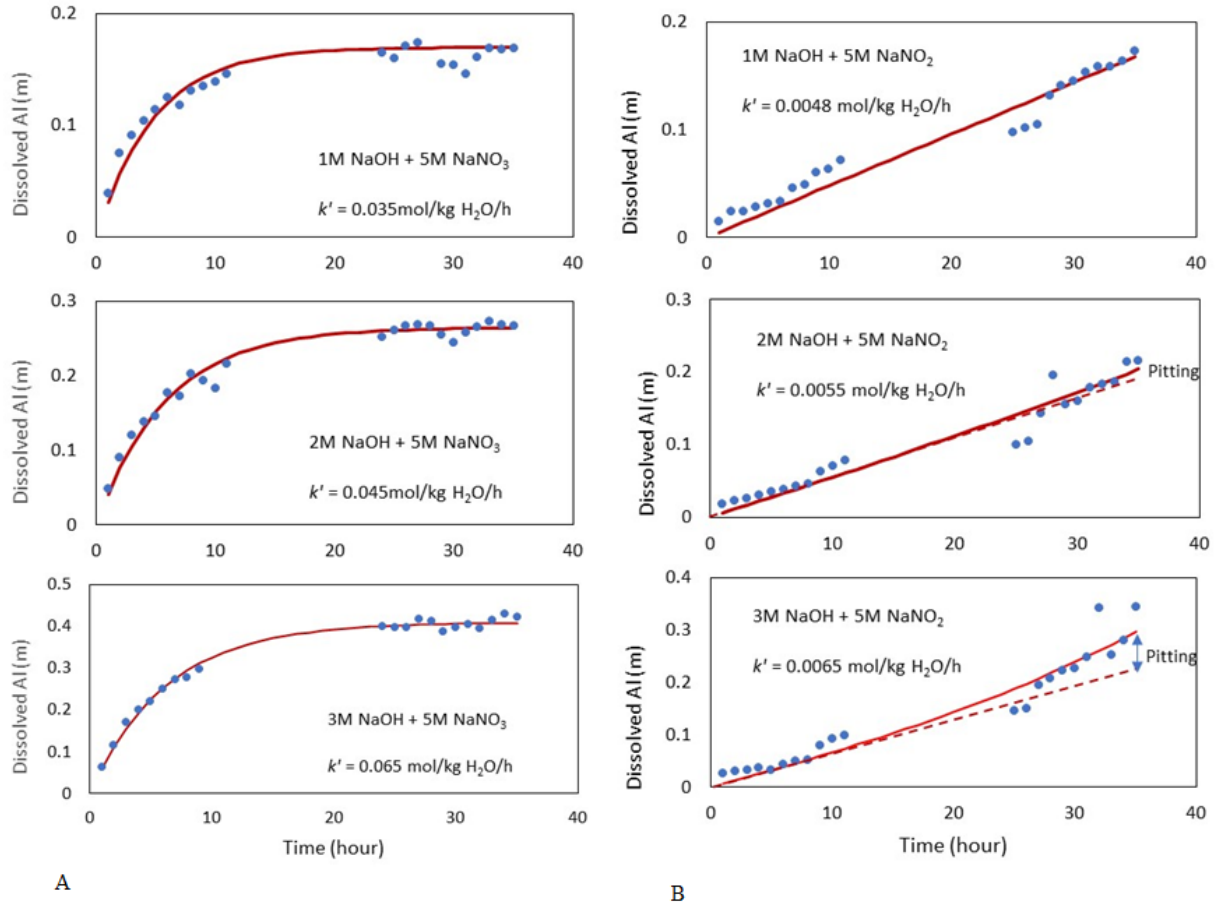


Figure 2.9. Model fit to experimental data for gibbsite dissolution in 5 M NaNO₃ or NaNO₂ media with various NaOH concentrations.

Dissolution in NaOH + NaNO₃ solutions: We first consider gibbsite dissolution in NaOH + NaNO₃ media. In this case, the total dissolved Al concentration approaches a plateau with time, indicating the system is near a chemical equilibrium, under which surface pitting generally diminishes, i.e., α approaches 0 (Beig and Lüttge, 2006). The equation (2.3) is then reduced to:

$$\frac{dm_{Al}}{dt} = k' \left(1 - \frac{m_{Al}}{\bar{m}_{Al}} \right) \quad (2.5)$$

By integration, we obtained

$$m_{Al} = \bar{m}_{Al} \left(1 - e^{-\frac{k'}{\bar{m}_{Al}} t} \right) \quad (2.6)$$

Equation (2.6) is then fit to experimental data. A subset of the model fitting results are shown in Figure 2.9A.

Table 2.2. Gibbsite apparent solubility in concentrated NaOH + NaNO₃ solutions

Solubility (mol/kg)	1.0 M NaOH	2.0 M NaOH	3.0 M NaOH
1.0 M NaNO ₃	0.121	0.203	0.290
2.5 M NaNO ₃	0.125	0.220	0.320
5.0 M NaNO ₃	0.170	0.265	0.410

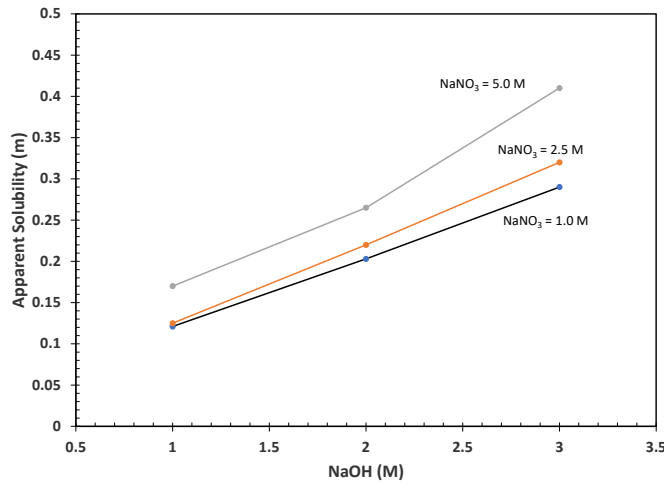


Figure 2.10. Dependence of gibbsite apparent solubility on NaOH concentration in NaNO₃ media

As shown in Figure 2.9A, the model fits the experimental data very well. The extracted solubility of gibbsite in NaOH + NaNO₃ media is summarized in Table 2.2 and ranges from 0.12 to 0.41 mol/kg H₂O. As expected in Equation (2.B8), the solubility increases almost linearly with NaOH concentration (Figure 2.10). Similarly, the extracted apparent rate constant is tabulated in Table 2.3 and ranges 0.029 to 0.065 mol/kg/h. With Equation (2.4) and the specific surface provided in Figure 2.1, the rate constant for gibbsite dissolution in concentrated NaOH + NaNO₃ solutions is estimated to be 1×10^{-7} to 3×10^{-7} mol/m²/s, approximately four orders of magnitude higher than that determined at pH 3 and 80 °C (Nagy and Lasaga, 1993). The rate

also increases approximately linearly with NaOH concentration (Figure 2.11). Based on this linear dependence, Equation (2.3) can be refined to:

$$\frac{dm_{Al}}{dt} \propto m_{OH} - (1 + \alpha t^2) \left(1 - \frac{m_{Al}}{\bar{m}_{Al}}\right) \quad (2.7)$$

Table 2.3. Apparent rate constant (k') for gibbsite dissolution in concentrated NaOH + NaNO₃ solutions

Apparent rate constant (k') (mol/kg/h)	1.0 M NaOH	2.0 M NaOH	3.0 M NaOH
1.0 M NaNO ₃	0.029	0.035	0.041
2.5 M NaNO ₃	0.031	0.039	0.050
5.0 M NaNO ₃	0.035	0.045	0.065

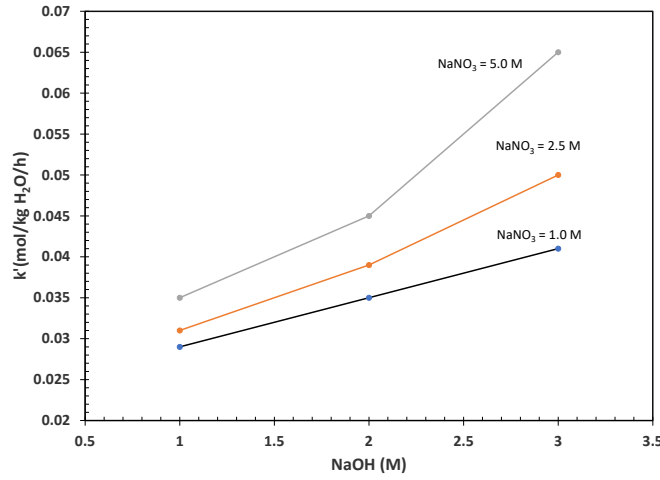


Figure 2.11. Dependence of apparent rate constant (k') on NaOH concentration in NaNO₃ media

Dissolution in NaOH + NaNO₂ solutions: In contrast, gibbsite dissolution in NaNO₂-bearing solutions did not reach a concentration plateau over the experimental duration (Figures 2.5 through 2.7), indicating that the system was still far from equilibrium, i.e., $\frac{m_{Al}}{\bar{m}_{Al}} \ll 1$. In this case, Equation (2.3) is reduced to:

$$\frac{dm_{Al}}{dt} = k'(1 + \alpha t^2) \quad (2.8)$$

By integration, and assuming the initial concentration of Al is zero at $t = 0$, we obtain:

$$m_{Al} = k' \left(t + \frac{\alpha}{3} t^3 \right) \quad (2.9)$$

As shown in Figure 2.9B, Equation (2.9) fits the data very well. Through the fitting, parameters k' and α can be extracted. The extracted apparent rate constants are tabulated in Table 2.4 and range from 0.0038 to 0.0065 mol/kg/h, approximately one order of magnitude lower than those in NaOH + NaNO₃ solutions (Table 2.3). This result indicates an inhibitory effect of nitrite on gibbsite dissolution. We postulate that NO_2^- attaches to the mineral surface replacing OH^- groups and forming a passivating layer for gibbsite dissolution. Therefore, NO_2^- plays two roles in gibbsite dissolution: It acts as a complexing agent in the solution to increase the apparent solubility of gibbsite and therefore force the system to be far from equilibrium. At the same time, it also forms a surface complex passivating the dissolving surface of gibbsite. It is interesting to note that, unlike the case in NaOH + NaNO₃ solutions, NaOH concentration here does not exhibit any consistent impact on gibbsite dissolution rate (Figure 2.12). This may also be attributed to the formation of a surface passivating layer by NO_2^- , which could reduce the sensitivity of dissolution reaction to OH^- groups.

Table 2.4. Apparent rate constant (k') for gibbsite dissolution in concentrated NaOH + NaNO₂ solutions

Apparent rate constant (k') (mol/kg/h)	1.0 M NaOH	2.0 M NaOH	3.0 M NaOH
1.0 M NaNO ₂	0.0038	0.0055	0.0055
2.5 M NaNO ₂	0.0038	0.0055	0.0050
5.0 M NaNO ₂	0.0048	0.0055	0.0065

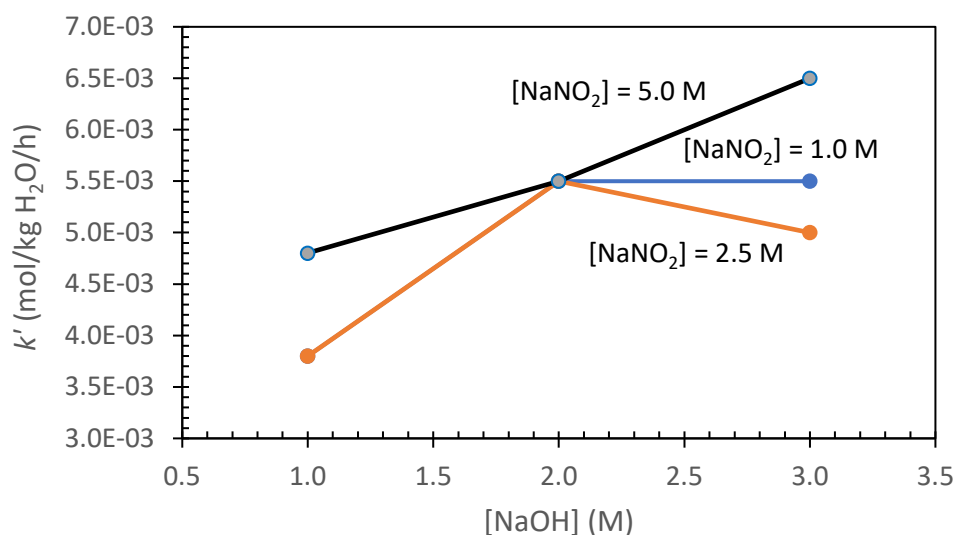


Figure 2.12. Plot showing apparent rate constant (k') vs. NaOH concentration in NaNO₂ media

Equation (2.9) provides a reasonable explanation for some salient features of gibbsite dissolution in concentrated NaOH + NaNO₂ solutions. For example, as shown in Figure 2.7, at

3.0 M NaOH, the trends of concentration data points curve up, indicating an acceleration of dissolution rate. Our model result shows that this behavior can be attributed to the pitting of dissolution surfaces, which would increase the effective surface area of the gibbsite. The model further shows the effect of pitting increases with NaOH concentration (Figure 2.13). This conclusion is directly supported by two other observations. Scanning electron microscopy (SEM) imaging shows that pitting did occur on the surfaces of reacted gibbsite samples (Figure 2.14). Furthermore, the BET measurements show that the specific areas of reacted samples are significantly higher than that of the initial material and increase with NaOH concentration (Figure 2.1).

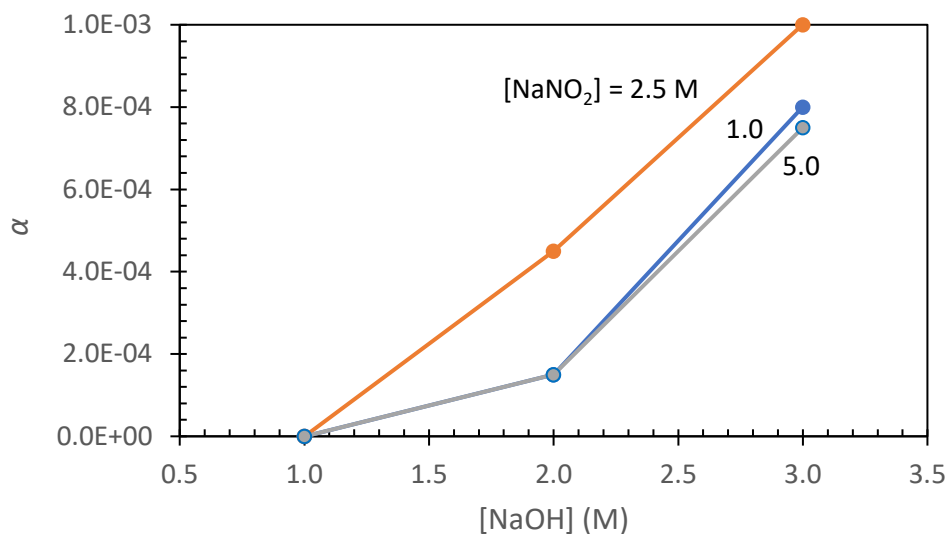


Figure 2.13. Plot showing pitting parameter α as a function of NaOH concentration in NaNO₂ media



Figure 2.14. Scanning electron microscopy (SEM) image showing dissolution pits on reacted gibbsite surfaces

2.5. Conclusions

We have experimentally investigated the dissolution kinetics of gibbsite in concentrated NaOH + NaNO₃ and NaOH + NaNO₂ solutions at 60 °C. The experimental results reveal distinct dissolution behaviors between the two solutions. A kinetic model has been formulated and fitted to the experimental data to extract key thermodynamic and kinetic parameters for gibbsite dissolution. The model results show that the dissolution rate constants of gibbsite in nitrite media are about one order of magnitude lower than that in corresponding nitrate media, indicating an inhibitory effect of nitrite on mineral dissolution. This inhibitory effect can possibly be attributed to the formation of a passivating layer of $>\text{Al-NO}_2^-$ on the mineral surface. In the solution, nitrite—a Lewis base—forms an aqueous complex of $\text{Al}(\text{OH})_3\text{NO}_2^-$ and thus increases the apparent solubility of gibbsite that forces the dissolution to be far-from-equilibrium, leading to etch pit development on the mineral surface. The results presented here bear important implications for the pretreatment of tank waste HLW sludge. Due to a large variability in nitrite concentration among different tanks, the dissolution rate of gibbsite is expected to vary greatly from tank to tank. This variation needs to be considered in designing an effective pretreatment strategy for an individual tank. If needed, the dependence of gibbsite dissolution kinetics on nitrite concentration may provide a means to control the mineral dissolution rate to optimize the process for washing/leaching of aluminum-rich waste sludges. The work presented here may also have implications to other industrial processes such as the Bayer process for Al and other metal extraction.

2.6. Appendix A. Density measurements of concentrated solutions

The densities of gibbsite-saturated NaOH + NaNO₃ and NaOH + NaNO₃ solutions were measured experimentally and are given in Tables 2.A1 and 2.A2. These measurements were used to calculate the molality of total dissolved aluminum from the concentration measurements by ICP-AES.

Table 2.A1. Density Measurements for Mixtures of NaOH + NaNO₃ Saturated with Gibbsite at 60 °C

Mixture	Density, g/cm ³ (g/mL)
1.00 mol·kg ⁻¹ NaOH + 1.00 mol·kg ⁻¹ NaNO ₃	1.0776±0.0003
1.00 mol·kg ⁻¹ NaOH + 2.50 mol·kg ⁻¹ NaNO ₃	1.1494±0.0003
1.00 mol·kg ⁻¹ NaOH + 5.00 mol·kg ⁻¹ NaNO ₃	1.2506±0.0006
2.00 mol·kg ⁻¹ NaOH + 1.00 mol·kg ⁻¹ NaNO ₃	1.1266±0.0003
2.00 mol·kg ⁻¹ NaOH + 2.50 mol·kg ⁻¹ NaNO ₃	1.1817±0.0003
2.00 mol·kg ⁻¹ NaOH + 5.00 mol·kg ⁻¹ NaNO ₃	1.2813±0.0003
3.00 mol·kg ⁻¹ NaOH + 1.00 mol·kg ⁻¹ NaNO ₃	1.1605±0.0003
3.00 mol·kg ⁻¹ NaOH + 2.50 mol·kg ⁻¹ NaNO ₃	1.2175±0.0003
3.00 mol·kg ⁻¹ NaOH + 5.00 mol·kg ⁻¹ NaNO ₃	1.2997±0.0006

Table 2.A2. Density Measurements for Mixtures of NaOH + NaNO₂ Saturated with Gibbsite at 60 °C

Mixture	Density, g/cm ³ (g/mL)
1.00 mol·kg ⁻¹ NaOH + 1.00 mol·kg ⁻¹ NaNO ₂	1.0787±0.0003
1.00 mol·kg ⁻¹ NaOH + 2.50 mol·kg ⁻¹ NaNO ₂	1.1255±0.0003
1.00 mol·kg ⁻¹ NaOH + 5.00 mol·kg ⁻¹ NaNO ₂	1.1997±0.0003
2.00 mol·kg ⁻¹ NaOH + 1.00 mol·kg ⁻¹ NaNO ₂	1.1217±0.0007

2.00 mol·kg ⁻¹ NaOH + 2.50 mol·kg ⁻¹ NaNO ₂	1.1584±0.0003
2.00 mol·kg ⁻¹ NaOH + 5.00 mol·kg ⁻¹ NaNO ₂	1.2345±0.0004
3.00 mol·kg ⁻¹ NaOH + 1.00 mol·kg ⁻¹ NaNO ₂	1.1502±0.0003
3.00 mol·kg ⁻¹ NaOH + 2.50 mol·kg ⁻¹ NaNO ₂	1.2038±0.0003
3.00 mol·kg ⁻¹ NaOH + 5.00 mol·kg ⁻¹ NaNO ₂	1.2729±0.0003

2.7 Appendix B. Derivation of kinetic model

List of symbols

K_1	Equilibrium constant of reaction (1)
K'_1	Apparent equilibrium constant of reaction (1)
K_2	Equilibrium constant of reaction (2)
K'_2	Apparent equilibrium constant of reaction (2)
k	Rate constant (mol/m ² /s)
k'	Apparent rate constant (mol/kg H ₂ O/s)
l	Slant height of conical dissolution pit (m) (Figure B1)
m_{Al}	Total dissolved Al concentration (mol/kg)
$\bar{m}_{Al}$	Solubility of gibbsite (mol/kg)
n_p	Pit density (number of pits/m ²)
Q	Solid/water ratio (g/kg H ₂ O)
R	Dissolution rate (mol/kg H ₂ O/s)
r	Radius of conical dissolution pit (m) (Figure B1)
S	Specific surface area (m ² /g)
S_0	Initial specific surface area (m ² /g)
t	Time (s)
v	Pit growth rate (m/s)
α	Pitting parameter characterizing the effect of surface pitting on dissolution rate (s ⁻²)
γ	Activity coefficient of the subscripted species
θ	Angle of conical dissolution pit (Figure B1)

The equilibrium constants of reactions (2.B1) and (2.B2) can be expressed:

$$K_1 = \frac{m_{Al(OH)_4^-}}{m_{OH^-}} \cdot \frac{\gamma_{Al(OH)_4^-}}{\gamma_{OH^-}} \quad (2.B1)$$

$$K'_1 = K_1 \frac{\gamma_{OH^-}}{\gamma_{Al(OH)_4^-}} = \frac{m_{Al(OH)_4^-}}{m_{OH^-}} \quad (2.B2)$$

$$K_2 = \frac{m_{Al(OH)_3NO_2^-} m_{OH^-}}{m_{Al(OH)_4^-} m_{NO_2^-}} \cdot \frac{\gamma_{Al(OH)_3NO_2^-} \gamma_{OH^-}}{\gamma_{Al(OH)_4^-} \gamma_{NO_2^-}} \quad (2.B3)$$

$$K'_2 = K_2 \cdot \frac{\gamma_{Al(OH)_3NO_2^-} \gamma_{OH^-}}{\gamma_{Al(OH)_4^-} \gamma_{NO_2^-}} = \frac{m_{Al(OH)_3NO_2^-} m_{OH^-}}{m_{Al(OH)_4^-} m_{NO_2^-}} \quad (2.B4)$$

Accordingly, the aqueous speciation of dissolved Al can be described by:

$$m_{Al} = m_{Al(OH)_4^-} + m_{Al(OH)_3NO_2^-} \quad (2.B5)$$

$$m_{Al(OH)_4^-} = \frac{m_{OH^-} m_{Al}}{m_{OH^-} + K'_2 m_{NO_2^-}} \quad (2.B6)$$

The dissolution rate of gibbsite is assumed to be:

$$R = kSQ \left(1 - \frac{m_{Al(OH)_4^-}}{K'_1 m_{OH^-}} \right) = kSQ \left[1 - \frac{m_{Al}}{K'_1 (m_{OH^-} + K'_2 m_{NO_2^-})} \right] \quad (2.B7)$$

The term in parentheses defines the degree of undersaturation of the solution with respect to gibbsite, a driving force for gibbsite dissolution. The solubility of gibbsite can then be defined as:

$$\bar{m}_{Al} = K'_1 (m_{OH^-} + K'_2 m_{NO_2^-}) \quad (2.B8)$$

The evolution of total dissolved Al concentration is then governed by:

$$\frac{dm_{Al}}{dt} = R = kSQ \left(1 - \frac{m_{Al}}{\bar{m}_{Al}} \right) \quad (2.B9)$$

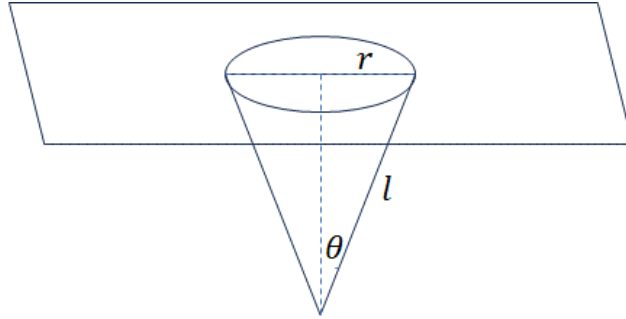


Figure 2.A1. Geometry of a conical dissolution pit

Now let us consider the effect of dissolution pits on gibbsite dissolution rate. We assume that a dissolution pit has a conical shape (Figure 2.A1). The evolution of the specific surface area can be described by:

$$S = S_0 \left[1 + n_p \pi \left(\frac{1}{\sin \theta} - 1 \right) r^2 \right] \quad (2.B10)$$

$$\frac{dr}{dt} = v \quad (2.B11)$$

We further assume the growth rate of a dissolution pit remains approximately constant. By integrating Equation (2.B11) and combining with Equation (2.B10), we obtain:

$$S = S_0 \left[1 + \pi n_p v^2 \left(\frac{1}{\sin \theta} - 1 \right) t^2 \right] = S_0 [1 + \alpha t^2] \quad (2.B12)$$

with

$$\alpha = \pi n_p v^2 \left(\frac{1}{\sin \theta} - 1 \right) \quad (2.B13)$$

Combining Equation (2.B13) with Equation (2.B9), we obtain Equation (2.B3).

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3. Equilibrium Aspects of Al Chemistry Part 1—A Thermodynamic Model for Interactions of Aluminate Ion ($\text{Al}(\text{OH})_4^-$) with Nitrate Based on Solubility Measurements at Elevated Temperatures

3.1. Summary

The interactions of aluminate ion ($\text{Al}(\text{OH})_4^-$) with nitrate are important to numerous fields including nuclear waste management and extraction of aluminum from bauxite ores. In the field of nuclear waste management, aluminum (Al) is the second most prevalent component in Hanford Tank Waste sludge phase, after sodium (Na). Aluminum accounts for one third of the total inventory of tank waste sludge and amounts to 4,140 metric tons. The three predominant Al-bearing solid phases are sodium aluminate [$\text{NaAl}(\text{OH})_4$], gibbsite [$\alpha\text{-Al}(\text{OH})_3$], and boehmite. Nitrate and nitrite have high concentrations in the supernatant liquids. Therefore, the knowledge of the interactions of aluminum with nitrate and nitrite is important to the realization of a scientifically sound and effective pretreatment approach for tank waste sludge.

To gain a deeper knowledge of such interactions, we are conducting systematic experiments coupled with the thermodynamic and molecular-level modeling. In this work, we report our solubility measurements at 60 °C. Based on our experimental data, we develop a thermodynamic model to describe the interactions of aluminate ion with nitrate. Then, the thermodynamic model is tested against the experimental data of gibbsite in mixtures of NaOH and NaNO_3 from the literature. Literature data are not utilized in the model development. The tests show that the values predicted by the model are in good agreement with the experimental data that are independent from the model development.

3.2. Background

The Hanford supernatants are characterized by high pH, high concentrations of sodium, nitrate, nitrite, and aluminate [$\text{Al}(\text{OH})_4^-$] (e.g., McCoskey et al., 2015). Nitrate and nitrite concentrations are high in the supernatant liquids and are important anions (e.g., Asmussen et al., 2024). The following are a few of examples: In the supernatant liquid from Tank 241-AN-105, the nitrate and nitrite concentrations are 4.08 and 4.58 $\text{mol}\cdot\text{kg}^{-1}$ (McCoskey et al., 2015), respectively. In Tank 241-AP-101, nitrite and nitrate are 0.911 $\text{mol}\cdot\text{dm}^{-3}$ and 2.13 $\text{mol}\cdot\text{dm}^{-3}$ on a molar scale (Fiskum et al., 2000), respectively, which are 1.01 $\text{mol}\cdot\text{kg}^{-1}$ and 2.37 $\text{mol}\cdot\text{kg}^{-1}$ for nitrite and nitrate respectively on a molal scale calculated by this study based on the density data from Fiskum et al. (2000). Similarly, the nitrate and nitrite concentrations in Tank 241-AP-105 analyzed in 1990's were 1.04 $\text{mol}\cdot\text{dm}^{-3}$ and 2.56 $\text{mol}\cdot\text{dm}^{-3}$ (DeLorenzo et al., 1994), respectively. Those concentrations correspond to 1.24 $\text{mol}\cdot\text{kg}^{-1}$ and 3.05 $\text{mol}\cdot\text{kg}^{-1}$ for the respective concentrations of nitrate and nitrite on a molal scale calculated by this study based on the density data from DeLorenzo et al. (1994). Recent analyses of the tank compositions have slightly higher nitrite but significantly lower nitrate concentrations (Ferriter, 2016; Fiskum et al., 2018), i.e., 1.42 $\text{mol}\cdot\text{kg}^{-1}$ for nitrite and 1.92 $\text{mol}\cdot\text{kg}^{-1}$ for nitrate calculated based on the raw chemical data and density data from Fiskum et al. (2018). In addition, sodium nitrate has been

considered as a component along with sodium hydroxide in leaching solutions to wash out Al-bearing solids including boehmite in pretreatment of sludge materials (Peterson et al., 2009).

Furthermore, gibbsite has been used to treat concentrated radioactive sodium nitrate solutions (Kononenko and Makarenkov, 2023). In scientific research, NaNO_3 solutions are used as supporting solutions for investigations of La (representing light rare earth elements) and Y (representing heavy rare earth elements) sorption onto gibbsite as a function of pH to understand the mechanisms of rare earth element enrichment in weathering environments (e.g., Zhou et al., 2023). Therefore, knowledge regarding interactions of nitrate and nitrite with aluminate ion is essential for accurate predictions of aluminum chemistry under the various conditions that will be beneficial to the scientific community in general as well as to the nuclear waste management in particular. In the latter aspect, such knowledge is highly relevant to Hanford tank waste, which can contribute to the development of a scientifically sound and effective pretreatment approach. Such an approach will be advantageous both for aluminum dissolution and removal from tank waste sludge, and for prevention of precipitation of aluminum phase(s) from supernatants.

Additionally, aluminum has numerous applications including its applications in aerospace industries and is essential to modern society. For this reason, it has been designated by US Department of Energy (US DOE) as a critical mineral/element. Aluminum is primarily extracted from bauxite ores in alkaline solutions. Therefore, a further understanding of Al(III) chemistry in alkaline solutions is beneficial to aluminum extraction.

In this work, we report on our experimental measurements of the solubility of gibbsite in mixtures of $\text{NaOH} + \text{NaNO}_3$ at elevated temperatures starting from 60 °C. Both gibbsite and boehmite are significant phases in Hanford Tank Waste (e.g., Peterson et al., 2009; Colburn and Peterson, 2021; Page et al., 2018; Westesen and Peterson, 2022; Westesen et al., 2023; Reynolds, 2024). In our solubility measurements, equilibrium is primarily approached from the direction of undersaturation. NaOH concentrations range from $1.0 \text{ mol} \cdot \text{kg}^{-1}$ to $3.0 \text{ mol} \cdot \text{kg}^{-1}$ in the mixtures. The concentrations of NaNO_3 are in a range from $1.0 \text{ mol} \cdot \text{kg}^{-1}$ to $5.0 \text{ mol} \cdot \text{kg}^{-1}$ in the mixtures. Together with our previously evaluated Pitzer parameters for $\text{Na}^+ - \text{Al}(\text{OH})_4^-$ (Xiong, 2014), our current experimental data with respect to gibbsite are utilized to describe the interactions of nitrate and nitrite with aluminate ion by using the Pitzer activity coefficient model. Our results for solubility constants of pseudo-boehmite according to the thermodynamic model developed in this study and based on our solubility measurements in mixtures of $\text{NaOH} + \text{NaNO}_3$ will be reported separately.

3.3. Experimental Section

3.3.1. Experimental Set-up and Experimental Procedure

In our solubility measurements, the starting material (i.e., the solubility-controlling phase) gibbsite ($\alpha\text{-Al}(\text{OH})_3$) is from Thermo Scientific (Figures 3.1 and 3.2). As shown by Figure 3.1, the particle size of gibbsite is usually larger than 1 μm . The XRD pattern of the starting material shown in Figure 3.2 indicates that it is pure gibbsite. Reagent grade NaOH , NaNO_3 and NaNO_2 used for preparation of supporting solutions are from Fisher Scientific, Sigma-Aldrich, and ACROS Organics, respectively. The compositions of the supporting solutions are tabulated in Table 3.1.

Aqueous solution samples are periodically sampled from each experiment. The sample size is usually 1 mL. After a solution sample is taken from an experiment, it is first filtered with a 0.22 μm syringe filter using a BD® 3 mL syringe from Becton, Dickinson and Company. The VMR® 0.22 μm nylon syringe filter with a diameter of 25 mm is from VMR®. After filtration, the mass of the sample is determined with a balance that is precise to four digits. Then, 0.5 mL of 1.0 mol·kg⁻¹ NaOH is pipetted into the sample and the sample is diluted to 10 mL with DI water. Right before analysis, aliquots of the original sample are further diluted by 10 or 100 times, depending upon the concentrations of the supporting solutions. Aluminum (Al) concentrations of solutions were analyzed with a Perkin Elmer dual-view inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Perkin Elmer DV 8300). Calibration blanks and standards were matched with experimental matrices. The instrument was warmed up for at least one and one-half hours to obtain a well-stabilized plasma before the calibration and analysis were performed. The instrument was calibrated with at least five standards (e.g., blank, 0.1 ppm Al; 1.0 ppm Al, 10 ppm Al, 100 ppm Al) with 1 ppm Sc as the internal standard. Immediately after the calibration, the samples were analyzed. In the analysis, the calibration standards were also analyzed as samples to check if there were significant shifts. At least one calibration standard and one blank were analyzed as samples after usually every eight samples were analyzed. If significant drift (e.g., higher than 5%) from the known concentrations of the standards was observed, the instrument was re-calibrated.

3.3.2. Experimental Results

The reaction products after the completion of experiments shown in Figure 3.3 are gibbsite, demonstrating that gibbsite is the solubility-controlling phase during the entire durations of experiments. The corresponding SEM images of the reaction products are illustrated in Figures 3.4A through 3.4I, showing the morphology of gibbsite with tabular crystals.

Experimental results are displayed in Figure 3.5. Figure 3.5 shows the solubility of gibbsite at 60 °C in mixtures of NaOH + NaNO₃ as a function of experimental time, suggesting that steady state in aluminum concentration is reached after about 80 days. NaOH concentrations range from 1.0 mol·kg⁻¹ to 3.0 mol·kg⁻¹ (Figure 3.5). The concentrations of NaNO₃ are at 1.0 mol·kg⁻¹, 2.5 mol·kg⁻¹, and 5.0 mol·kg⁻¹. The experimental results indicate that the effect of NaNO₃ on the solubility of gibbsite at the level of 1.0 mol·kg⁻¹ NaOH is indistinguishable, as Al concentrations from experiments with different NaNO₃ concentrations are close to each other (Figure 3.5). However, at the level of 3.0 mol·kg⁻¹ NaOH, the effect of NaNO₃ on the solubility of gibbsite is weak but distinguishable. Of note, in our kinetic investigations of gibbsite dissolution in similar matrices at the same temperature, which will be published elsewhere, we have systematically evaluated the experimental uncertainty regarding Al(III) concentrations. The experimental uncertainty is smaller than or similar to the symbol size in Figure 3.5.

3.4. Thermodynamic Model

3.4.1. Model Development

In the thermodynamic model development, the computer code EQ3/6 version 8.0a (Wolery et al., 2010; Xiong, 2011) was utilized as a modeling platform.

The dissolution of gibbsite in alkaline solutions can be expressed as,



Using our solubility data for gibbsite in mixture of NaOH + NaNO₃ at 60 °C, and based on the relevant thermodynamic data including Pitzer parameters from Pabalan and Pitzer (1987), the temperature-dependent equilibrium constants of gibbsite and Pitzer parameters from Wesolowski (1992), and Pitzer parameters from Archer (2000) (Table 2), the interaction of Al(OH)₄⁻ with NO₃⁻ was modeled. Among those Pitzer parameters from the literature, Pabalan and Pitzer (1987) evaluated Pitzer interaction parameters for Na⁺–OH⁻ from 0–350 °C at NaOH concentrations ranging from 0 to 10 mol·kg⁻¹. The temperature function for Na⁺–OH⁻ in Table 3.2 is valid to 250 °C, and is from Wolery and Jarek (2003), Wolery and Jove-Colon (2004), and Wolery and Sutton (2011). Wesolowski (1992) determined the interaction parameters for Na⁺–Al(OH)₄⁻ and assumed that those parameters are constant in the temperature range from 25 °C to 100°C. In the high-temperature Pitzer model of Xiong (2014), those parameters were adopted for the temperature range from 25 °C to 100 °C, and above 100 °C the interaction parameters for Na⁺–Al(OH)₄⁻ are temperature dependent. Archer (2000) evaluated the Pitzer parameters for Na⁺–NO₃⁻ up to 152 °C. The temperature function for Na⁺–NO₃⁻ interaction parameters in Table 3.2 was refitted to the EQ3/6 format (Wolery and Jarek 2003, Wolery and Jove-Colon, 2004, and Wolery and Sutton, 2011), based on Archer (2000).

In accordance with the above parameters from the literature, the interaction of Al(OH)₄⁻–NO₃⁻ was modeled. The value of the theta parameter, $\theta_{\text{Al(OH)}_4^-, \text{NO}_3^-}$, is 0.04638 (Table 3.2). This parameter is assumed to be constant between 25 °C and 100 °C.

3.4.2. Model Verification and Validation Tests

By verification tests, we mean that values predicted by the model are compared with the values used for the development of the model. By validation tests, we mean values predicted by the model are tested against the values that are independent from the development of the model, i.e., experimental values not used in the model development. Figure 3.6 shows solubilities of gibbsite in terms of Al(III) concentrations on a molal scale predicted by the model in comparison with the experimental data for the model development. Figure 3.6 demonstrates excellent agreement between the model-predicted values and the experimental data.

Validation tests are the key part for development of a valid thermodynamic model (e.g., Xiong and Wang, 2025). In the following, the model developed in this work is tested against the experimental data that were not used in the model development. Figure 7 compares the predicted values at 25 °C with the experimental data at 23 °C from Felmy et al. (1994). The experimental data from Felmy et al. (1994) covered a wide range of NaNO₃ concentrations from 0 mol·kg⁻¹ to 8 mol·kg⁻¹, and NaOH concentrations from 0.1 mol·kg⁻¹ to 3.54 mol·kg⁻¹. Of note, the upper NaOH concentration in Felmy et al. (1994) was labeled as 3.0 mol·dm⁻³ in the original report. That value must have been a typographical error* as the solubility of gibbsite is sensitive to an NaOH concentration and a 3.0 mol·dm⁻³ concentration of NaOH cannot produce those high Al(III) concentrations as they presented. This point can be quantitatively assessed for pure NaOH solutions in the following. According to Misra (1970), the solubility of gibbsite as a function of temperature and NaOH concentration, on the basis of the regression of experimental data, can be expressed as below,

$$\ln C_{Al(III)}(\text{mol} \cdot \text{dm}^{-3}) = 5.7128 - \frac{2486.7}{273 + T^{\circ}\text{C}} + \frac{33.713 \times (\text{NaOH})(\text{mol} \cdot \text{dm}^{-3})}{273 + T^{\circ}\text{C}} + \ln(\text{NaOH})(\text{mol} \cdot \text{dm}^{-3}) \quad (3.2)$$

Based on the above equation, the calculated Al(III) concentrations at 23 °C for 3.0 mol·dm⁻³ mol and 3.5 mol·dm⁻³ NaOH are 0.287 mol·dm⁻³ and 0.355 mol·dm⁻³, respectively, corresponding to 0.291 mol·kg⁻¹ and 0.360 mol·kg⁻¹ respectively on a molal scale. In Felmy et al. (1994), the Al(III) concentration for the experiment with 0 mol·dm⁻³ NaNO₃ at 23 °C labeled with “3.0” mol·dm⁻³ NaOH was 0.346 mol·kg⁻¹. This value is close to the Al(III) concentration for a 3.5 mol·dm⁻³ NaOH solution, but much higher than, and far away from, that for a 3.0 mol·dm⁻³ NaOH solution, as calculated above. Additionally, the Al(III) concentration for the experiment with 0 mol·dm⁻³ NaNO₃ in 1.0 mol·dm⁻³ NaOH at 23 °C was 0.0719 mol·kg⁻¹ in Felmy et al. (1994), close to a value of 0.0763 mol·dm⁻³ calculated from Eq. (3.2) for a solution with 1.0 mol·dm⁻³ NaOH at 23 °C. Therefore, the above quantitative comparisons with an independent source suggest that it is likely that the NaOH concentration for the data is 3.5 mol·dm⁻³ instead of 3.0 mol·dm⁻³ in Felmy et al. (1994). In our validation test, that concentration on a molar scale is converted the one on a molal scale, which is 3.54 mol·kg⁻¹, based on the density of NaOH solutions from Söhnel and Novotný (1985). In Figure 3.7, the solubility of gibbsite is presented as a function of NaNO₃ concentrations at three constant concentrations of 0.10 mol·kg⁻¹, 1.0 mol·kg⁻¹, and 3.54 mol·kg⁻¹ NaOH, respectively. Figure 3.7 shows that the model-predicted values are in good agreement with the experimental values.

Figure 3.8 displays the comparisons of the model-predicted gibbsite solubilities at 20 °C with the experimental data at 20 °C from Russell et al. (2009). The concentrations of NaNO₃ range from 0 mol·kg⁻¹ to 4.63 mol·kg⁻¹. The original concentrations of NaNO₃ and NaOH are

* We have tried to confirm our assessment directly with the authors of that report. However, the first author (Andrew Felmy) has passed away. The co-authors are no longer at Pacific Northwest National Laboratory (PNNL), and we have either been unable to contact them or they were not able to provide the answer.

on a molar scale, and they are converted to those on a molal scale based on the density data in Russell et al. (2009). Figure 3.8 indicates that the model performs well in the validation test.

The test against the experimental data at 22 °C from Herting (2014) is shown in Figure 3.9. The concentrations of NaNO₃ and NaOH in his experiments are up to 3.75 mol·kg⁻¹ and 4.0 mol·kg⁻¹, respectively. As shown by Figure 3.9, the model performs reasonably well.

Figure 3.10 illustrates comparisons of the model-predicted solubilities of gibbsite at 30 °C with the experimental data at 30 °C from Bénézeth et al. (2016), and at 27 °C from Delegard et al. (2018). In the experiments of Bénézeth et al. (2016), the total ionic strengths ranged from 0.1 mol·kg⁻¹ to 5.2 mol·kg⁻¹ in mixtures of NaOH + NaNO₃. In Delegard et al. (2018), the total ionic strengths are 1.0 mol·kg⁻¹ and 5.9 mol·kg⁻¹. Figure 3.10 suggests that the model performs quite well against the experimental data that were not used in the model parameterization.

Figure 3.11 depicts the validation test against the experimental results at 63 °C from Bénézeth et al. (2016), and at 60 °C from Russell et al. (1955). The model-predicted values are at 60 °C. The experiments in Bénézeth et al. (2016) were performed with NaNO₃ concentrations ranging from 0 mol·kg⁻¹ to 4.9 mol·kg⁻¹, and the experiments of Russell et al. (1955) were carried out without the presence of NaNO₃. Figure 3.11 shows that the model-predicted values are in good agreement with the experimental data.

The validation test based on the experimental data at 89.8 °C from Bénézeth et al. (2016), and at 90 °C from Russell et al. (1955) is shown in Figure 3.12. The values predicted by the model are at a temperature of 90 °C. The concentrations of NaNO₃ present in the experiments of Bénézeth et al. (2016) range from 0 mol·kg⁻¹ to 4.9 mol·kg⁻¹, and the experiments of Russell et al. (1955) were without NaNO₃. Figure 3.12 demonstrates that the solubility of gibbsite in NaOH + NaNO₃ solutions predicted by the model is in excellent agreement with the experimental data.

3.5. Conclusions

In this study, solubilities of gibbsite in NaOH + NaNO₃ solutions at 60 °C have been investigated. The NaOH + NaNO₃ solutions have nine matrices with NaOH concentrations ranging from 1.0 mol·kg⁻¹ to 3.0 mol·kg⁻¹ and NaNO₃ concentrations ranging from 1.0 mol·kg⁻¹ to 5.0 mol·kg⁻¹. Among them, nitrate concentrations range over the majority of those observed in the tank waste. Based on our experimental data and the thermodynamic parameters from the literature, we have developed a thermodynamic model to describe the interactions of Al(OH)₄⁻ with NO₃⁻. The model is valid from ambient temperature to 100 °C, as demonstrated by validation tests against the experimental data that are independent from the model development.

3.6. References

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3.7. Supporting Data

Table 3.1. Experimental matrices for investigations of interactions of $\text{Al}(\text{OH})_4^-$ with nitrate

Nitrate Matrices
$1.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 1.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$
$1.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 2.5 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$
$1.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 5.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$
$2.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 1.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$
$2.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 2.5 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$
$2.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 5.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$
$3.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 1.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$
$3.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 2.5 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$
$3.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 5.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$

Table 3.2. Pitzer binary and mixing interaction parameters used in this work

Pitzer binary interaction parameter				
Interactions	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	Reference and Remarks
$\text{Na}^+ - \text{Al}(\text{OH})_4^-$	0.05100	0.2500	-9.000E-04	Wesolowski (1992), assuming constant between 25 °C and 100 °C. Adopted in Xiong (2013, 2014)
$\text{Na}^+ - \text{OH}^-$	Temperature dependence equations in Footnote A			Pabalan and Pitzer (1987). Coefficients were fitted in DATA0.YPF
$\text{Na}^+ - \text{NO}_3^-$	Temperature dependence equations in Footnote B			Archer (2000). Coefficients were fitted in DATA0.YPF
Pitzer mixing parameter				
Interaction	θ_{ij}			
$\text{NO}_3^- - \text{Al}(\text{OH})_4^-$	0.046375			This Study, constant between 25 °C and 100 °C.

A:

$$\beta^{(0)} = 0.0883443913 - 1197.84571 \times \left(\frac{1}{T} - \frac{1}{298.15} \right) - 6.1098033 \times \ln \frac{T}{298.15} + 0.00743325156 \times (T - 298.15)$$

$$\beta^{(1)} = 0.244421177 - 1627.02502 \times \left(\frac{1}{T} - \frac{1}{298.15} \right) + 9.48250496 \times \ln \frac{T}{298.15} - 0.0115788697 \times (T - 298.15)$$

$$C^\phi = 0.00399943679 - 88.2475511 \times \left(\frac{1}{T} - \frac{1}{298.15} \right) + 0.46876285 \times \ln \frac{T}{298.15} - 0.00047566612 \times (T - 298.15)$$

B:

$$\beta^{(0)} = 0.00357079096 - 703.084301 \times \left(\frac{1}{T} - \frac{1}{298.15} \right) - 3.34763961 \times \ln \frac{T}{298.15} + 0.00398160930 \times (T - 298.15)$$

$$\beta^{(1)} = 0.231962722 - 2726.23493 \times \left(\frac{1}{T} - \frac{1}{298.15} \right) - 13.0356312 \times \ln \frac{T}{298.15} + 0.0206884555 \times (T - 298.15)$$

$$C^\phi = -0.0000415037562 + 64.7822983 \times \left(\frac{1}{T} - \frac{1}{298.15} \right) + 0.318330659 \times \ln \frac{T}{298.15} - 0.0000384315789 \times (T - 298.15)$$

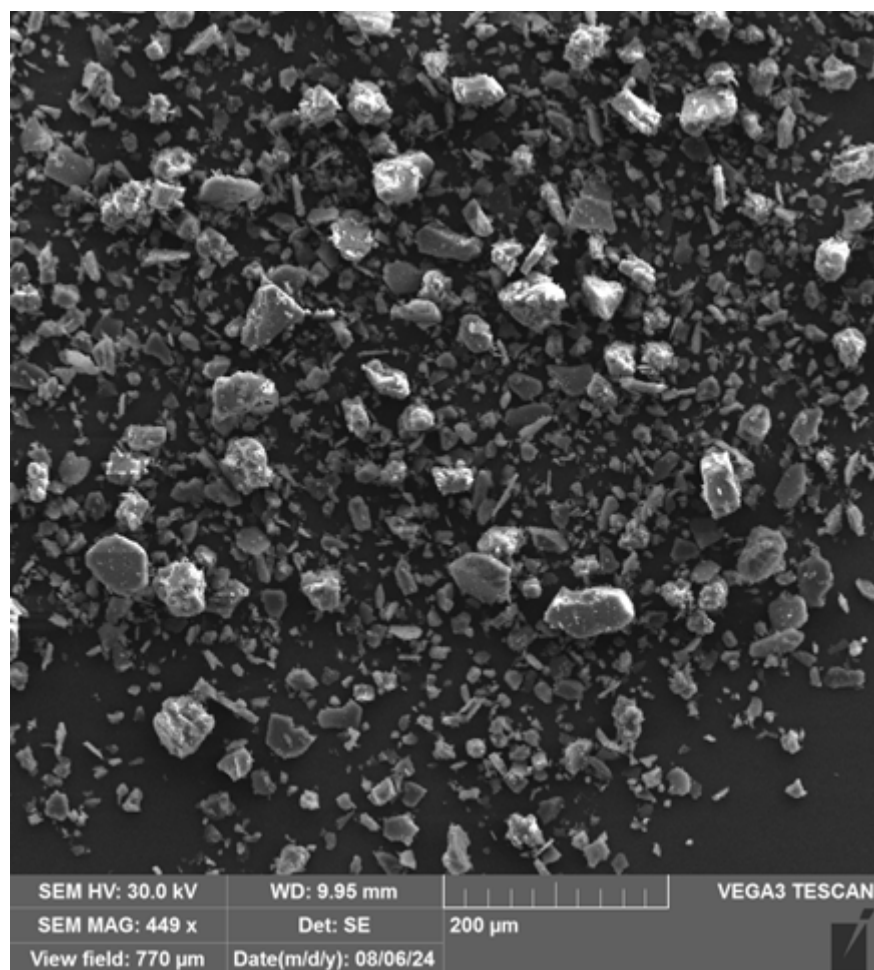


Figure 3.1. SEM images of the starting material, gibbsite.

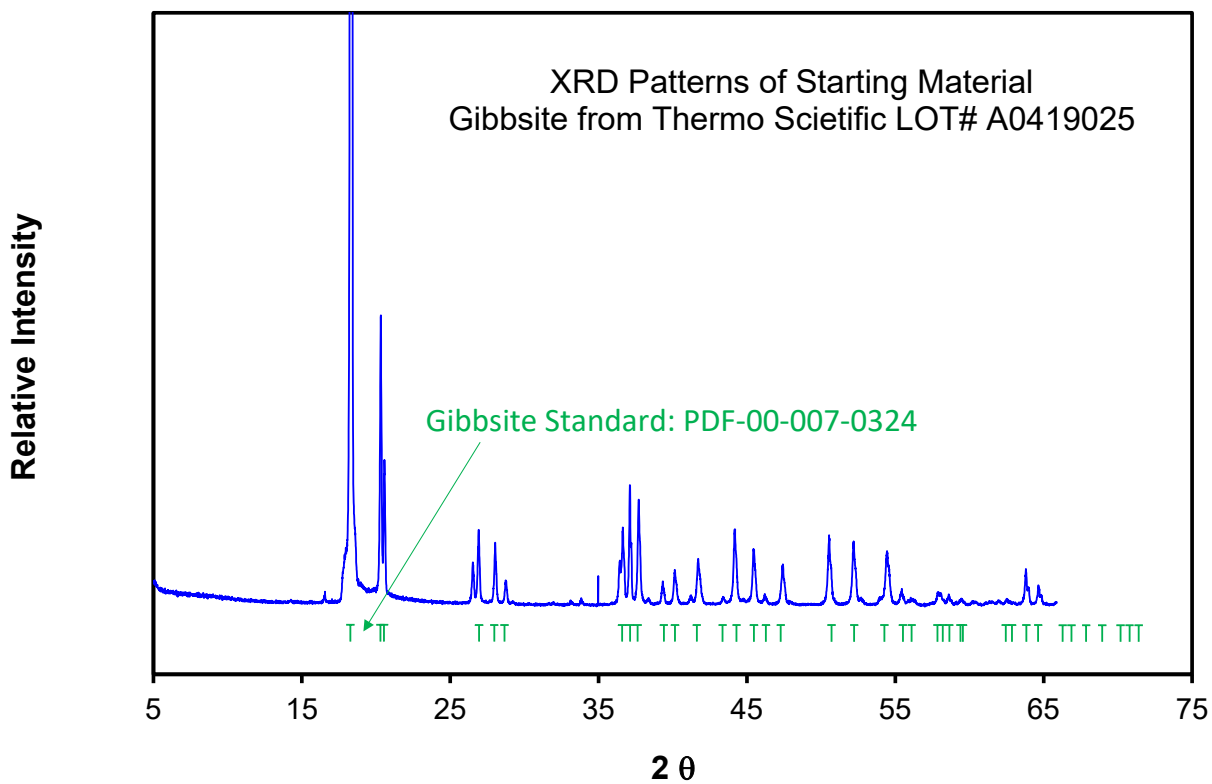


Figure 3.2. XRD patterns of the starting material, gibbsite.

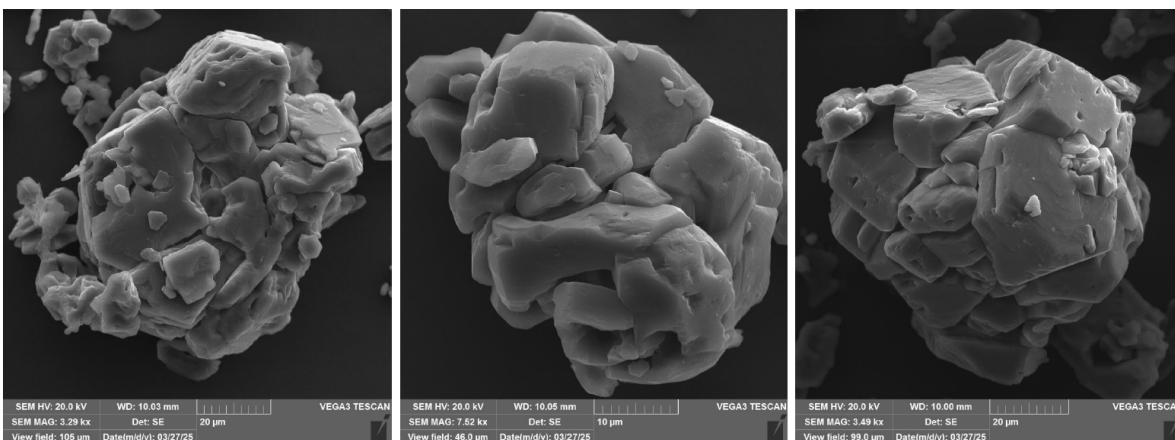


Figure 3.4A. SEM images for the reaction products of the experiment GIB60-A1, $1.0 \text{ mol} \cdot \text{kg}^{-1}$ NaOH + $1.0 \text{ mol} \cdot \text{kg}^{-1}$ NaNO₃

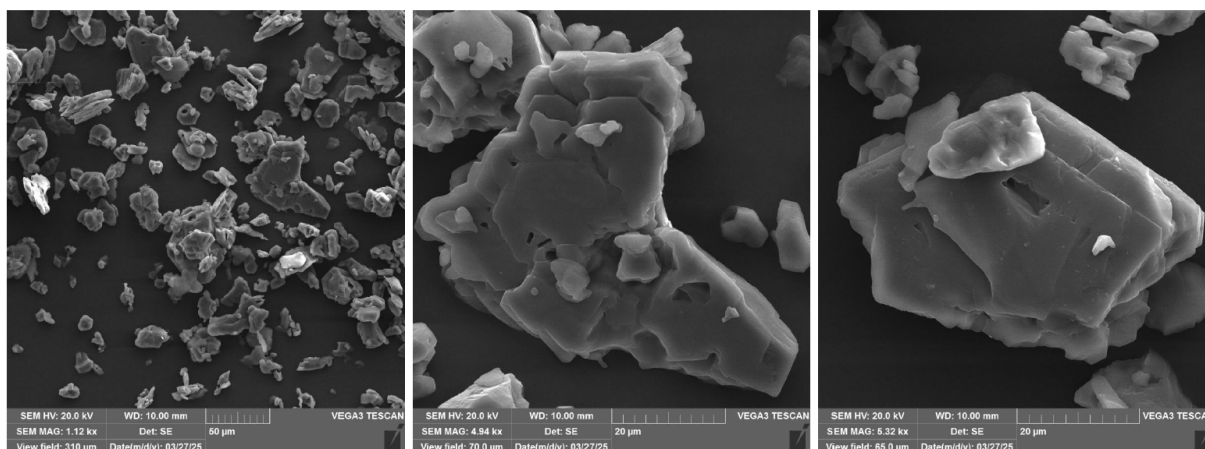


Figure 3.4B. SEM images for the reaction products of the experiment GIB60-A2, $1.0 \text{ mol} \cdot \text{kg}^{-1}$ NaOH + $2.5 \text{ mol} \cdot \text{kg}^{-1}$ NaNO₃

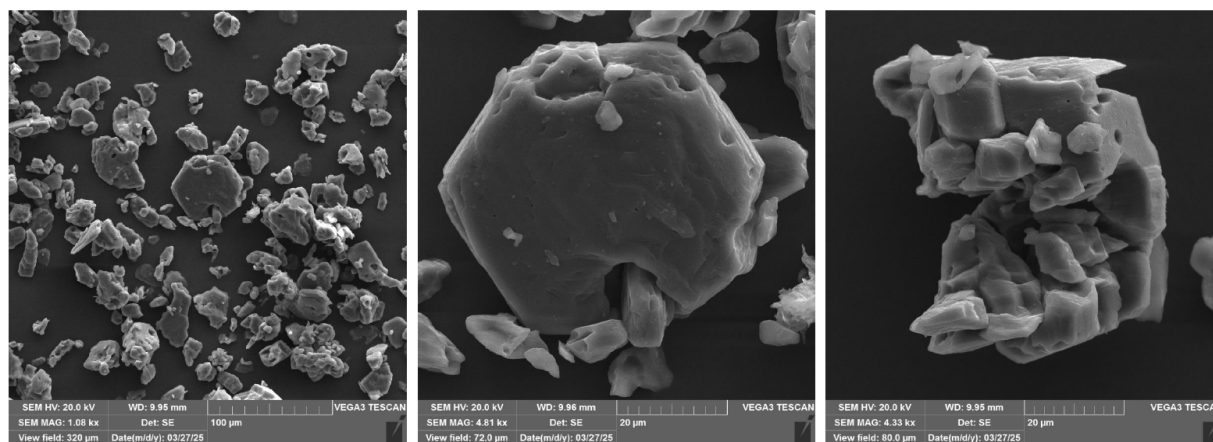


Figure 3.4C. SEM images for the reaction products of the experiment GIB60-A3, $1.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 5.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$

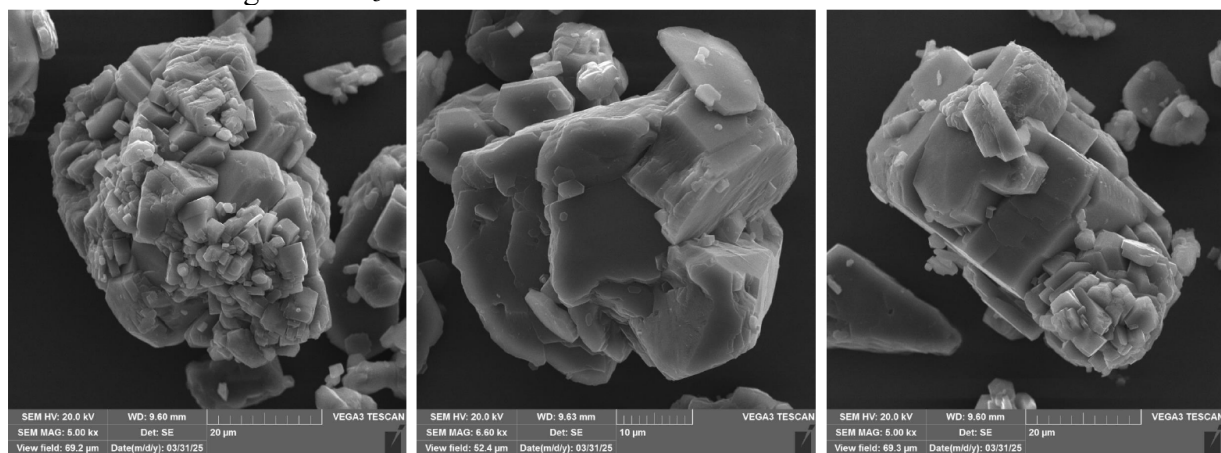


Figure 3.4D. SEM images for the reaction products of the experiment GIB60-B1, $2.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 1.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$

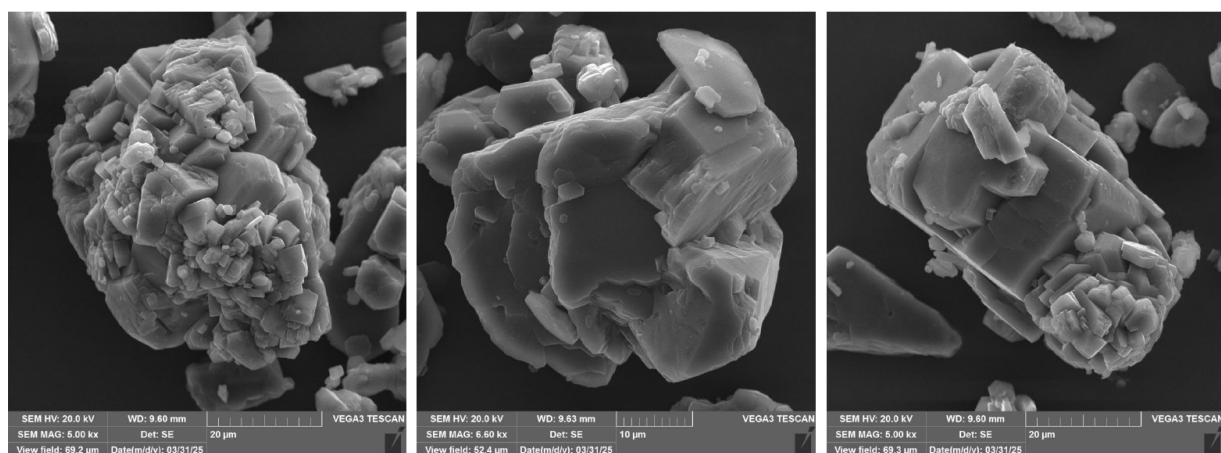


Figure 3.4E. SEM images for the reaction products of the experiment GIB60-B2, $2.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 2.5 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$

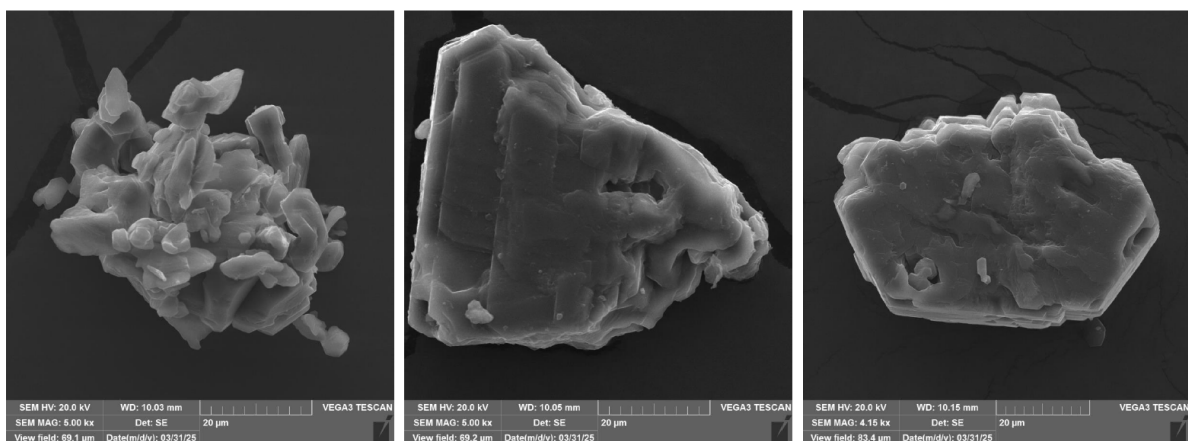


Figure 3.4F. SEM images for the reaction products of the experiment GIB60-B3, $2.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 5.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$

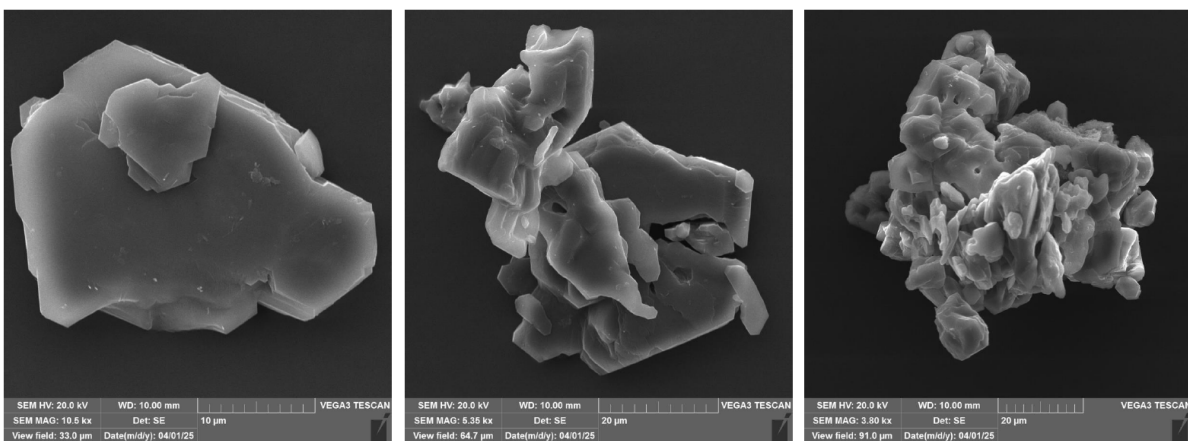


Figure 4G. SEM images for the reaction products of the experiment GIB60-C1, $3.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 1.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$

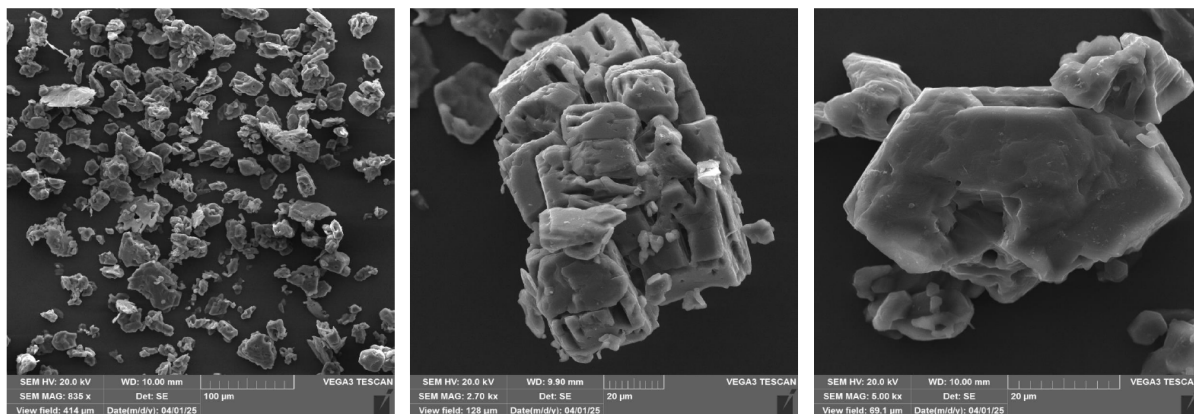


Figure 3.4H. SEM images for the reaction products of the experiment GIB60-C2, $3.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 2.5 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$

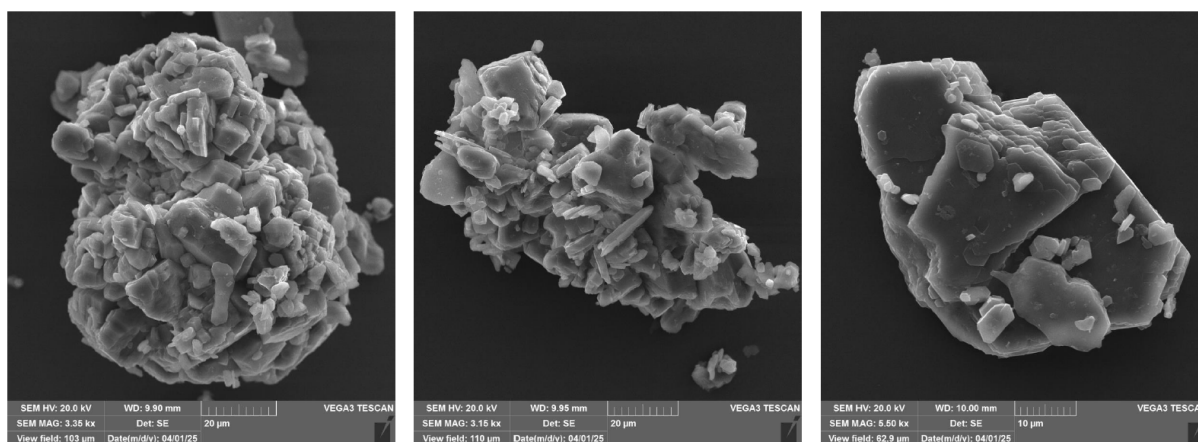


Figure 3.4I. SEM images for the reaction products of the experiment GIB60-C3, $3.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaOH} + 5.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$

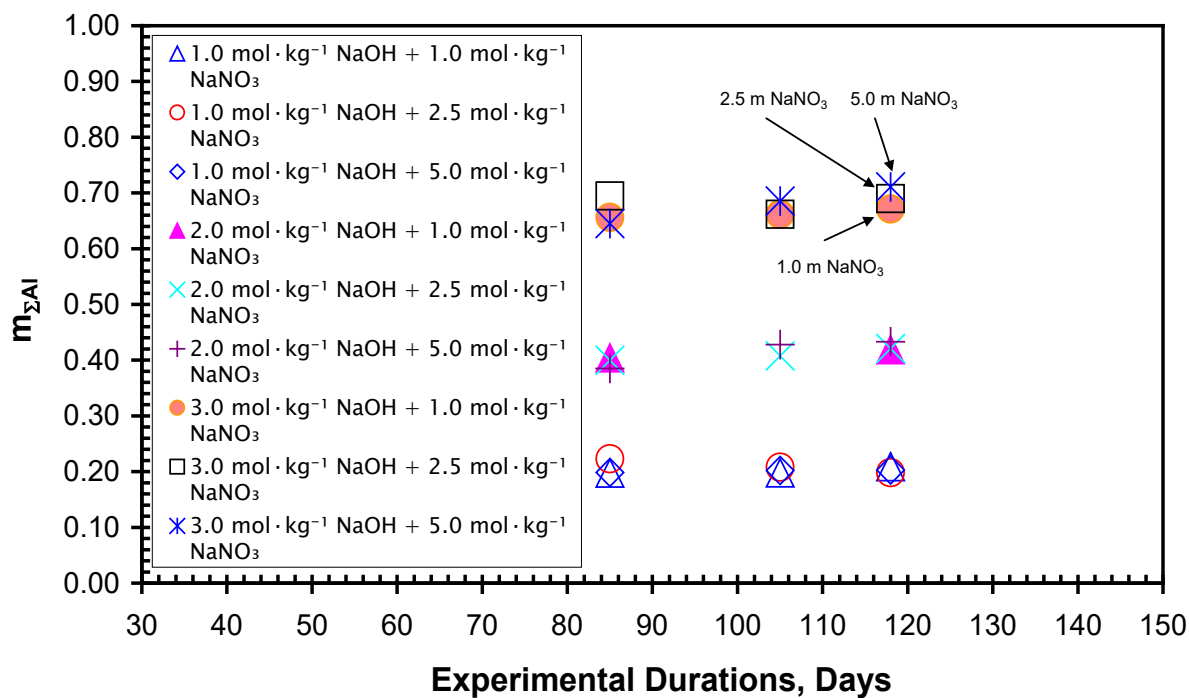


Figure 3.5. Experimental concentrations of solutions in contact with gibbsite in total molality of Al(III) in mixtures of NaOH + NaNO $_3$ as a function of experimental time at 60 °C in this work.

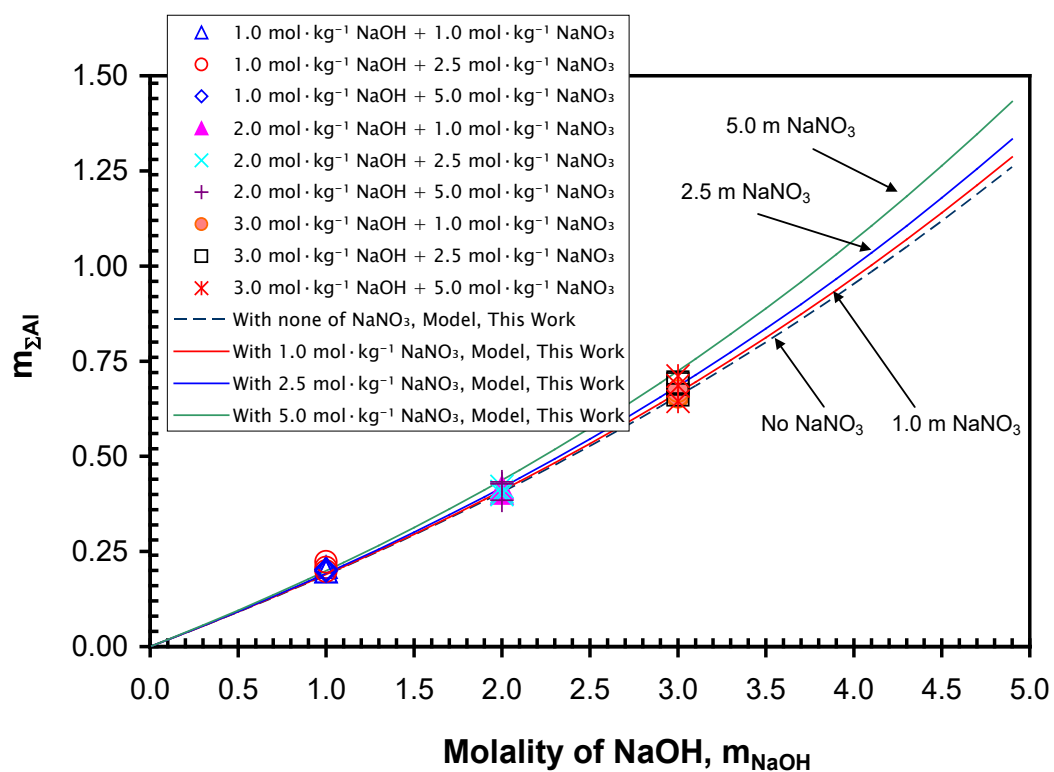


Figure 3.6. Solubilities of gibbsite in total molality of Al(III) in mixtures of NaOH + NaNO_3 as a function of NaOH molality at 60 °C predicted by the model developed in this work, in comparison with the experimental values at 60 °C produced by this study.

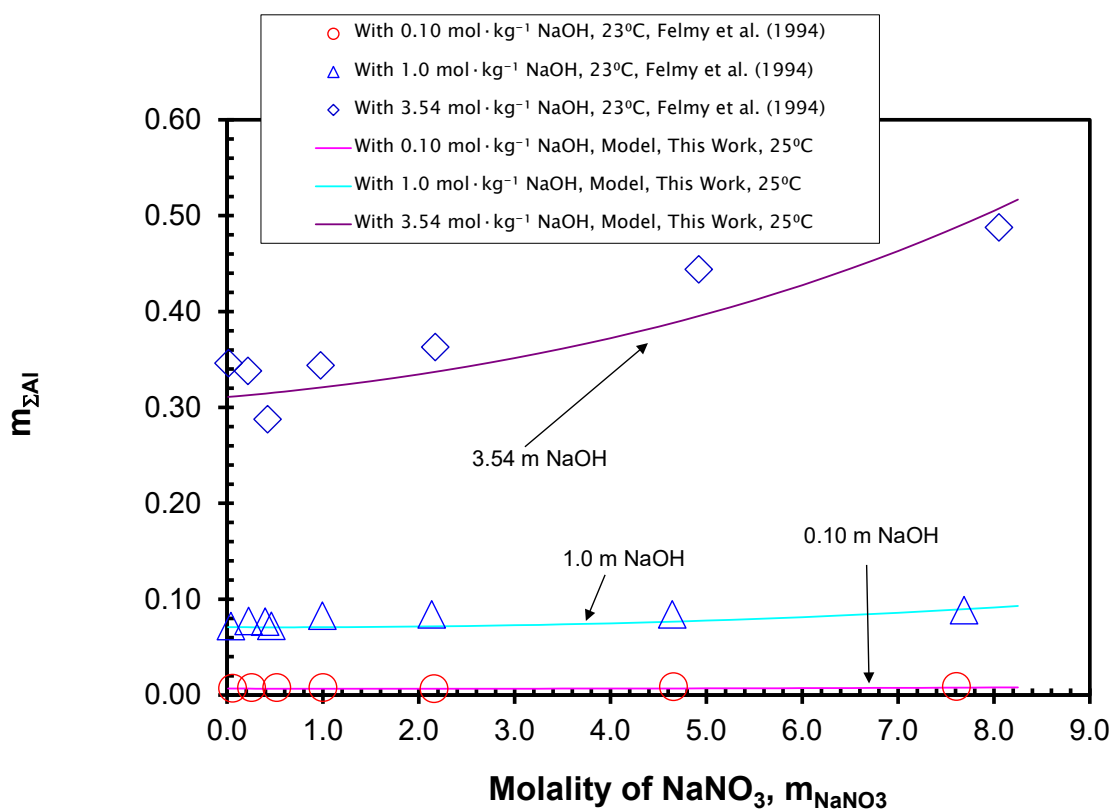


Figure 3.7. Solubilities of gibbsite in total molality of Al(III) in mixtures of NaOH + NaNO_3 as a function of NaNO_3 molality at 25 °C predicted by the model developed in this work, in comparison with the experimental values at 23 °C from Felmy et al. (1994).

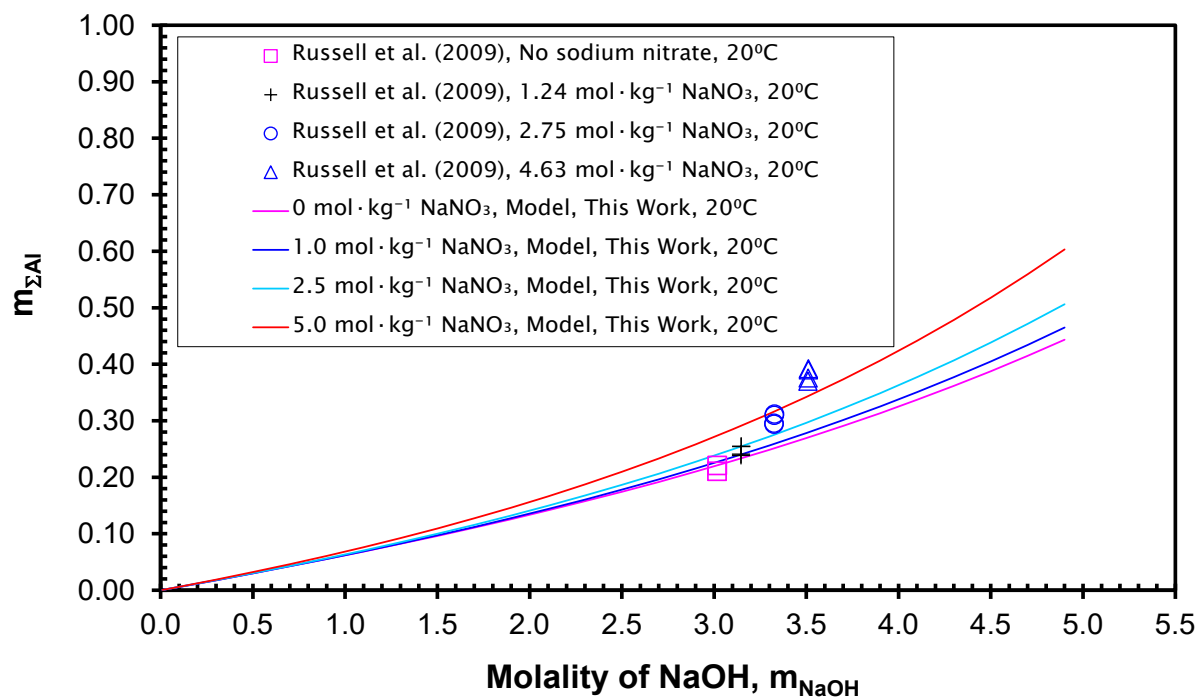


Figure 3.8. Solubilities of gibbsite in total molality of Al(III) in mixtures of NaOH + NaNO₃ as a function of NaOH molality at 20 °C predicted by the model developed in this work, in comparison with the experimental values at 20 °C from Russell et al. (2009).

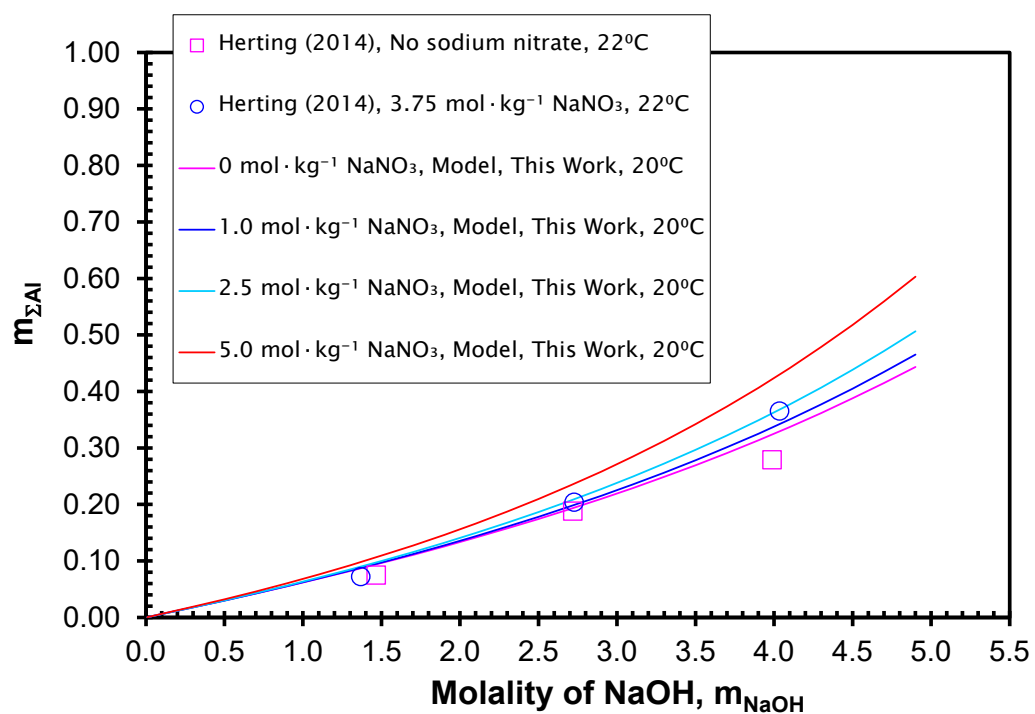


Figure 3.9. Solubilities of gibbsite in total molality of Al(III) in mixtures of NaOH + NaNO₃ as a function of NaOH molality at 20 °C predicted by the model developed in this work, in comparison with the experimental values at 22 °C from Herting (2014).

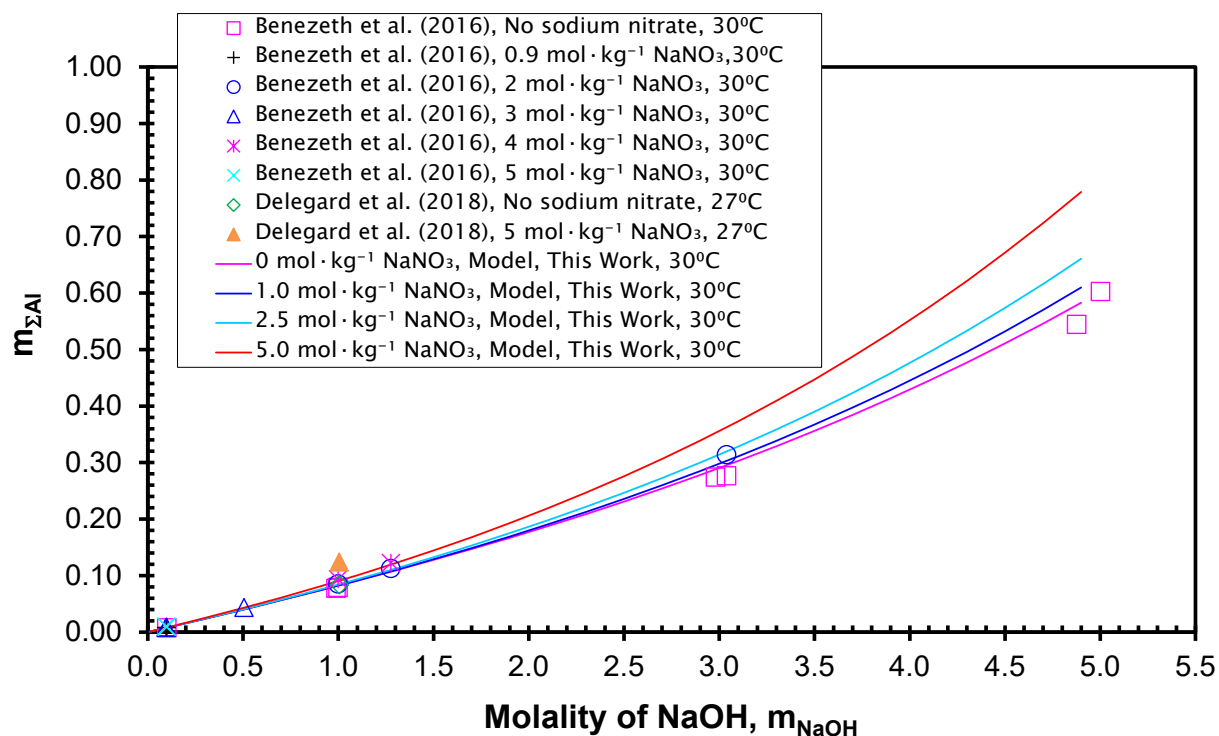


Figure 3.10. Solubilities of gibbsite in total molality of Al(III) in mixtures of NaOH + NaNO₃ as a function of NaOH molality at 30 °C predicted by the model developed in this work, in comparison with the experimental values at 30 °C from Bénézeth et al. (2016), and at 27 °C from Delegard et al. (2018).

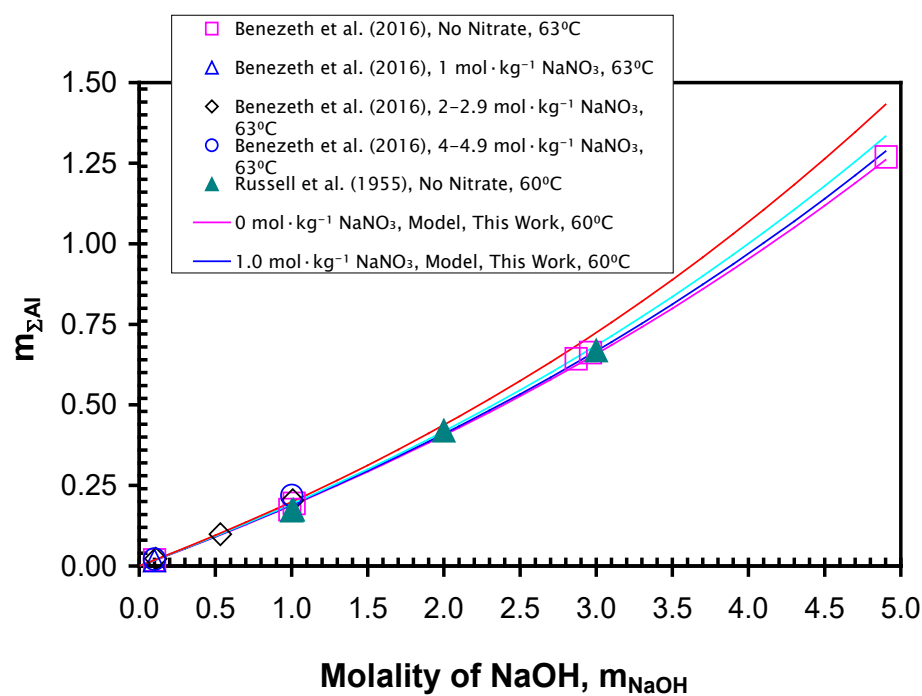


Figure 3.11. Solubilities of gibbsite in total molality of Al(III) in mixtures of NaOH + NaNO₃ as a function of NaOH molality at 60 °C predicted by the model developed in this work, in comparison with the experimental values at 63 °C from Bénézech et al. (2016), and at 60 °C from Russell et al. (1955).

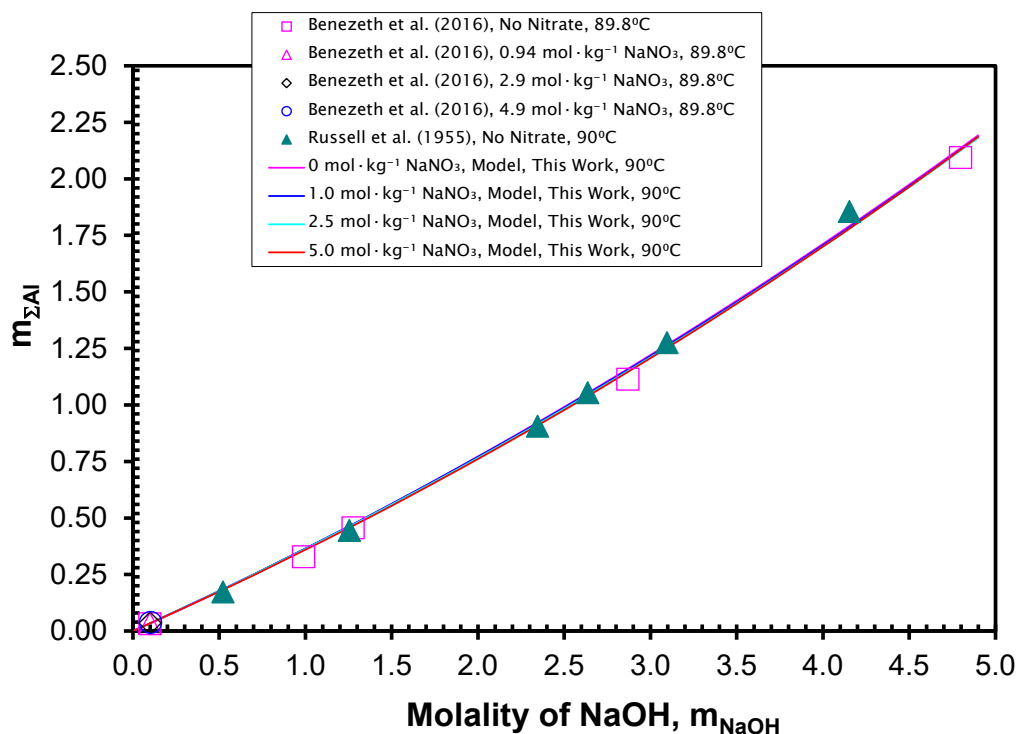


Figure 3.12. Solubilities of gibbsite in total molality of Al(III) in mixtures of NaOH + NaNO₃ as a function of NaOH molality at 90 °C predicted by the model developed in this work, in comparison with the experimental values at 89.8 °C from Bénézech et al. (2016), and at 90 °C from Russell et al. (1955).

4. Equilibrium Aspects of Al Chemistry Part 2—Solubility measurements of gibbsite and boehmite in mixtures of NaOH + Na₂B₄O₇ and NaOH + NaB(OH)₄ (or alternatively expressed as NaBO₂•2H₂O)

4.1. Experimental Set-up

In this work, gibbsite and boehmite have been used as a solubility-controlling phase in solubility measurements. The first set of experiments was in mixtures of NaOH + Na₂B₄O₇ (Table 4.1).

Table 4.1. Experiments investigating gibbsite solubility in NaOH + Na₂B₄O₇ solutions at 60 °C.

Experimental Number	NaOH, m	Na ₂ B ₄ O ₇ , m	Solubility-controlling phase
GBT60-B4O7-1	0.10	0.025	Gibbsite
GBT60-B4O7-2	0.10	0.050	Gibbsite
GBT60-B4O7-3	0.10	0.10	Gibbsite
GBT60-B4O7-4	0.10	0.15	Gibbsite

The second set of experiments was set-up in pure NaBO₂ solutions to investigate the effect of borate on the solubility of gibbsite (Table 4.2).

Table 4.2. Experiments investigating gibbsite solubility in NaBO₂ solutions at 60 °C.

Experimental Number	NaB(OH) ₄ , m	Solubility-controlling phase
GBT-BO2-0.1	0.10	Gibbsite
GBT-BO2-0.5	0.50	Gibbsite
GBT-BO2-1.0	1.0	Gibbsite
GBT-BO2-2.0	2.0	Gibbsite
GBT-BO2-3.0	3.0	Gibbsite
GBT-BO2-4.0	2.0	Gibbsite

Under this subtask, the third set of experiments was set-up in mixtures of NaOH + NaBO₂ solutions to investigate the effects of borate and hydroxyl concentrations on the solubility of gibbsite (Table 4.3)

Table 4.3. Experiments investigating gibbsite solubility in NaOH + NaBO₂ solutions at 60 °C.

Experimental Number	NaOH, m	NaB(OH) ₄ , m	Solubility-controlling phase
GBT60-BO2-A1	1.0	0.50	Gibbsite
GBT60-BO2-A2	2.0	0.50	Gibbsite
GBT60-BO2-A3	3.0	0.50	Gibbsite
GBT60-BO2-B1	1.0	1.0	Gibbsite
GBT60-BO2-B2	2.0	1.0	Gibbsite
GBT60-BO2-B3	3.0	1.0	Gibbsite

In the fourth set of experiments under this task, the solubility-controlling phase was boehmite hydrothermally synthesized at 175°C. The supporting solutions were mixtures of NaOH + Na₂B₄O₇ (Table 4.4).

Table 4.4. Experiments investigating boehmite solubility in NaOH + Na₂B₄O₇ solutions at 80°C.

Experimental Number	NaOH, m	Na ₂ B ₄ O ₇ , m	Solubility-controlling phase
HBMT80-B4O7-0	0.10	0.00	Boehmite
HBMT80-B4O7-0.1	0.10	0.10	Boehmite
HBMT80-B4O7-0.2	0.10	0.20	Boehmite
HBMT80-B4O7-0.3	0.10	0.30	Boehmite
HBMT80-B4O7-0.4	0.10	0.40	Boehmite
HBMT80-B4O7-0.6	0.10	0.60	Boehmite

4.2. Representative SEM Images of Reaction Products

The solution chemical compositions of the above experiments have been determined, and those results would be modeled, if the project is to be continued in the future. The reaction products have been characterized. In Figures 4.1 and 4.2, the representative SEM images for experiments such as those listed in Table 4.3 are shown.

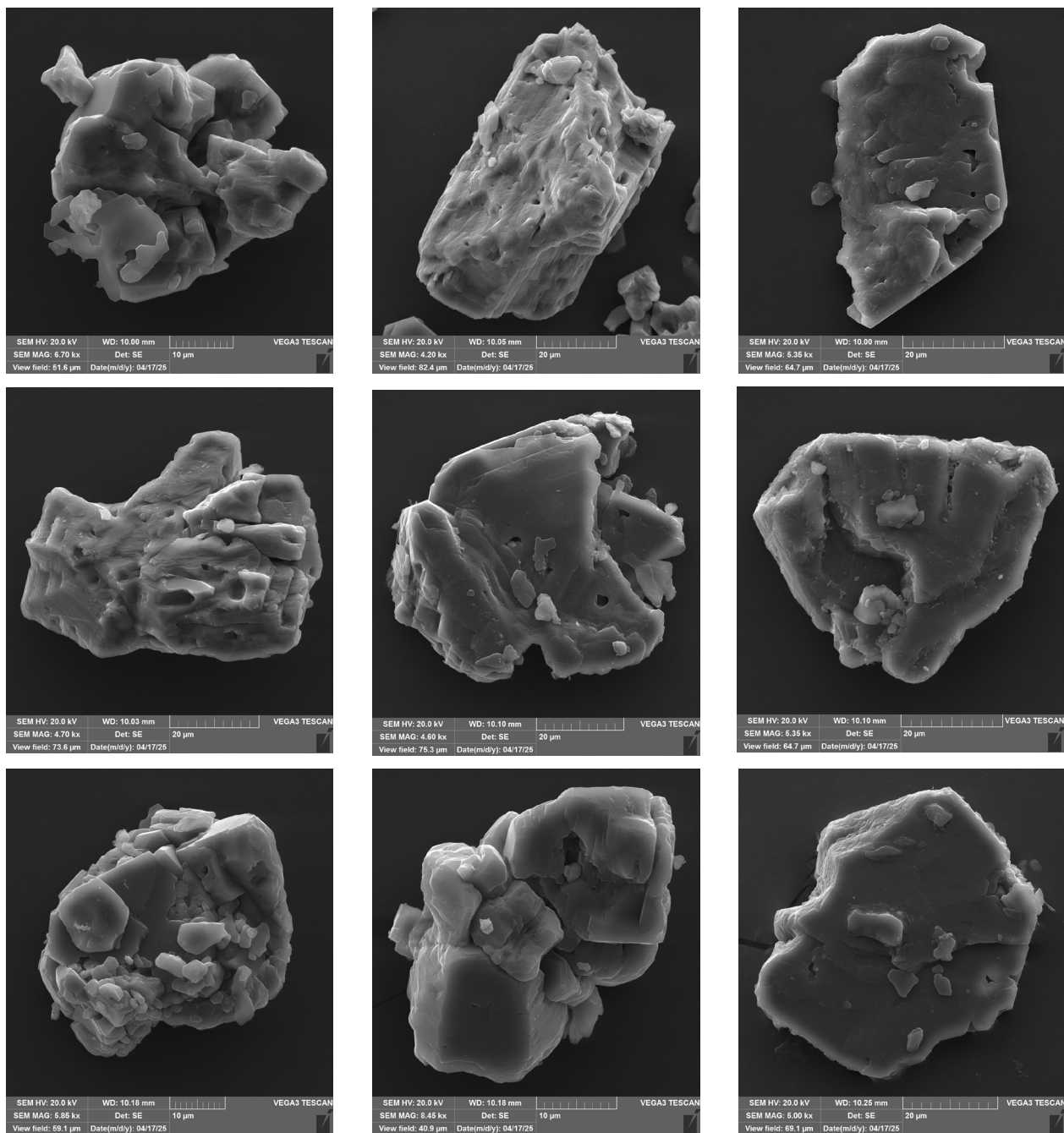


Figure 4.1. SEM images of the reaction products for Series A experiments listed in Table 4.3. Top Panel: SEM images of reaction products from experiment GBT60-BO2-A1. Middle Panel: SEM images of reaction products from experiment GBT60-BO2-A2. Bottom Panel: SEM images of reaction products from experiment GBT60-BO2-A3.

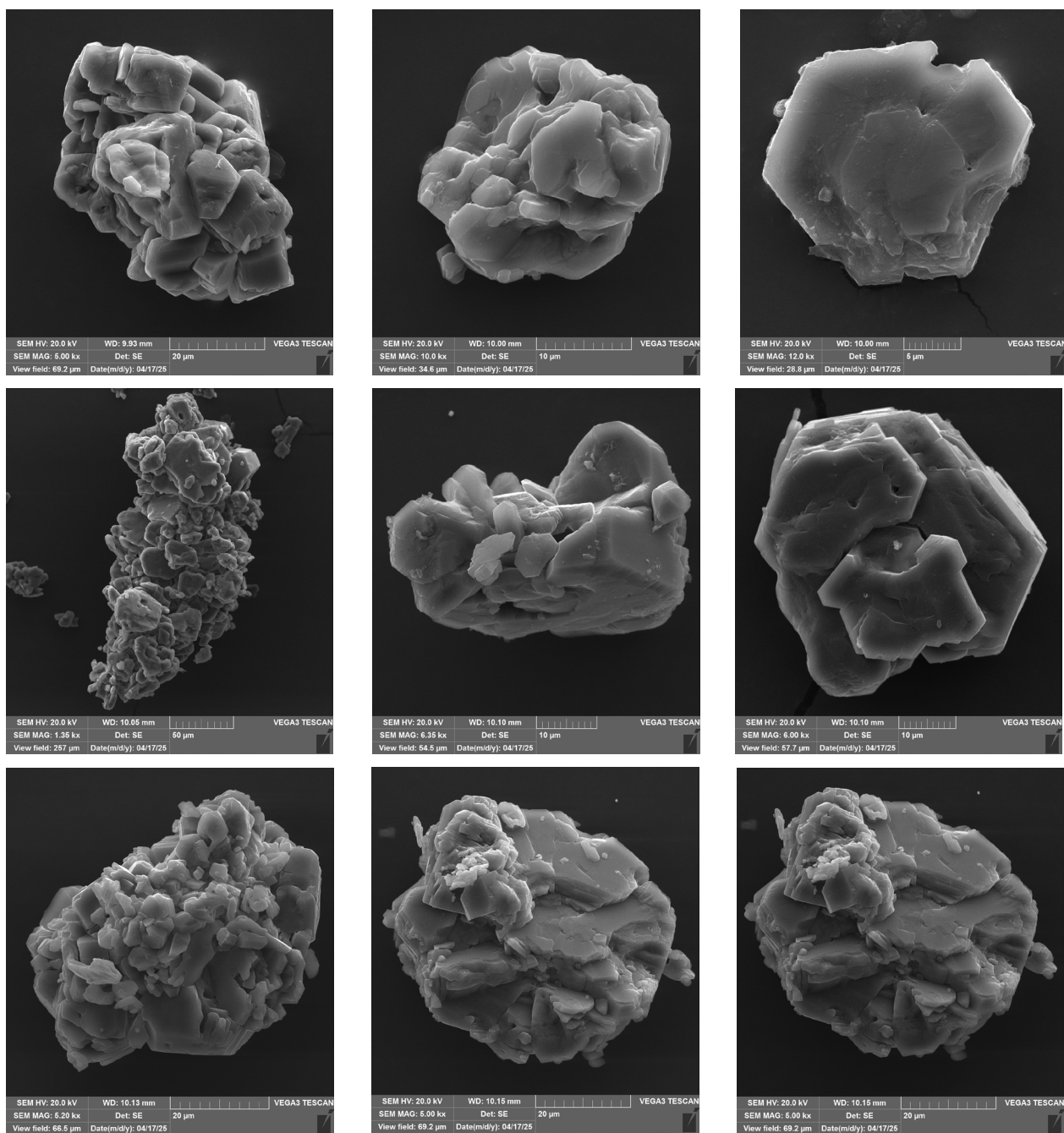


Figure 4.2. SEM images of the reaction products for Series B experiments listed in Table 4.3. Top Panel: SEM images of reaction products from experiment GBT60-BO2-B1. Middle Panel: SEM images of reaction products from experiment GBT60-BO2-B2. Bottom Panel: SEM images of reaction products from experiment GBT60-BO2-B3.

5. Kinetic Aspects of Al Chemistry Part 2—Kinetics of Gibbsite Dissolution in Concentrated Ternary Mixtures of NaOH + NaNO₃ + NaNO₂

This work belongs to Task 4.4—Experimental and modeling of the effects of co-anions on the dissolution/precipitation kinetics of HLW Al-bearing sludge. The University of Idaho team lead by Dr. Leslie Baker is in charge of performing this subtask.[§]

5.1. Experimental Setup

The primary objective of this subtask is to carry out experiments in order to assess the effects of common co-anions in Hanford tank waste on the dissolution kinetics of gibbsite. The experimental system consists of aqueous solutions of 1-5 *m* NaOH + 1-5 *m* NaNO₃ + a co-anion at a concentration comparable to that observed in tank waste. Co-anions to be studied include nitrate (1-5 *m* NaNO₂), sulfate (0.02 *m* Na₂SO₄), phosphate (0.02 *m* Na₃PO₄), and chromate (0.01 *m* NaCr(OH)₄).

Initial experiments were performed in the NaOH-NaNO₃-NaNO₂ system. Static experiments at ambient temperature were performed as follows. For each specific solution composition of interest, a set of replicate tubes was prepared containing ~2g of gibbsite each. At the start of the experiment, 10 mL of the prepared solution was pipetted into each tube and the exact mass recorded. The tubes were placed on a mixer and mixed continuously at room temperature. At fixed time intervals ranging from 15 minutes to 64 days, replicate pairs of tubes were removed from the shaker and centrifuged. The supernatant was decanted and filtered through a 0.2 μm polyethersulfone (PES) membrane. The gibbsite pellet in the tube was rinsed with 10 mL of deionized water, shaken, centrifuged, and the supernatant filtered and mixed with the original supernatant. The gibbsite pellet was air-dried, and selected dried samples were analyzed by XRD to confirm that the final mineralogy was unchanged.

Initial experiments were carried out for up to 64 days. As discussed below, results from these experiments suggested that equilibration required much less time, and the longest experiment duration was subsequently shortened to 16 days, in order to use experimental resources in the most cost-efficient manner.

The experimental solutions were diluted 1:5000 and acidified for Al analysis on an Agilent 5110 ICP-OES. Solution blanks (experimental solution with no gibbsite) and gibbsite blanks (gibbsite in DI water) were also analyzed, and quality control samples were analyzed every 15 samples to monitor for drift. Although the initial samples were basic, analysis of duplicate samples indicated that sample acidification for analysis did not affect dissolved Al content and improved instrument performance.

[§] The start of the work at University of Idaho was significantly delayed by negotiations between the University of Idaho and Sandia National Laboratories regarding contract terms until late January of 2025, nine months after the project was funded by DOE.

5.2. Experimental Results

Five experiments were performed (Table 5.1 and Figure 5.1). Several observations may be made from the results of these initial experiments. The dissolved Al concentrations observed at equilibrium are comparable to published data for similar solutions (Dembowski et al., 2020), near 3000 ppm for 1 *m* NaOH and 6000 ppm for 1 *m* NaOH. Increasing nitrate or nitrite concentration appears to cause a modest increase in Al solubility, but further experimental results are needed for confirmation of this.

Gibbsite dissolution occurs rapidly at the start of the experiments. Dissolved Al concentrations in 1 *m* NaOH approach equilibrium concentrations after approximately one day, and plateau by approximately two days (Figure 5.2). In 2 *m* NaOH, near-equilibrium concentrations are achieved after three to four days and concentrations plateau after approximately one week.

A sample XRD scan of dried gibbsite from a completed experiment is shown in Figure 5.3. No differences are observed between the run product, the starting gibbsite, or the gibbsite standard pattern, indicating that no new phases were precipitated during the experiment.

Experiments to complete the planned NaOH-NaNO₃-NaNO₂ series are currently under way. Future experiments will address the other anions discussed above and will include experiments carried out in a shaking water bath at 60 °C.

Table 5.1. Experiments performed at University of Idaho

Experiment	NaOH (m)	NaNO ₃ (m)	NaNO ₂ (m)
1	1	1	1
2*	1	2.5	1
3	1	1	2.5
4	2	2.5	1
5	2	1	1

*Experiment 2 was discovered to not have been at the stipulated concentrations due to a transcription error. Data from it are not included on Figures 5.1 and 5.2.

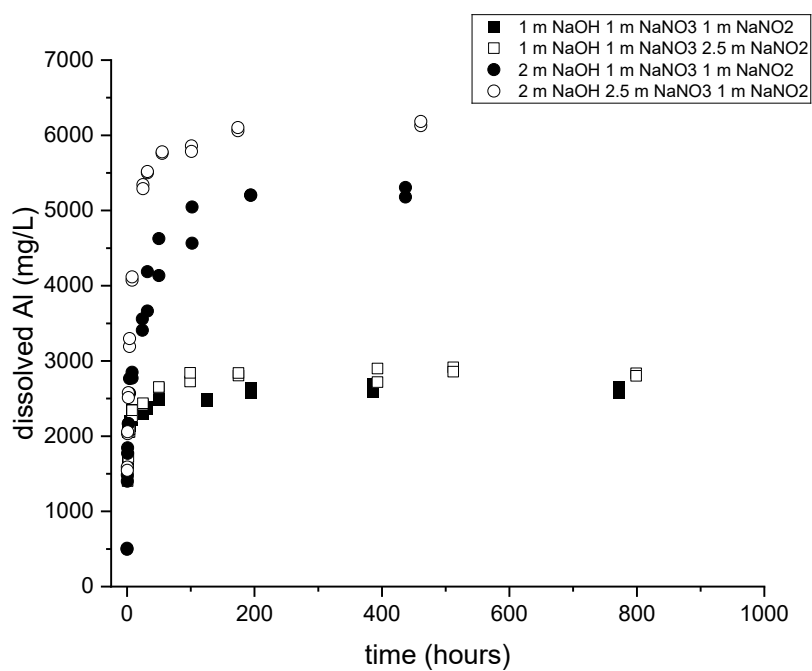


Figure 5.1. Dissolved Al concentrations in experimental supernatants as a function of time

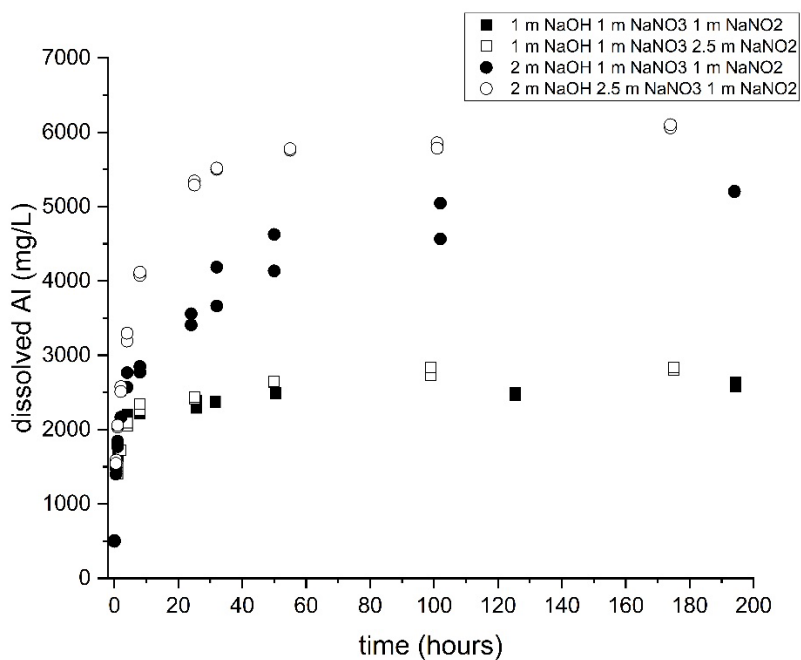


Figure 5.2. X-axis expanded in Figure 5.1 to more clearly show equilibration times

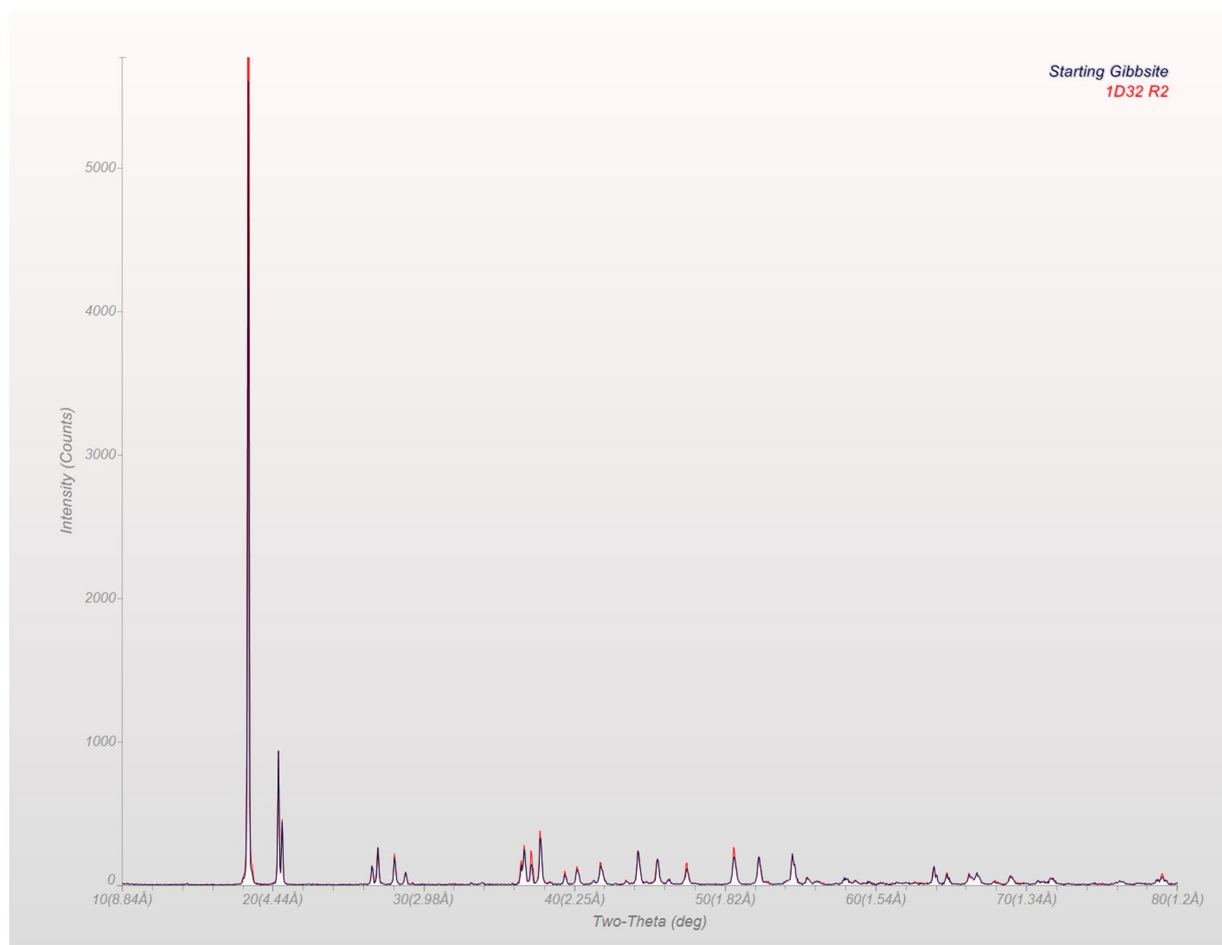


Figure 5.3. X-ray diffractogram of starting gibbsite powder (black) and dried experimental run product (red) from experiment 1, time = 32 days.

6. Development of a Machine Learning (ML) model to predict/estimate Pitzer interaction parameters

This work belongs to Task 5.3—Development of a Machine Learning (ML) model to predict/estimate Pitzer interaction parameters. The preliminary results have been presented at a conference (Chowdhury et al., 2025).

Understanding the behavior of electrolyte solutions in various environments is essential to nuclear waste management, including evaluating the safety and effectiveness of waste pretreatment and treatment of tank waste. The Specific Ion Interaction Theory (SIT) and Pitzer models are thermodynamic models used to determine the activity coefficients of aqueous

species. While the SIT model provides mathematical simplicity, the Pitzer model extends to much higher ionic strength range such as those in tank waste. The utility of the Pitzer model to multiple component systems such as the tank waste at the Hanford and Savannah River sites in US, however, is constrained by the limitations of existing Pitzer parameters, as those model parameters are experimentally derived. Experimental limitations impose various challenges for obtaining model parameters, including the vast experimental matrices requiring enormous resources and time, and the likely experimental inaccessibility (e.g., species of interest being radiologically toxic on one hand, and the availability and obtainment of them being difficult on the other hand).

Machine Learning (ML) can potentially facilitate parameter estimations for the Pitzer model where experimental data are scarce or lacking, based on available fundamental properties of elements/species. For instance, Lopez et al. (2023) successfully applied machine learning techniques to estimate the interaction coefficients in the SIT model. Building on that approach taken by Lopez et al. (2023), this work aims to employ machine learning techniques to estimate interaction parameters of the Pitzer model. In order to accomplish the objectives, we first collect and compile Pitzer parameters from open and public literature and build a database. The public and open literature includes journal publications, government reports, university degree theses, company online documents, etc. The collected parameters were up to May 2026. Once new parameters are published and evaluated according to the key guiding principles (Xiong and Wang, 2025), the database is updated. We plan to do so until the completion of this project.

We use the artificial neural network (ANN), Random Forest (RF), and XGBoost (XGB) models to evaluate $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ parameters of simple electrolytes that do not involve aqueous complexes. Our results demonstrate that the RF model has the best performance in estimation of parameters and the XGB model has the second-best performance. The ANN model has a strong performance in predicting data cluster assignments and a strong performance in estimation of parameters. The ML model development reported in this work shows that ML models can play a supplementary role in predicting/estimating the Pitzer parameters that are unknown, and in guiding further experimental work. We are in a process of preparing a journal manuscript based on this work. We are further developing our models to estimate Pitzer parameters involving aqueous complexes and parameters in mixed systems.

6.1. References

- Chowdhury, N., Mercado, V., Xiong, Y., 2025. Estimation of Pitzer Parameters using Neural Network, Random Forest, and exTreme Gradient Boosting: A comparative analysis of machine learning applications in critical mineral extraction and nuclear waste management (Abstract for Geological Society of America Rocky Mountain Section Annual Meeting in May, 2026).
- Lopez, C.M., Zhang, P., Favela, S.D., Xiong, Y. and Wang, Y., 2023. Application of machine learning for modeling brønsted-guggenheim-scatchard specific ion interaction theory (SIT) coefficients. *Applied Geochemistry*, 155, p.105730.

7. IN SITU & EX SITU CHARACTERIZATION OF AL-BEARING PHASES FORMED IN SIMULATED TANK WASTE SOLUTIONS

Our goal in this task is to perform detailed characterization of Al-bearing phases in simulated tank waste solutions using *ex-situ* and *in-situ* mass spectrometry of liquid samples. Two unique mass spectrometry (MS) techniques, time-of-flight secondary ion mass spectrometry (ToF-SIMS) and vacuum ultraviolet single photon ionization mass spectrometry (VUV SPI-MS) were employed primarily. The Al-bearing solids of interest include gibbsite, boehmite, aluminosilicates, dawsonite, nitrate-cancrinite, and soluble sodium aluminate. We used *in situ* VUV SPI-MS and *in-situ* liquid SIMS to characterize simulated tank waste solutions and determine the dependence of Al chemical speciation on ionic strength in the alkaline pH range. This task can provide critical experimental information about aqueous speciation and the related solubility-controlling mineral phases for the development of the proposed thermodynamic model in Task 5.

7.1. In situ VUV SPI-MS analysis of chemical composition

A paper was published based on results reported in this chapter (Sui et al. 2025). Synchrotron-based single-photon ionization mass spectrometry (SPI-MS) using vacuum ultraviolet (VUV) photons, or VUV SPI-MS, is a powerful technique used to investigate properties of chemical systems (Komorek et al. 2018). VUV SPI-MS is a “soft” method of ionization, allowing complex system detection with fewer fragments compared to other ionization methods such as electron impact or charged particles (Komorek et al. 2018). The “system for analysis at the liquid–vacuum interface (SALVI)” device is a vacuum-compatible microreactor that can be integrated with VUV SPI-MS, which allows high-vacuum analysis of biological and environmental chemistry at the liquid interface (Komorek et al. 2018). Tiny apertures in the SALVI slow evaporation with no temperature or composition change and proton beam ionization of the surface (Komorek et al. 2018; Yang et al. 2011a).

7.1.1. Materials and methods

7.1.1.1. SALVI fabrication

The SALVI device is a portable and vacuum compatible microfluidic reactor (Yang et al. 2011a; Yang et al. 2011b; Yu 2020). The rectangular microchannel is 200 μm (width) $\times$ 300 μm (depth) in a polydimethylsiloxane (PDMS) block. This channel is covered by a 100 nm thick silicon nitride (SiN) membrane (Norcada, 1.5 $\times$ 1.5 mm² in area) on a supporting 200 μm thick silicon frame of 7.5 $\times$ 7.5 mm² in area to form the detection area. **Figure 7.1** depicts the schematic of the SALVI device setup coupled with VUV SPI-MS at the Advanced Light Source (ALS) beamline 9.0.2. After microfluidics fabrication using soft lithography, two micropores (2 μm in diameter and 100 μm apart, **Figure 7.1b**) were milled on the center of the channel using a scanning electron microscopy-focused ion beam (SEM-FIB, ThermoFisher Helio Dual Beam

Quanta) to allow evaporation of molecules in vacuum and provide ions for ionization in high vacuum (Komorek et al. 2018; Komorek et al. 2020). The chamber vacuum was kept on the order of 10^{-7} Torr during analysis. More details of SALVI integration to VUV SPI-MS are described in our recent studies (Komorek et al. 2018; Komorek et al. 2020).

7.1.1.2. Boehmite sample preparation

The boehmite stock solution of 1 mg/mL was prepared using 10 mg of AOH60 powder (AOH60 powder, Apyral, particle size 0.4 to 1.6 μm with D_{50} 1 μm) and deionized water (DI water) with resistance of 18.2 $\text{M}\Omega$ (Barnstead water purification system, Nanopure diamond). The stock solution was then ultrasonicated for 5 min. The 10 $\mu\text{g/mL}$ boehmite solution was made by diluting 1 mL boehmite stock solution into 99 mL DI water. Afterwards, a series of samples with different pH conditions of the 10 $\mu\text{g/mL}$ boehmite (including pH 1, 3, 7, 9, and 13) were prepared. The pH of boehmite solution was adjusted by adding a suitable amount of hydrochloric acid (HCl) and sodium hydroxide (NaOH) prior to VUV SPI-MS analysis and the solution pH can be regarded as constant over time. The solution pH was determined using a pH meter (Fisherbrand™ accumet™ AP110 Portable pH Meter Kit). To reduce possible interference of polydimethylsiloxane (PDMS) signals in mass spectral analysis, each device was kept at 70 °C in a vacuum oven (ThermoFisher, Fisherbrand™ Isotemp™ Model 281A Vacuum Oven) overnight prior to usage. The prepared boehmite solutions were then injected into the microchannel and sealed with PEEK fittings (Agilent Technologies) for VUV SPI-MS analysis.

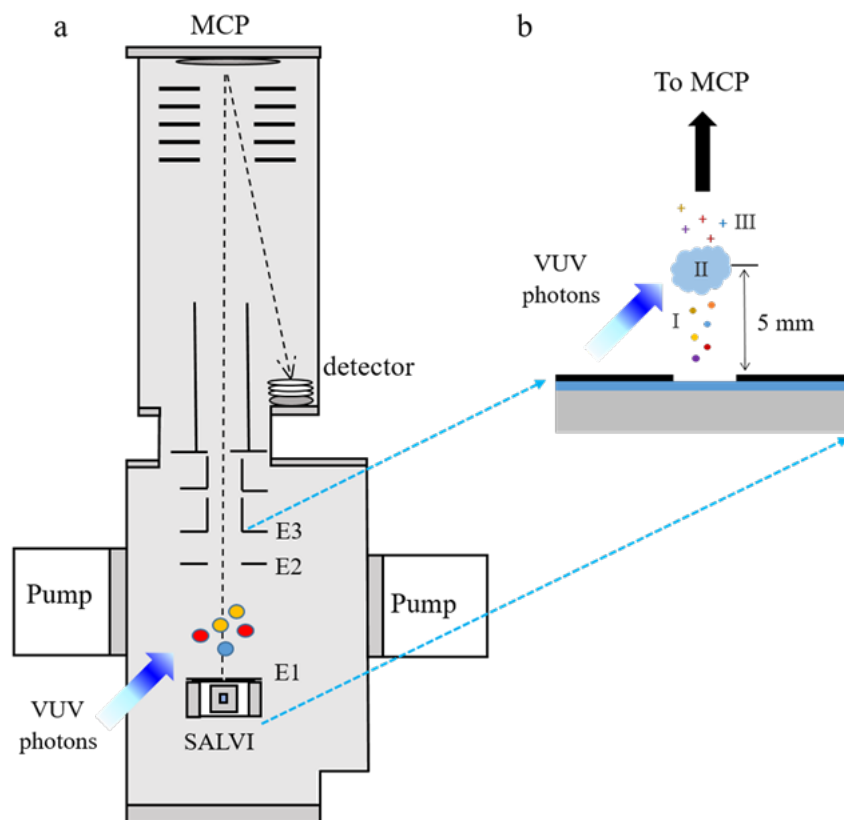


Figure 7.1. The experimental schematics of solvated boehmite particle study using VUV SPI-MS: a) instrument diagram showing microchannel plate (MCP) with E1 as the bottom electrode plate, E2 the electrode held at 1,000 V nominally, and E3 the electrode held at 0 V; and b) the position of the VUV photon flux relative to evaporated molecules (I), photon beam (II), and molecules charged to positive ions (III) for detection, adapted from our recent papers (Komorek et al. 2018; Sui et al. 2024; Sui et al. 2021; Sui et al. 2025).

7.1.1.3. VUV SPI-MS liquid analysis

The SALVI device was attached to the bottom electrode plate of the microchannel plate (MCP) after the pH adjusted boehmite solutions injected into the microchannel (**Figure 7.1a**). The VUV SPI-MS analysis was carried out by a three-meter VUV monochromator at the 9.0.2 Chemical Dynamics Beamline at the ALS of the Lawrence Berkeley National Laboratory (Ahmed & Kostko 2020). The VUV photon flux was adjusted to about 5 mm above the SiN membrane by optimizing the height of the mass spectrometer before data collection (Komorek et al. 2018; Komorek et al. 2020; Sui et al. 2021). After ~20 minutes pump down process, the chamber was maintained at the intended vacuum (10^{-7} Torr) during sample analysis. Molecules were evaporated at a rate of about 10^8 molecules·cm⁻²·s⁻¹ (calculated by a custom code), from the two holes on the SiN membrane. The evaporated molecules were subsequently ionized by the bright and tunable synchrotron VUV photon light (**Figure 7.1a**) (Komorek et al. 2018; Yang et al. 2011a). Meanwhile, surface tension at the aqueous surface holds the liquid in the micrometer-sized aperture along the microchannel and keep the vacuum stable. Recently, gamma

irradiation was found to facilitate the aggregation of boehmite particles in solution (Liu et al. 2022). Nevertheless, as a “soft” ionization method, the VUV irradiation will not likely change the structure of evaporated molecules from the microchannel. Thus, the mass spectral results can provide more insights into the pH effect on boehmite dissolution in liquids. To optimize signals, the MCP voltage was tuned for detection of ions of interest. Ions were collected and detected by the ToF mass spectrometer. SPI-MS measurements were acquired for photon energies ranging from 8.0 to 12.6 eV for all boehmite samples. The energy step was 0.1 electron volt (eV) to obtain the photo ionization energy (PIE) curve of each mass by integrating the peak intensities at each photon energy.

7.1.1.4. Data analysis

Mass calibration of the VUV SPI-MS was performed by using reference chemical compounds like water, oxygen, or rare gases.¹³ During data acquisition, a continuous wave ion beam was converted to a pulsed one to obtain more photons (Kostko et al. 2016). The resulting mass resolution was not uniform over the mass range because higher relative energy is acquired by small molecules, which leads to narrower peaks. On the contrary, lower relative energy acquired by larger molecules can produce wider peaks. Thus, unit mass at the peak center was used for peak identification. The peak centers are slightly different at various photon energies for a particular species. However, the peak identifications based on the unit mass are consistent among different PIEs. For example, the ions detected at 12.5 eV, 12.0 eV, and 11.5 eV were consistent. All mass spectra were plotted and integrated in Origin[®] 2018.

In this study, the appearance energies (AEs) of key solvated boehmite ions were all smaller than 11.5 eV according to mass spectral analysis as shown in **Figure 7.2**. However, identification of ions may be more difficult at lower ionization energies (IEs) because the characteristic peaks have lower ion counts. Therefore, mass spectra at 12.5 eV were chosen for peak identification after evaluation of all spectra. The AE was determined to be the first point on the PIE curve where ion counts began to increase from the background signal. There was a slight difference in the total counts of different aqueous solutions of boehmite particles because of random surface topography and instrument efficiency.

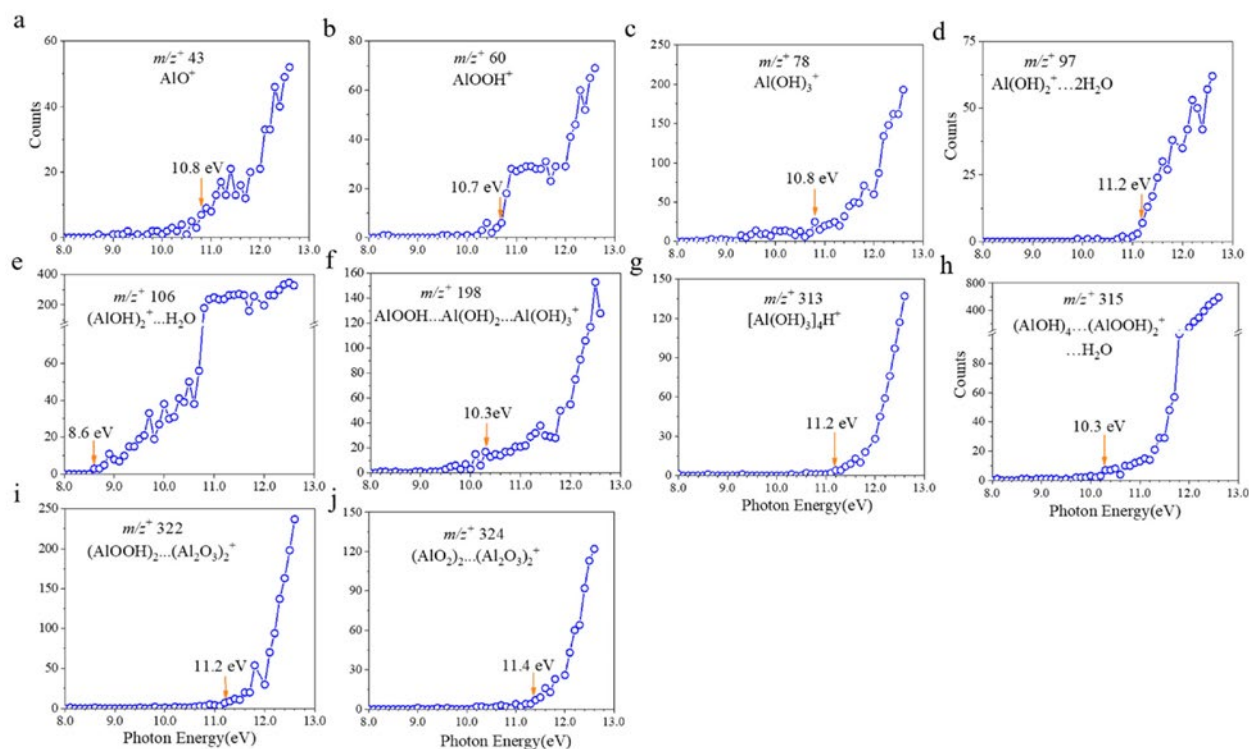


Figure 7.2. AEs of key observed ions of the dissolved boehmite particles using VUV SPI-MS: (a) $m/z^+ 43$ AlO^+ , (b) $m/z^+ 60$ AlOOH^+ , (c) $m/z^+ 78$ Al(OH)_3^+ , (d) $m/z^+ 97$ $\text{Al(OH)}_2 \dots 2\text{H}_2\text{O}$, (e) $m/z^+ 106$ $(\text{AlOH})_2 \dots \text{H}_2\text{O}$, (f) $m/z^+ 198$ $\text{AlOOH} \dots \text{Al(OH)}_2 \dots \text{Al(OH)}_3^+$, (g) $m/z^+ 313$ $[\text{Al(OH)}_3]_4\text{H}^+$, (h) $m/z^+ 315$ $(\text{AlOH})_4 \dots (\text{AlOOH})_2 \dots \text{H}_2\text{O}$, (i) $m/z^+ 322$ $(\text{AlOOH})_2 \dots (\text{Al}_2\text{O}_3)_2^+$, and (j) $m/z^+ 324$ $(\text{AlO}_2)_2 \dots (\text{Al}_2\text{O}_3)_2^+$.

As discussed above, the mass of ions could not be absolutely determined because unit mass is used for peak identification. However, peak separation is not a problem since peak positions can be identified to two decimal places of accuracy. To improve the accuracy of identification, the key reactants/products were identified according to the following criteria: First, the magnitude of peaks was higher than their neighboring peaks and at least three times higher than the base lines. Second, product peaks reported in previous papers relevant to boehmite hydrogen and/or hydroxide behavior were included and searched in the spectra to verify their observations. Furthermore, three approaches were adopted to improve the likelihood and reliability of peak identification. First, peaks—except interference from system residuals from previous experiments and PDMS fragments—that have higher intensities than adjacent peaks were selected as alternative key products, reactants, or fragments. To minimize the interference from PDMS peaks in peak identification, all possible PDMS peaks are smoothed (counts divided by 10) in the spectra. Second, the identities of peaks were proposed based on existing knowledge of boehmite solvation products (Kerisit et al. 2019; Yu et al. 2018; Zhang et al. 2018a). Third, peak identification was based on the AEs and PIE curves comparison with the reported values of chemicals coupled together with molecular mass determined from the spectral analysis. As to the observed species where AEs and/or structures that have not been found in previous studies, the new makeup and structure was deduced by considering the spectrum, PIE

curve, and the most likely structures based on knowledge of the boehmite dissolution and known literatures (as shown in **Table 7.1**) (Sassi et al. 2020; Verdier et al. 2007).

7.1.2. Results and discussion

7.1.2.1. VUV SPI-MS spectral and AE analysis of boehmite dissolution

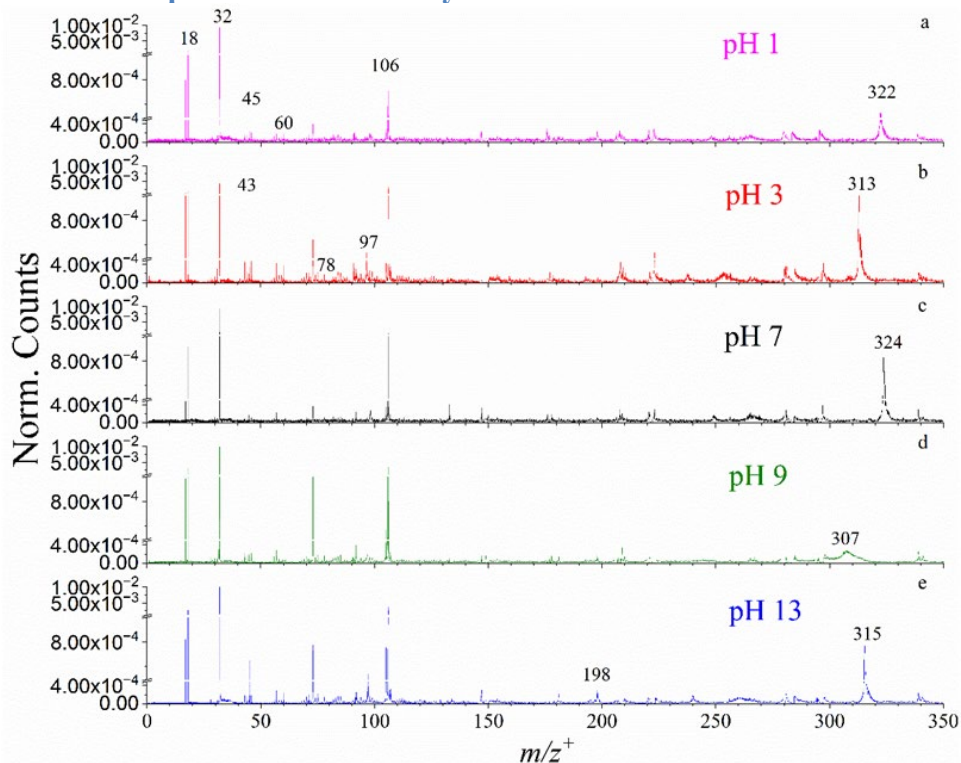


Figure 7.3. Normalized VUV SPI-MS spectral plots of boehmite at different pH observed at 12.5 eV: (a) pH 1, (b) pH 3, (c) pH 7, (d) pH 9, and (e) pH 13.

Representative VUV SPI-MS spectra were illustrated in **Figure 7.3** and **Figure 7.4**. The findings suggest that boehmite dissolution in different pH conditions produce more than the known γ -AlOOH solute in the molecular form. Furthermore, all AEs of the key products have been determined the first time in this study to our knowledge (**Table 7.1**). Specifically, several peaks related to boehmite, aluminum oxides, and hydroxides were identified from mass spectral analysis, such as m/z^+ 43 (AlO^+), m/z^+ 60 (AlOOH^+), m/z^+ 78 ($\text{Al}(\text{OH})_3^+$). Their AEs were 10.8, 10.7 and 10.8 eV, respectively. In comparison, AlOOH and $\text{Al}(\text{OH})_3$ were also detected by static SIMS on the powder surface (Sassi et al. 2020; Verdier et al. 2007). Additionally, the mass spectral results show peaks that were not reported before. For example, aluminum hydroxides with water clusters including m/z^+ 97 ($\text{Al}(\text{OH})_2^+ \dots 2\text{H}_2\text{O}$, 11.2 eV) and m/z^+ 106 ($(\text{AlOH})_2^+ \dots \text{H}_2\text{O}$, 8.6 eV) were observed for the first time.

Table 7.1. Identified key ions of dissolved boehmite particles at 12.5 eV in VUV SPI-MS.

¹ m/z^+ _{obs}	² m/z^+ _{the}	Possible Identification	³ AEs (eV)
43	42.98	AlO^+	10.8
60	59.99	AlOOH^+	10.7
78	78	$\text{Al}(\text{OH})_3^+$	10.8
97	96.94	$\text{Al}(\text{OH})_2^+ \dots 2\text{H}_2\text{O}$	11.2
106	105.99	$(\text{AlOH})_2^+ \dots \text{H}_2\text{O}$	8.6
198	197.98	$\text{AlOOH} \dots \text{Al}(\text{OH})_2 \dots \text{Al}(\text{OH})_3^+$	10.3
313	313.02	$[\text{Al}(\text{OH})_3]_4\text{H}^+$	11.2
315	314.93	$(\text{AlOH})_4 \dots (\text{AlOOH})_2 \dots \text{H}_3\text{O}^+$	10.3
322	321.88	$(\text{AlO}_2)_2 \dots (\text{Al}_2\text{O}_3)_2^+$	11.4
324	323.9	$(\text{AlOOH})_2 \dots (\text{Al}_2\text{O}_3)_2^+$	11.2

¹ m/z^+ _{obs}: observed mass to charge ratio (m/z) obtained in this experiment; ² m/z^+ _{the}: theoretical m/z ;

³ AEs: appearance energy values determined in this work.

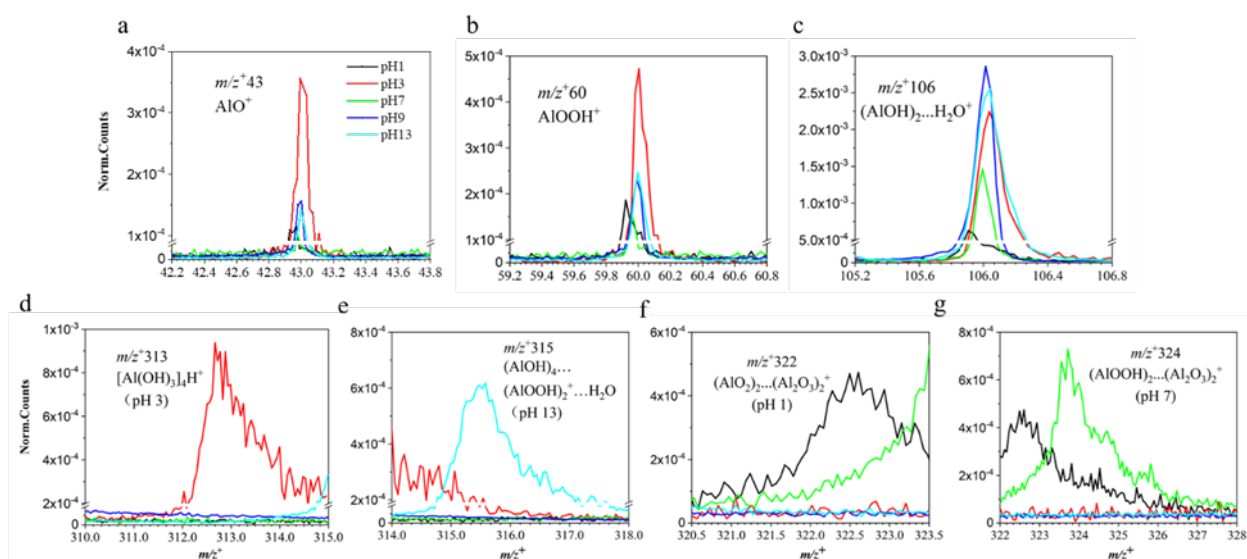


Figure 7.4. Normalized VUV-SPIMS spectral plots of boehmite at 12.5 eV showing key peaks: (a) m/z^+ 43 AlO^+ , (b) m/z^+ 60 AlOOH^+ , (c) m/z^+ 106 $\text{Al}(\text{OH})_2 \dots \text{H}_2\text{O}^+$, (d) m/z^+ 313 $[\text{Al}(\text{OH})_3]_4\text{H}^+$, (e) m/z^+ 315 $(\text{AlOH})_4 \dots (\text{AlOOH})_2 \dots \text{H}_2\text{O}$, (f) m/z^+ 322 $(\text{AlO}_2)_2 \dots (\text{Al}_2\text{O}_3)_2^+$, (g) m/z^+ 324 $(\text{AlOOH})_2 \dots (\text{Al}_2\text{O}_3)_2^+$, (h) $(\text{AlOH})_4 \dots (\text{AlOOH})_2 \dots \text{H}_2\text{O}$.

Another type of important dissolved ions observed in VUV SPI-MS spectra are cluster ions. These ions indicate ion pairs formed via weak intermolecular forces in the aqueous solution (Sui et al. 2017). For example, m/z^+ 198 was identified as $(\text{AlOOH} \dots \text{Al}(\text{OH})_2 \dots \text{Al}(\text{OH})_3)^+$, 10.3 eV) based on previous results of static SIMS analysis of solid boehmite (Strange et al. 2022b; Verdier et al. 2007). These cluster ions have not been reported in liquid to the authors' knowledge. m/z^+ 313 was primarily assessed as $([\text{Al}(\text{OH})_3]_4)^+$, 11.2 eV). Besides, dissolved boehmite can form ion clusters like m/z^+ 315 $(\text{AlOH})_4 \dots (\text{AlOOH})_2 \dots \text{H}_2\text{O}$, 10.3 eV) and m/z^+

322 ((AlO₂)₂...(Al₂O₃)₂)⁺, 11.4 eV) in solutions in different pH conditions. The peak of m/z^+ 324 was identified as ((AlOOH)₂...(Al₂O₃)₂)⁺, 11.2 eV) based on the solute composition and mass matching. As shown in **Figure 7.4d – 7.4g**, the broad peaks consisting of the parent and protonated ions were likely caused by the proton-transfer process during VUV analysis (Bell et al. 2013). It is worth noting that the PIE of these cluster ions exhibit similar features, implying that these newly detected cluster ions are possibly combined by semblable functional compounds, like aluminum oxides and aluminum hydroxides.

Furthermore, AEs of boehmite, aluminum oxides, hydroxides, and cluster ions were presented in **Figure 7.2**. The red arrows indicate the values of the AEs for each detected key ion. These values acquired from the VUV SPI-MS are summarized in **Table 7.1**. Many cluster ions were first detected by VUV SPI-MS coupled with the SALVI microreactor. Besides hydration and hydroxyl configuration of boehmite particles, solvated ions and ion fragments can form more complex cluster ions in water as a solvent, presenting more insights into the fundamental process of solvation at the molecular level (Kerisit et al. 2019; Sassi et al. 2020).

7.1.2.2. The pH effects on boehmite dissolution

The normalized intensities were used to compare key observed ions from the VUV SPI-MS spectra. The pH dependence of representative ions on boehmite dissolution was depicted in **Figure 7.4**. It is interesting to note that boehmite solvation products are detected with different intensities under different pH conditions. The new findings suggest that the dissolution of boehmite and solvation of particles in solvent actually produce more complex solvated ions and cluster ions with water, presenting a new understanding compared to the existing simpler picture of the presence of molecular form of boehmite solvated in water. Specifically, the peaks of smaller aluminum oxides and hydroxides, for example m/z^+ 43 AlO⁺, m/z^+ 60 AlOOH⁺, and m/z^+ 78 Al(OH)₃⁺, have highest intensities in the acidic environment at pH 3. Also, alkaline conditions (i.e., pH 9, pH 13) can stimulate the formation of aluminum oxides and hydroxides, like AlOOH⁺ and Al(OH)₃⁺ (**Figure 7.5a**). In contrast, these ions show lower normalized counts in the neutral solution at pH 7. Aluminum hydroxides with water clusters, including m/z^+ 97 Al(OH)₂⁺...2H₂O and m/z^+ 106 (AlOH)₂⁺...H₂O revealed different features among the studied pH solutions. For example, m/z^+ 97 (Al(OH)₂⁺...2H₂O), its abundance in the acidic solution at pH 3 was slightly larger than in the strong alkaline solution at pH 13. As to m/z^+ 106 (AlOH)₂⁺...H₂O, the higher intensities in alkaline solutions at pH 9 and 13. Also, the acidic condition of pH 3 can promote its formation.

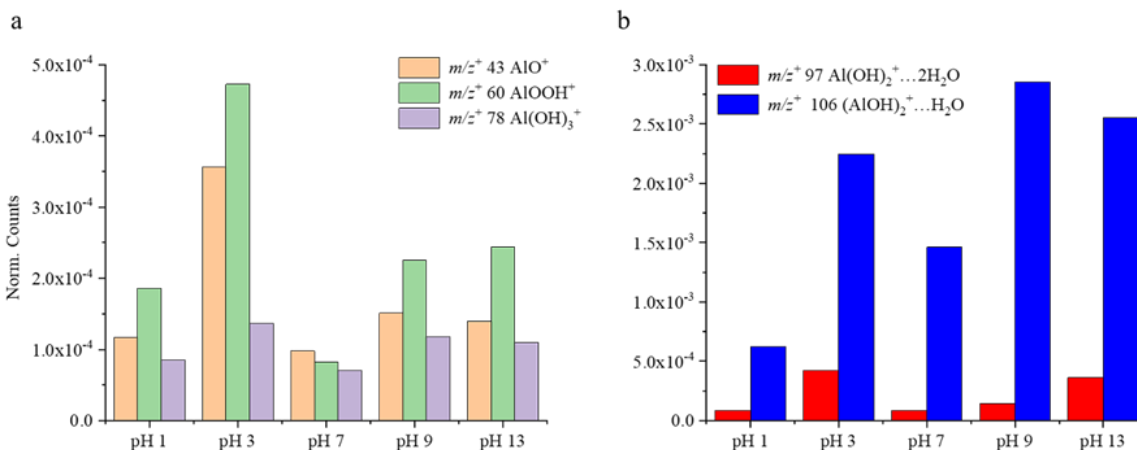


Figure 7.5. Comparison of pH dependence of representative boehmite AOH 60 components observed by VUV SPI-MS: a) $m/z^+ 43 \text{ AlO}^+$, $m/z^+ 60 \text{ AlOOH}^+$, and $m/z^+ 78 \text{ Al(OH)}_3^+$, and b) $m/z^+ 97 \text{ Al(OH)}_2 \dots 2\text{H}_2\text{O}$ and $m/z^+ 106 (\text{AlOH})_2 \dots \text{H}_2\text{O}$. Normalization is to total ion intensities.

Compared with aluminum oxides, aluminum hydroxides, and small cluster ions, the formation of larger cluster ions shows stronger dependence on pH conditions. As seen **Figure 7.3**, cluster ions are prominent at certain pH solutions. For instance, $m/z^+ 198 \text{ AlOOH} \dots \text{Al(OH)}_2 \dots \text{Al(OH)}_3^+$ was observed in alkaline conditions, namely pH 9 and 13, while $m/z^+ 313 [\text{Al(OH)}_3]_4^+$ can only be detected in the acidic (pH 3) solution. Besides, dissolved boehmite can form $m/z^+ 315 (\text{AlOH})_4 \dots (\text{AlOOH})_2 \dots \text{H}_2\text{O}$ in strong alkalis condition (pH 13), $m/z^+ 322 (\text{AlO}_2)_2 \dots (\text{Al}_2\text{O}_3)_2^+$ in strong acidic condition (pH 1), and $m/z^+ 324 (\text{AlOOH})_2 \dots (\text{Al}_2\text{O}_3)_2^+$ in neutral solution (pH 7). As summarized in **Table 7.1**, most cluster ions were detected at 12.5 eV for the first time. Cluster ions that contain boehmite and aluminum oxides tend to form in acidic solutions. In contrast, cluster ions that have boehmite hydroxides could be easily observed in alkaline solutions. As to the neutral pH 7 solution, boehmite, aluminum oxides, and hydroxides were detected; however, the detected species and intensities are fewer and their counts lower than those in acidic and alkaline conditions. Additional product identification of boehmite were summarized in **Table 7.1**. Our results show that, in addition to the molecular form of boehmite, a variety of aluminum oxides, hydroxides, and cluster ions incorporating water molecules coexist in the solvent cage. Varying pH could influence the formation of hydrogen bonds, which will change the structure of cluster ions. Their relative abundances also vary depending on the pH condition, suggesting the hydronium ions and hydroxide ions actively participate in the dissolution process at the molecular level. Specifically, boehmite tends to form 1D nanorods or nanofibers in acidic conditions; whereas 2D and 3D nanostructures are detected in alkaline conditions (Zhang et al. 2018a). In terms of composition, nanofibers are mainly made up by smaller aluminum oxides elements (i.e., AlO and AlO_2 as shown in **Figure 7.3a**, **7.3e**, and **7.3f** at acidic conditions, such as pH 1 and pH 3, respectively. In more alkaline conditions like pH 9 and pH 13, our results suggest that 2D nanoplates and 3D nanotubes contain more aluminum hydroxide units, like Al(OH) and Al(OH)_2 , as shown in **Figure 7.3c**, **7.3d**, and **7.3g**.

7.1.2.3. Conclusion

In this study, we performed *in-situ* VUV SPI-MS analysis of dissolved boehmite particles in different pH conditions in high vacuum. Liquid analysis in VUV SPI-MS was made possible by using the vacuum compatible SALVI microreactor. The dissolution pathways of boehmite at the solid-liquid interface, particularly in liquid water are more complex than previously conceived. Specifically, known dissolved products of boehmite, such as AlO^+ and AlOOH^+ , are confirmed by their AEs determined from the PIE curves in addition to mass spectral analysis. Moreover, the AE values of newly found dissolution products have been reported, and their molecular structures reported with mass spectral analysis for the first time. Different types of dissolved ions were observed with distinct intensities at different pH conditions. These new findings show that the solvation of boehmite depends on pH and that pH could indicate the change of the water microenvironment, affecting hydrogen bonding in aqueous solutions. Our results imply that future studies on boehmite in liquid, such as temperature and ionic strength dependence, is highly important to understand how boehmite dissolution could be impacted in the microenvironment where cluster ions exist in waste streams. We provided new insights into the pH dependence effect of boehmite; such fundamental understanding is important to design nuclear waste processing and environmental mitigation solutions. In future studies, quantum chemical calculations are desirable to determine the products more precisely by comparing the experimentally obtained AEs of ions with theoretical predications.

8. *In situ* liquid ToF-SIMS analysis of chemical compositions

This subtask will investigate the solid–liquid (s–l) interface of the dissolution and solvation of boehmite in different pH conditions using advanced *in situ* liquid ToF-SIMS technique developed in Dr. Yu’s laboratory (Yang et al. 2011a; Yang et al. 2011b; Yu 2020). Optimization of *in situ* liquid SIMS was performed using DI water to increase peak detection sensitivity using a slightly different instrument herein (Zhou et al. 2016). Afterwards, commercial boehmite, commercial gibbsite, and synthesized nano-boehmite samples were analyzed utilizing the single-pulse switching mode to acquire data. The hydration and hydroxyl reaction pathways of boehmite were investigated and expanded based on the detected ion clusters using *in situ* liquid SIMS. The observation of boehmite-containing cluster peaks indicates that the solvated structures of boehmite depend on pH. Our results showed that more complex solute molecules exist at the s–l interface than conventionally perceived in liquid. These findings provide new understanding of chemical processes at the interfaces from boehmite solvation and dissolution in liquid.

8.1. SALVI fabrication

As discussed in prior sections, the SALVI device preparation is a multistep process involving the construction of a portable, vacuum compatible microfluidic reactor. Mainly, soft lithography is used. The epoxy-based photoresist SU-8 molding, plasma activation of PDMS and the SiN surface bonding in a cleanroom were coupled. This process creates a microchannel $200\ \mu\text{m} \times 150\ \mu\text{m}$ enclosed in a PDMS block. The channel is covered by a 100 nm thick SiN membrane (Norcada, Edmonton, AB, Canada, $1.5 \times 1.5\ \text{mm}^2$ in area) supported by a 200 μm thick silicon frame with dimensions $7.5 \times 7.5\ \text{mm}^2$ to form the detection area (Yang et al. 2011a; Yang et al. 2011b; Yu 2020).

8.2. Sample preparation

Boehmite (APYRL AOH 60, AlOOH, Nabaltec, Schwandorf, Germany), Gibbsite (R6011, $\gamma\text{-Al(OH)}_3$, Noah Technologies, San Antonio, Texas, USA) and in-house synthesized nano-boehmite particles suspended into DI water then injected into SALVI devices for analysis. Liquid samples were prepared using DI water in the concentration of 10 $\mu\text{g/mL}$ before getting injected into the microchannel. The liquid mixture was vortexed for 1 min and sonicated for 5 min prior to analysis.

8.3. Optimization of *in situ* liquid ToF-SIMS

Optimization of *in situ* liquid ToF-SIMS has been conducted using the ToF-SIMS V spectrometer (IONTOF, GmbH, Münster, Germany) at the CNMS facility. To determine suitable primary beam and acquisition settings, approximately 1 mL of DI water was filled into the microchannel of the SALVI device. The device was then installed on a top mount sample holder and transferred into the load lock chamber of the ToF-SIMS to pump down to reach vacuum at

about 10^{-6} Torr. The device was then pushed to the main chamber for in situ analysis. The vacuum was maintained on the order of 10^{-6} Torr during data acquisition.

The base setting of the liquid SIMS is to use the Liquid Metal Ion Gun (LMIG) in fast imaging mode, where highest spatial resolution is possible. The Bi_3^+ primary ion beam was rastered onto the SiN membrane that was used to protect the liquid within the microchannel. The primary ion beam was set in the interlocked milling mode with an energy of 30 kV, beam emission current of $0.8\mu\text{A}$ and cycle time of $100\mu\text{s}$ (Yang et al. 2011a; Yang et al. 2011b; Yu 2020). The probing area was set to be $2\mu\text{m}$ in diameter circle on the SiN membrane. The beam raster pattern was in the random mode with a spatial resolution of 128 by 128 pixels. At least 200 data points were collected after the SiN membrane was punched through. The flood gun was set as 300 V during all acquisitions (Yu et al. 2016). Each sample was analyzed in five different spots in the positive ion mode and the negative ion mode, respectively, to obtain replicate data.

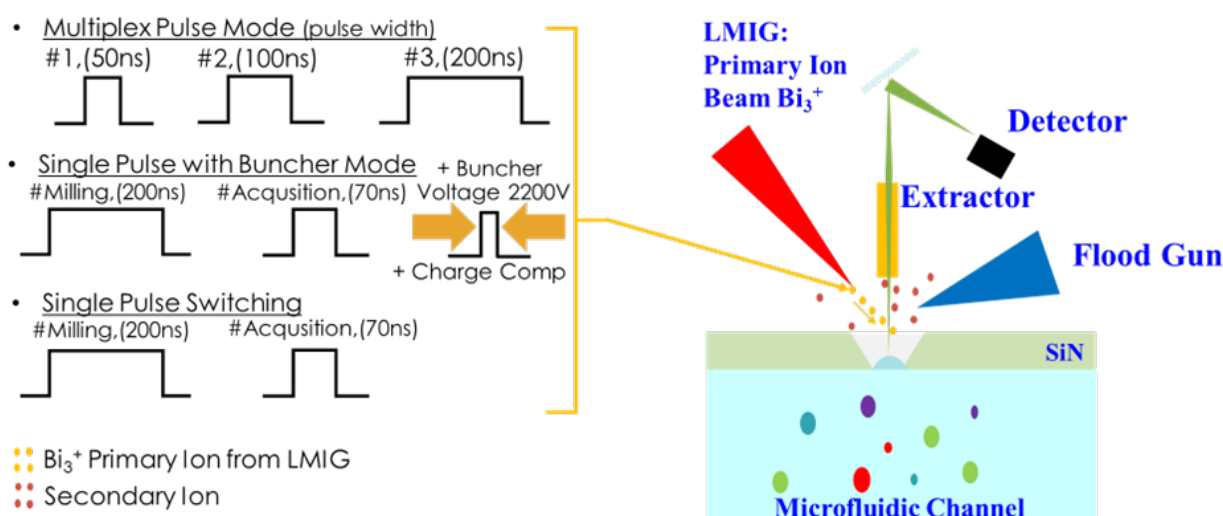


Figure 8.1. Schematics of *in situ* liquid ToF-SIMS optimization using three different modes.

The optimization of liquid SIMS was focused on primary ion beam settings, such as pulse width, single-pulse width, pulse bunching, and charge compensation (**Figure 8.1**). We utilized three different operation modes, namely, the multiplex pulse mode, single-pulse buncher mode, and single-pulse switching mode. The multiplex pulse mode contains three different primary beam pulse widths within the primary beam raster mode: 50 ns, 100 ns and 200 ns. These three different pulses were applied sequentially, allowing repeatedly rastering of the primary ion beam onto the surface during a scan. The 200 ns pulse widths were selected for SiN membrane milling, while 50 ns and 100 ns pulse beams were utilized for data acquisition. Since this mode utilized three different pulse widths sequentially, it took more than 1000 s to punch through the $2\mu\text{m}$ diameter aperture on the SiN membrane.

The single pulse with buncher mode contains very short ion pulse with increased energy through the bunching system of the time-of-flight (ToF) analyzer. The milling of the SiN membrane was done by using the 200 ns pulse width beam, which took $\sim 500 - 600\text{s}$ for the membrane punch-through. After the punch-through, the pulse width was set to 70 ns with a

buncher voltage up to 2200 V and charge compensation to -40V . The bunching system allows the reduction of the pulse width from the range of several tens of nanosecond (ns) to sub ns. As a result, the energy of the primary ion beam is increased, which reduces the lateral resolution in high-current bunched modes to a few micrometers.

The single-pulse switching mode used the 200 ns pulse width during milling and switched to the 70 ns pulse width after the punch-through for data acquisition. It took about 500 – 600 s for the SiN punch-through used the 200ns pulse width. After the punch-through, the pulse width was manually adjusted to 70 ns to acquire at least 200 data point for each sample run.

The acquired ToF-SIMS data was processed using the SurfaceLab 7.0 (IONTOF) software. Each raw data file was reconstructed based on the depth profiles (see **Figure 8.2**). Reconstructed data were calibrated using peaks $m/z^+ 12 \text{ C}^+$, $m/z^+ 18 \text{ H}_2\text{O}^+$, $m/z^+ 91 (\text{H}_2\text{O})_5\text{H}^+$, $m/z^+ 127 (\text{H}_2\text{O})_7\text{H}^+$, $m/z^+ 42 \text{ AlO}^+$, $m/z^+ 208 \text{ Al}_3\text{O}_2\text{HF}_5^+$ in the positive mode and $m/z^- 15 \text{ O}^-$, $m/z^- 35 (\text{H}_2\text{O})\text{OH}^-$, $m/z^- 71 (\text{H}_2\text{O})_3\text{OH}^-$, $m/z^- 42 \text{ AlO}_2^-$, and $m/z^- 160 \text{ Al}_3\text{O}_5^-$ in the negative mode, respectively.

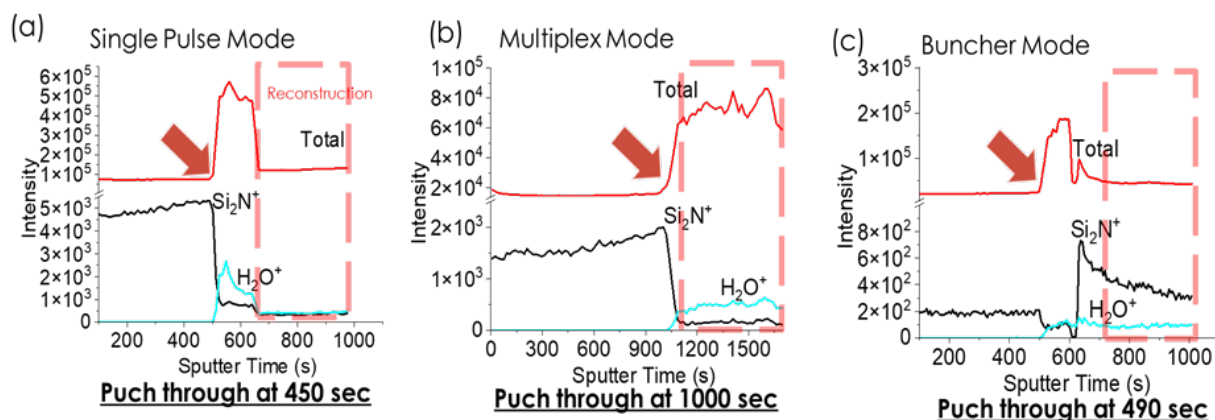


Figure 8.2. Secondary ion intensity profile comparison among (a) single pulse, (b) multiplex, and (c) buncher mode. Red profile represents the total secondary ion count. blue profile represents H_2O^+ , black profile represents Si_2N^+ . The red arrow points to the SiN membrane breakthrough point and red box represent reconstruction data range for further analysis. Of note, “Puch” in the figure should be “Punch”.

8.4. *In situ* liquid ToF-SIMS optimization using DI water

Comparisons of secondary ion intensity profiles of the single pulse, multiplex, and buncher modes were shown in **Figure 8.2**. Each profile depicted the punch-through process of the SiN, when the total secondary ion count was significantly increased as shown in all profile plots, indicating that liquid water is being detected compared to the analysis of the SiN only. The punch-through time of the single pulse and buncher mode was within 500 s while the multiplex mode took more than 1000 s. After the punch-through using the single and buncher mode, manual pulse width changed to 70 ns, causing a decreased plateau for stable data acquisition

(**Figure 8.3a-c**). The narrow pulse width was selected to improve the peak resolution and consequently the mass accuracy during data collection (Zhou et al. 2016).

Figure 8.3 shows ToF-SIMS spectral comparison of DI water acquired in three different primary ion beam modes in the positive ion mode. The SIMS spectral plot uses blue bars to mark representative water cluster peaks, such as $m/z^+ 19$ (H_2O) H^+ , $m/z^+ 37$ (H_2O) $_2\text{H}^+$, $m/z^+ 55$ (H_2O) $_3\text{H}^+$, $m/z^+ 73$ (H_2O) $_4\text{H}^+$, and $m/z^+ 91$ (H_2O) $_5\text{H}^+$ (Ding et al. 2016; Yu et al. 2020). In the mass range of $m/z^+ 0 - 200$, most water cluster peaks can be detected from all three modes (**Figure 8.3a**). However, beyond $m/z^+ 200$ mass, single pulse mode spectral results show more water cluster peaks compared to the multiplex and buncher mode (**Figure 8.3b-c**), such as $m/z^+ 217$ (H_2O) $_{12}\text{H}^+$, $m/z^+ 235$ (H_2O) $_{13}\text{H}^+$. This trend continues in a higher mass range ($m/z^+ 400 - 600$). This means single-pulse switching mode offers relatively superior spectral detection of cluster ions than the other two modes.

Interestingly, there are some newly found benefits from the buncher and multiplex modes. Buncher mode spectral data showed higher mass resolution (i.e., 1100) of $m/z^+ 553$ (H_2O) $_3\text{H}^+$ peak compared to other two modes (i.e., 200), which is a difference of five times. This is because the bunched ion beam effect offers higher mass resolution (**Figure 8.3-d**) as effective as those in static SIMS data acquisition. However, this mode has relatively lower secondary ion counts, which limits exploration of higher spectral mass range compared to other two modes using the current setting (**Figure 8.3-b, c**). The multiplex mode was less aggressive in the beam current compared to the other two modes and it provides a softer and slower milling/data acquisition process due to sequential scanning, which led to less damage on the SiN membrane and liquid volume surface during the scan. This means relatively less risk of SiN membrane rupture and liquid volume leaking through the aperture by beam damaging. However, the longer analysis time is not effective for data acquisition.

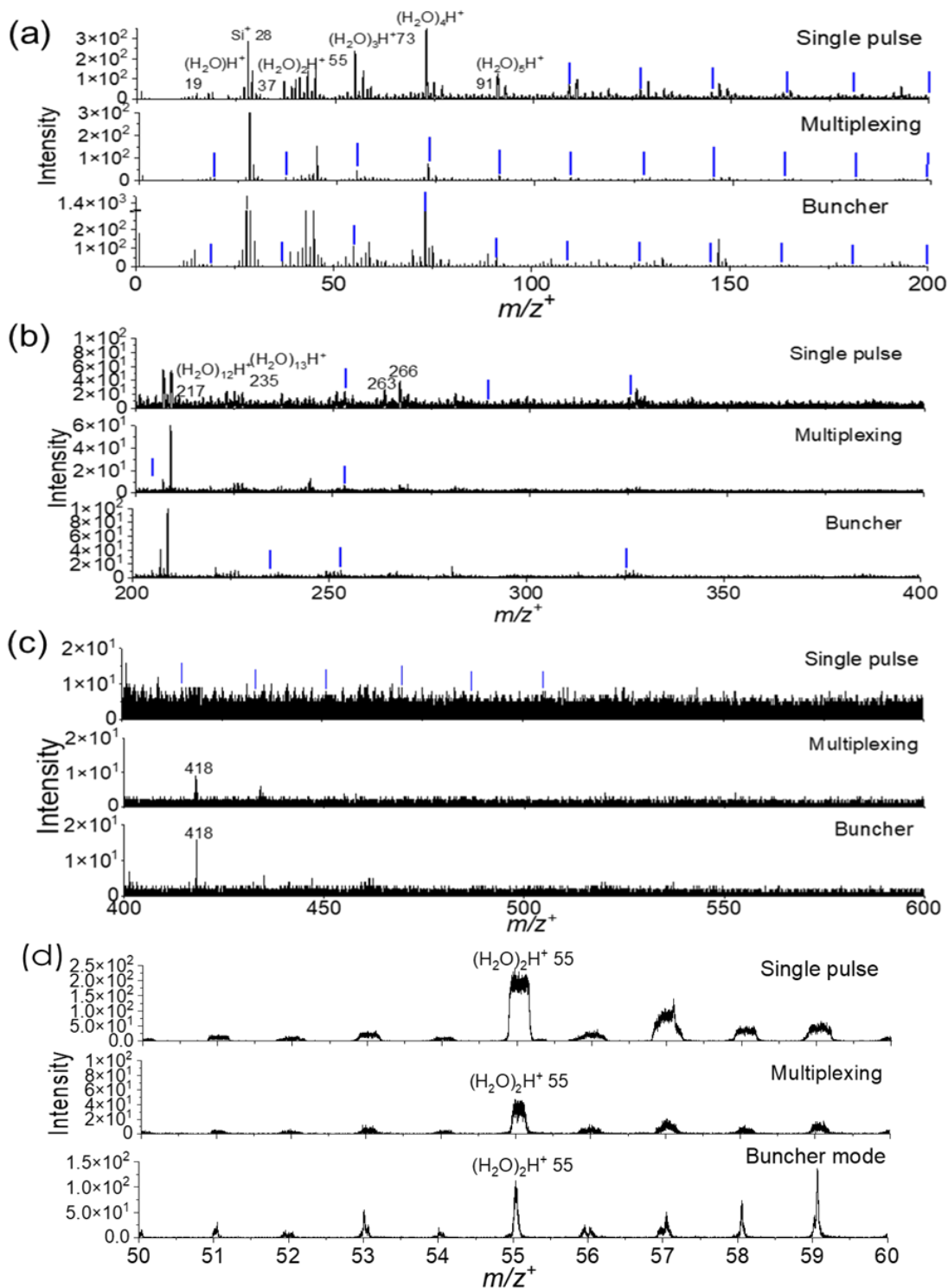


Figure 8.3. ToF-SIMS spectral data comparisons of DI water using three different primary beam modes, (a) m/z^+ 0 – 200, (b) m/z^+ 200 – 400, (c) m/z^+ 400 – 600 , and (d) m/z^+ 50 – 60 in the positive ion mode.

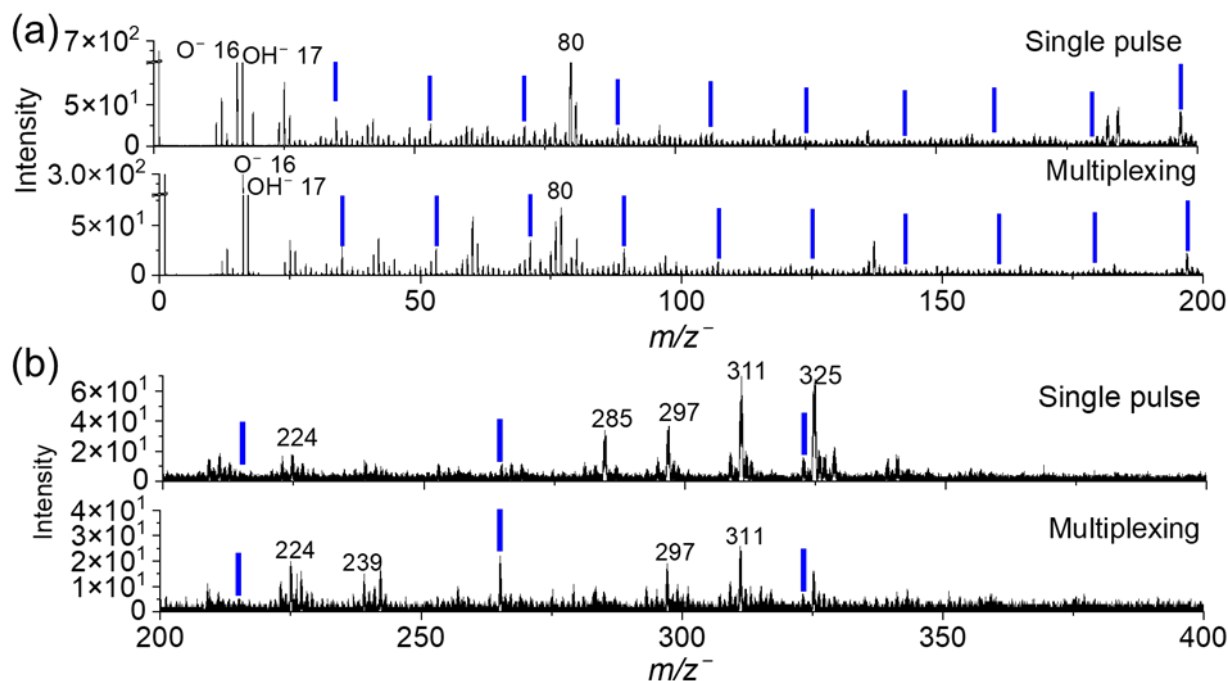


Figure 8.4. ToF-SIMS spectra data comparisons of DI water using two different primary beam modes (a) m/z^- 0 – 200, and (b) m/z^- 200 – 400 in the negative ion mode.

Figure 8.4 shows ToF-SIMS DI water spectral comparison of two different primary ion beam modes, namely single pulse and multiplexing in the negative mode. The buncher application in the negative ion mode did not work as in the positive ion mode because the negative mode generates significantly less secondary ion. Total secondary ions were insufficient to detect any prominent spectral peaks. In **Figure 8.4a-b**, each spectral plot shows detection of representative water cluster peaks (Ding et al. 2016; Yu et al. 2020), such as m/z^- 35 (H_2O) OH^- , m/z^- 53 (H_2O) $_2\text{OH}^-$, and m/z^- 71 (H_2O) $_3\text{OH}^-$. In situ SIMS spectral results from single-pulse and multiplexing modes show relatively similar detection of water cluster peaks (blue bars) and prominent peaks, such as m/z^- 80, and m/z^- 224.

Based on the DI water spectral comparisons, it is determined that the single-pulse fast-imaging mode is most suitable for more systematic studies of the key tank waste components such as boehmite and gibbsite within this task.

8.5 *In situ* liquid ToF-SIMS analysis of boehmite and gibbsite

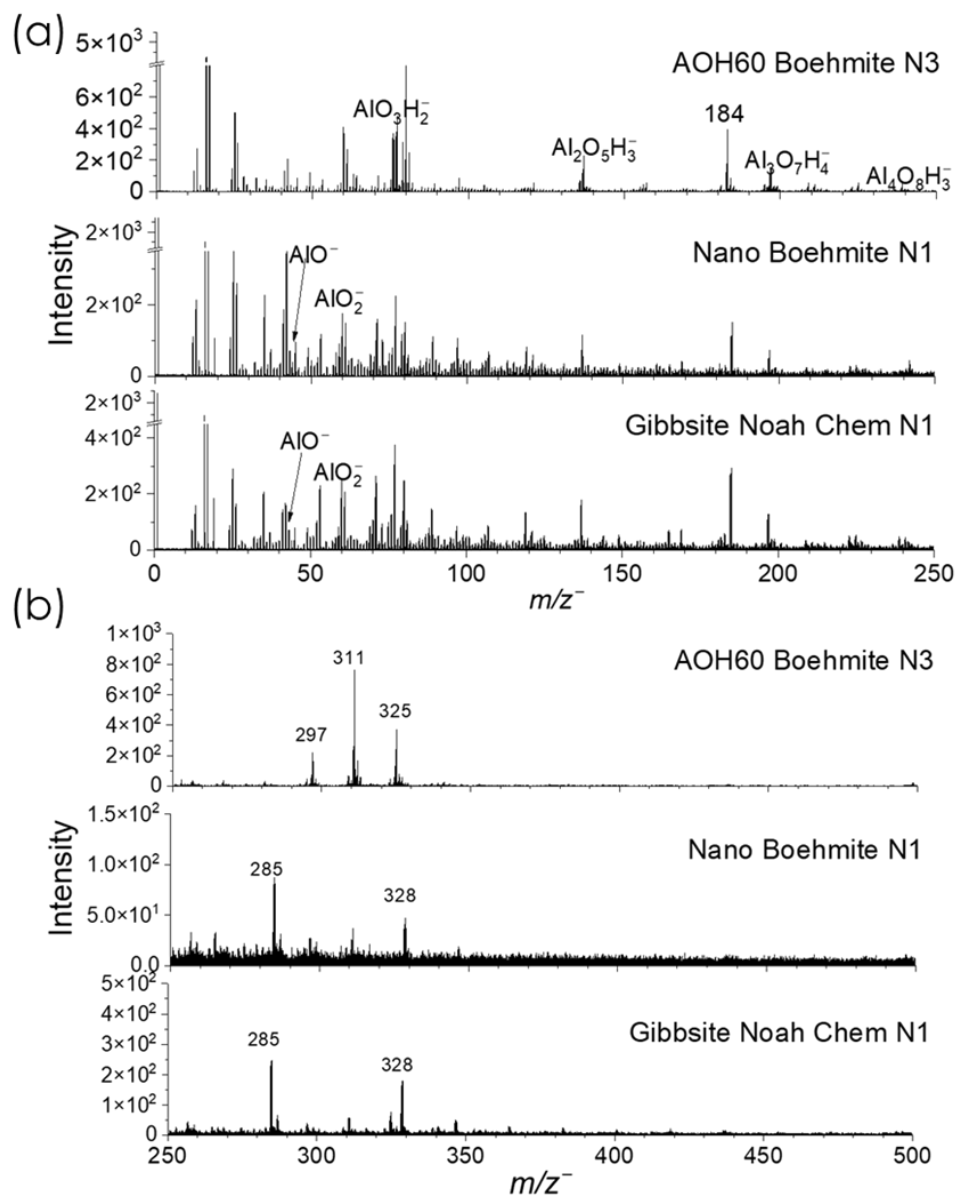


Figure 8.5. *In situ* liquid ToF-SIMS spectral comparisons of AOH 60, nano-boehmite, and gibbsite, (a) m/z^- 0 – 250, and (b) m/z^- 250 – 500 in the negative ion mode.

We used the optimized single-pulse mode setting to study commercial boehmite, gibbsite, and nano-boehmite particles dissolved in DI water at natural pH. **Figure 8.5** shows *in situ* liquid ToF-SIMS negative mode spectra of the commercial boehmite, gibbsite, and nano-boehmite. Peaks such as m/z^- 43 AlO^- and m/z^- 59 AlOO^- appeared in nano boehmite and commercial gibbsite. However, they are missing in the commercial boehmite, namely AOH60, spectra. There are also prominent peaks such as m/z^- 285 and 328, from nano-boehmite and commercial gibbsite; while AOH60 spectrum shows m/z^- 297, 311, and 325. This kind of prominent similar

and different peaks could offer more understanding of the different phases of aluminum hydroxide with different crystal structure in the simulated waste conditions.

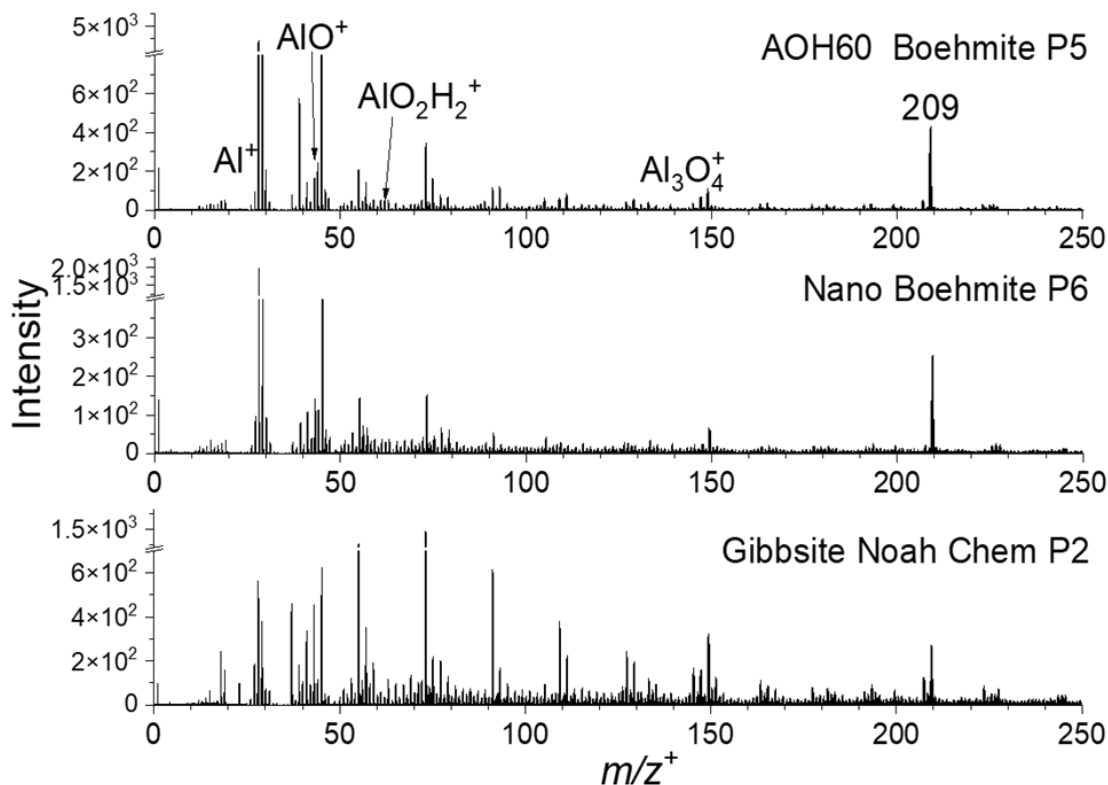


Figure 8.6. ToF-SIMS spectral comparisons of AOH 60 boehmite, nano-boehmite, and gibbsite in the range of m/z^+ 0 – 250 in the positive ion mode.

Figure 8.6 shows *in situ* liquid ToF-SIMS spectra of boehmite, nano-boehmite, and gibbsite in the range of m/z^+ 0 – 250 in the positive ion mode. Peaks such as m/z^+ 43 AlO^+ , m/z^+ 61 $AlO_2H_2^+$, and m/z^+ 144 $Al_3O_4^+$ are observed. These prominent peaks can be used to distinguish characteristics of different phases of aluminum hydroxide in the dissolved state.

Table 8.1. A selected peak list of *in situ* liquid SIMS of boehmite in the position ion mode.

¹ m/z^+_{theo}	² $m/z^+_{obs.(amu)}$	Species	Note	Reference
19.0183	19	(H ₂ O)H ⁺	Water Cluster	Yu et.al. 2020 ³⁰
26.9815	27	Al ⁺	Boehmite	Verdier et al. 2007 ²³
27.9769	28	Si ⁺	Silicon	This work
42.9764	43	AlO ⁺	Boehmite	Verdier et al. 2007 ²³
55.0395	55	(H ₂ O) ₃ H ⁺	Water Cluster	Yu et al. 2020 ³⁰
73.05	73	(H ₂ O) ₄ H ⁺	Water Cluster	Yu et al. 2020 ³⁰
91.0606	91	(H ₂ O) ₅ H ⁺	Water Cluster	Yu et al. 2020 ³⁰
145.932	146	AlOOH(AlO) ₂ ⁺	Boehmite	This work
217.135	217	(H ₂ O) ₁₂ H ⁺	Water Cluster	Yu et al. 2020 ³⁰
235.145	235	(H ₂ O) ₁₃ H ⁺	Water Cluster	Yu et al. 2020 ³⁰

Note: m/z^+ represents the mass-to-charge ratio for positively charged ions

¹ m/z^+_{theo} represents the theoretical mass to charge ratio

² $m/z^+_{obs.(amu)}$ represents the observed mass to charge ratio represented in atomic mass unit form.

All peak identification are possibilities identified by SurfaceSpectra software.

Table 8.1 lists selected prominent peaks related to water clusters and dissolved boehmite observed in the *in-situ* liquid ToF-SIMS spectral analysis in the positive polarity. Spectral results provide evidence of water clustering of (H₂O)_x where x = 2 to 13. Also observed are boehmite clusters, for example aluminum oxide cluster (AlO)₂ at m/z^+ 146.

Table 8.2. A selected peak list of *in-situ* liquid SIMS of boehmite in the negative ion mode.

¹ m/z^-_{theo}	² $m/z^-_{obs.(amu)}$	Species	Note	Reference
15.9949	16	O ⁻		-
17.0027	17	OH ⁻		-
35.0133	35	(H ₂ O)OH ⁻	Water Cluster	Yu et.al. 2020 ³⁰
53.0238	53	(H ₂ O) ₂ OH ⁻	Water Cluster	Yu et.al. 2020 ³⁰
71.0344	71	(H ₂ O) ₃ OH ⁻	Water Cluster	Yu et.al. 2020 ³⁰
76.9819	77	AlO(OH) ₂ ⁻	Boehmite	This work
118.9505	119	Al ₂ O ₃ ·OH ⁻	Boehmite	This work
136.9611	137	Al ₂ O ₃ ·H ₂ OOH ⁻	Boehmite	This work
193.0080	193	AlO·AlOOH·(H ₂ O) ₅ ⁻	Boehmite	This work

Note: m/z^- represents the mass-to-charge ratio for negatively charged ions

¹ m/z^-_{theo} represents the theoretical mass to charge ratio

² $m/z^-_{obs.(amu)}$ represents the observed mass to charge ratio represented in atomic mass unit form.

All peak identification are possibilities identified by SurfaceSpectra software.

Table 8.2 gives a summary of several prominent peaks related to water clusters and dissolved boehmite that were observed in the *in situ* liquid ToF-SIMS spectral analysis in the negative ion mode. The liquid SIMS spectral analysis provides evidence of water clusters, for

instance $(\text{H}_2\text{O})_x$ where $x = 2$ to 3 . Also observed are peaks indicative of boehmite clusters with aluminum hydroxide and hydroxide in water. Both **Table 8.1** and **Table 8.2** provide peak identification of molecular interactions of the boehmite dissolution and interactions with the water solvent at the molecular level using advanced in situ liquid ToF-SIMS.

In this subtask, *in situ* liquid ToF-SIMS was used to acquire spectral analysis of compositional evolution of aluminum containing components in water. We used DI water to determine the optimal conditions of in situ liquid ToF-SIMS using the CNMS ToF-SIMS instrument, which has different configurations from a previous instrument used to invent this technology. The primary beam conditions were varied to collect spectral data and secondary ion intensity profile data. In situ SIMS spectral data were processed and compared to determine the optimal condition. Using the optimized conditions, boehmite and gibbsite dissolved in DI water were studied to confirm detection of molecular ions and study dissolution. Compared to VUV SPI-MS (Sui et al. 2024; Sui et al. 2021; Sui et al. 2025), *in situ* ToF-SIMS spectral analysis offers different yet complementary mass spectral characteristics. The observed differences arise due to different ionization and detection sensitivities between the two techniques.

9. *Ex Situ* Multimodal Imaging and Analysis of Al-Bearing Phases: Synthesis and Characterization of Nanoboehmite

9.1. Experimental procedure

The synthesis of boehmite nanoparticles was conducted using a hydrothermal synthesis technique adopted from reports by Zhang *et al.* (Zhang *et al.* 2018a; Zhang *et al.* 2018b). Prior to synthesis, a 1 M NaOH solution was prepared by dissolving NaOH pellets (ACS reagent, $\geq 97\%$, MilliporeSigma) in deionized (DI) water. Similarly, a 0.25 M $\text{Al}(\text{NO}_3)_3$ solution was prepared by dissolving $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (ACS reagent, $\geq 98\%$, MilliporeSigma) in DI water. DI water required for synthesis was filtered with a Milli-Q water purification system (Merck KGaA, Darmstadt, Germany), and pH measurements were recorded using a Thermo Scientific Orion Star A215 digital pH probe. As a precautionary measure, the aluminum nitrate solution was stored in a glass bottle covered with aluminum foil to prevent light-induced degradation.

The sodium hydroxide solution was used to titrate 78 mL of aluminum nitrate solution until the pH reached 10. The resulting solution was allowed to stir while being covered for one hour. $\text{Al}(\text{OH})_3$ gel-like precipitates that formed were collected from the solution via centrifugation at 5000 rpm for 5 minutes. Excess salts were removed by washing the gel precipitates three times with DI water. The precipitates were resuspended in deionized water, and a diluted 1 M sodium hydroxide solution (pH 12) was used to titrate the suspension to pH 10. The suspension was then loaded into two 45 mL Teflon lined stainless steel autoclaves. Both autoclaves were sealed before being secured in a rotary oven set to 200 °C and 10 rpm for 48 hrs. After heating, the autoclaves were placed in a 1-gal utility bucket filled with room-temperature water for cooling overnight. The solids recovered from the vessels were dried in an electric oven at 90 °C for 72 hours before being transferred into storage vials. Synthesis conducted with a total of 0.53 g of aluminum yields roughly 7.60 g of boehmite solids. **Figure 9.1** displays an overview of experimental procedures.

9.2. Analysis of synthesized nanoboehmite

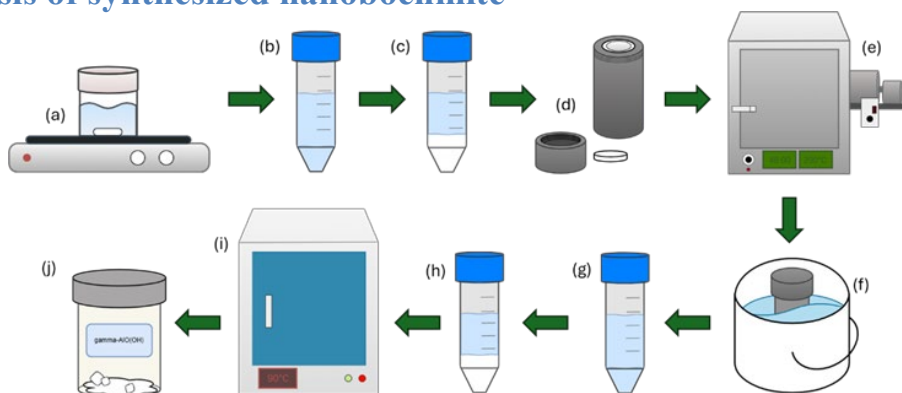


Figure 9.1. Schematic showing the steps of hydrothermal synthesis of boehmites as follows: (a) mixing, (b) transfer, (c) centrifuge and wash, (d) titrate and transfer, (e) heat, (f) cool, (g) transfer, (h) centrifuge and wash, (i) dry, and (j) store.

Two distinct sample preparation methods were utilized in preparation for SEM and ToF-SIMS analysis. Silicon wafer chips, with an area of $1 \times 1 \text{ cm}^2$ and $500 \text{ }\mu\text{m}$ thickness taken from a 100 mm diameter silicon (Si) wafer (P type, (100) crystal orientation, one side polished, UniversityWafer, Inc., Massachusetts, United States) were sterilized. The first method created a suspension of synthesized boehmite powder in DI water ($10 \text{ }\mu\text{L}/\text{mg}$) by vertexing and drop-casting the mixture onto a sterile Si wafer to form a uniformly distributed coating of material (Strange et al. 2022a; Strange et al. 2022b). The second method entailed directly applying the dry powder to double sided carbon tape dot on a Si wafer. All wafers were then fixed into a back mount holder. The commercially available boehmite in a powdered form was sourced from Nabeltec (200SM, Nabaltec GmbH, Schwandorf, Germany) and utilized as a control group against which to compare the synthesized material to. The commercial boehmite sample was prepared by drop-casting a powder slurry ($5 \text{ mg}/\text{mL}$) onto sterile silicon wafers, which were then transferred into the back-mount holder for analysis (Strange et al. 2022a; Strange et al. 2022b).

Samples required for TEM analysis were prepared-by drop casting a particle-containing solution composed of synthesized boehmite particles suspended in DI water onto a TEM grid. The deposited solution dried on the grid prior to imaging.

9.2.1. SEM analysis

SEM images of boehmite samples were obtained with a Zess Merlin SEM (Carl Zeiss AG, Oberkochen, Germany) utilizing 5 kV electron high tension and a 6.4 mm working distance. The magnification required to differentiate individual nanoparticles was 127.87 KX (Yu et al. 2019).

9.2.2. TEM analysis

STEM imaging and energy dispersive X-ray spectroscopy (STEM-EDS) was performed using a FEI Talos F200X S/TEM operated at 200 kV (Thermo Fisher Scientific Inc., Massachusetts, United States). Bitmap images were uploaded to ImageJ 1.54p 2025 software to perform particle size analysis. The measurements were exported as a CSV file before the data was imported and plotted with OriginPro 2024. The CSV file was also imported to Excel® to perform additional statistical analysis.

9.2.3. ToF-SIMS analysis

Prepared sub micrometer boehmite samples were back mounted and loaded into the main ToF-SIMS (IONTOF ToF-SIMS V, IONTOF GmbH, Münster, Germany) chamber after the instrument reached $3.1 \times 10^{-8} \text{ mbar}$. Static ToF-SIMS spectral data was acquired using an IONTOF ToF-SIMS V (IONTOF GmbH, Münster, Germany) with a 30keV Bi_3^+ primary ion beam rastered over an area of $500 \times 500 \text{ }\mu\text{m}^2$ with 60 scans per spectrum and 128×128 spectral pixel resolution. The Bi_3^+ beam was $5 \text{ }\mu\text{m}$ in diameter with a current of 30.8 nA. The extraction cone had bias of -21V and 0V for the negative and positive spectra, respectively. The filament current of the flood gun remained at 2.35A for both spectral modes.

Calibration and peak identification ToF-SIMS data were performed using IONTOF SurfaceLab v7 software. Calibration of the negative mass spectra data included m/z^- 18.9990 F^- , m/z^- 24.0005 C_2^- , m/z^- 31.9904 O_2^- , m/z^- 14.0162 CH_2^- , m/z^- 58.9719 AlO_2^- , and m/z^- 118.9511 $Al_2O_4H^-$, while the positive mass spectra data was calibrated with m/z^+ 1.0073 H^+ , m/z^+ 22.9892 Na^+ , m/z^+ 26.9810 Al^+ , m/z^+ 27.9888 AlH^+ , m/z^+ 60.9865 $AlO_2H_2^+$, and m/z^+ 69.9574 Al_2O^+ . Peak identification was carried out by utilizing features suggesting mass formulas that aligned with observed peaks and the analyst's knowledge of the analytes. Mass formulas assigned through the systems suggestions did not exceed a mass deviation of 65 ppm. The data was then exported as ASCII files before getting plotted in OriginPro 2024 software. Data from the SIMS spectral analysis of peak areas and heights was exported to Excel® prior to arriving at the summary of peak identification.

9.2.4. X-Ray Diffraction Analysis

XRD analysis was conducted using a Rigaku SmartLab X-ray diffractometer with a HyPix-3000 Hybrid Pixel 2-Dimensional detector and Cu radiation source (Rigaku Holdings Corporation, Akishima-shi, Tokyo). The instrument performed a 1-Dimensional scan with a $K\beta$ filter for 1D Cu with an intensity ratio of 2:1 $K\alpha_1:K\alpha_2$. Characteristic X-ray wavelengths include 1.54056 Å for λ_1 and 1.54439 Å for λ_2 . Raw XRD data was exported as an XY file to be refined and analyzed using Materials Analysis Using Diffraction (MAUD) 2.999 2023 software in conjunction with the Crystallography Open Database (COD). Refined data was then exported as CSV file and transferred to OriginPro 2024 software for graphing and Gaussian data analysis.

9.3. Multimodal *ex-situ* characterization

9.3.1. SEM

Scanning electron (SE) images of the boemite nanoparticle sample fixed with carbon tape were obtained. **Figure 9.2** provides estimates of individual particle diameter from 39 – 90 nm. One of the most notable crystalline features is the range of shape from orthorhombic nanoparticles to nanorods. When compared to literature findings, the particles observed here are larger than the anticipated 35 nm particle diameter expected based on hydrothermal synthesis conditions (Strange et al. 2022a; Strange et al. 2022b; Zhang et al. 2018a; Zhang et al. 2018b). The deviation in particle size can be attributed to slight variations in experimental methodology, including pH, heating duration, and heating temperature, which affects the size and shape of nanoparticles.

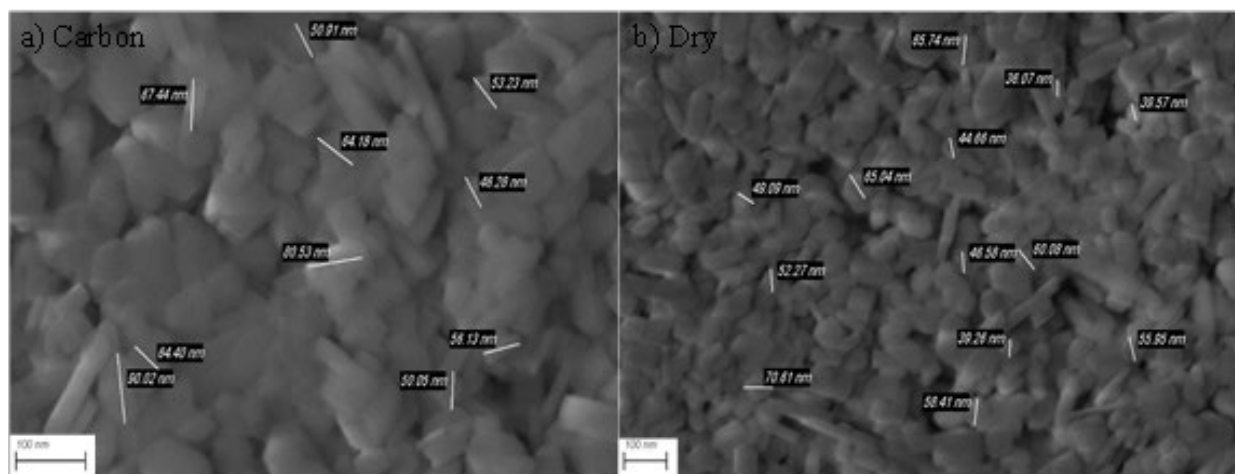


Figure 9.2. SEM images of boehmite nanoparticles acquired on carbon tape (a) and dry cast (b).

9.3.2. TEM

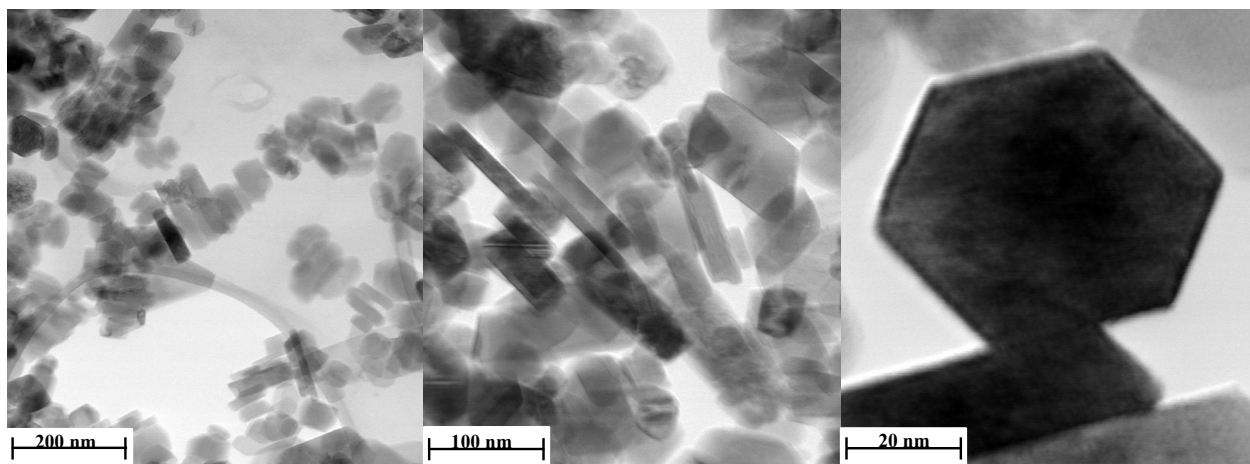


Figure 9.3. TEM images of boehmite nanoparticles.

TEM images (**Figure 9.3**) and EDX mapping provide additional information regarding particle size and elemental distributions. **Figure 9.4** shows the size distribution of the nanoparticles present in **Figure 9.3**. The particle size data was fitted using a single modal normal distribution. Particle sizes ranged from 12.31 – 192.00 nm, with an average size of 57.06 nm and a standard deviation of 26.42 nm. The higher magnification capability of TEM enabled the detection of smaller particles that were difficult to observe using SEM. EDX analysis shown in **Figure 9.5** highlights the abundance of aluminum and oxygen within the sample, supporting ToF-SIMS spectral findings that the synthesized nanoparticles have Al and O as main components of boehmite.

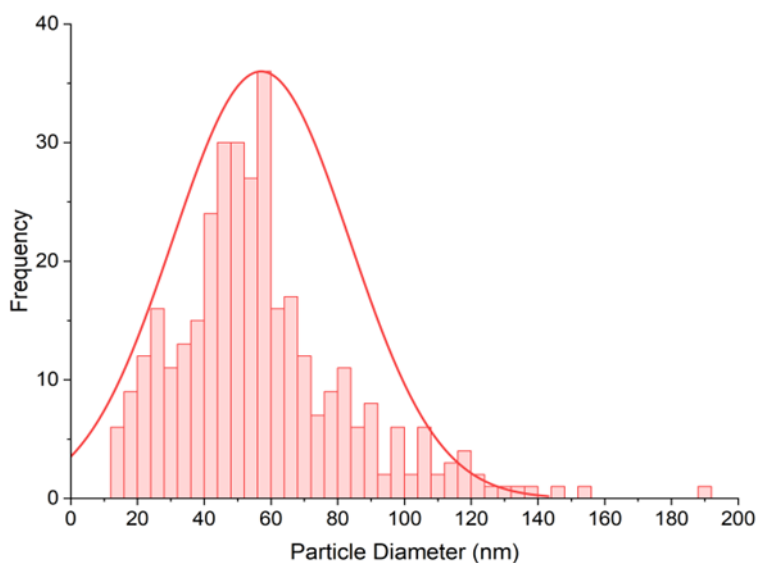


Figure 9.4. Boehmite nanoparticle size distribution.

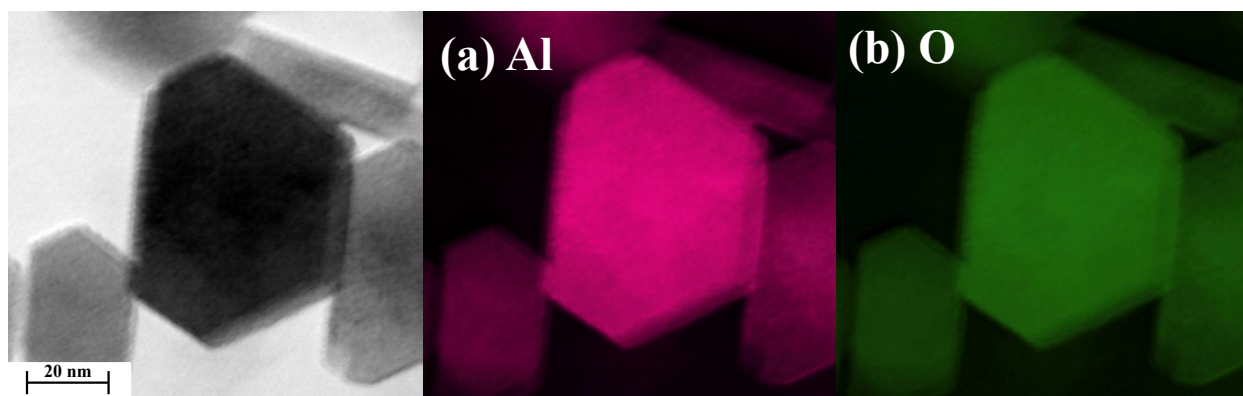


Figure 9.5. EDX mapping images of (a) aluminum and (b) oxygen presence in the boehmite sample.

9.3.3. ToF-SIMS

Secondary ion (SI) images collected with ToF-SIMS show the spatial distribution of chemical compounds in the boehmite samples prepared via carbon tape and dry-casting (**Figure 9.6**). Negatively charged ions identified in the images include m/z^- 26.9821 Al^- , m/z^- 42.9761 AlO^- , m/z^- 59.9759 AlO_2H_4^- , and m/z^- 119.9765 $\text{Al}_2\text{O}_4\text{H}^-$. A higher abundance of aluminum containing ions can be viewed in the dry cast sample. These ions are less present and not as evenly distributed between carbon compounds the sample prepared with carbon tape, indicating that ToF-SIMS spectra results are more complex to interpret in confirming the presence of boehmite due to interferences from carbon.

Figures 9.7 and **Figure 9.8** display stacked ToF-SIMS spectral datasets corresponding with the different sample preparation methods used. The comparison illustrates a closer correlation between the boehmite sample prepared via suspension and the commercial data. Similarly, the sample prepared with carbon tape was compared against the commercial boehmite. When examining the normalized mass spectra of the suspension-based sample and commercial data between $m/z^{+/+} 20 - 70$ in **Figures 9.9** and **Figure 9.10**, there is a strong agreement of $m/z^{+} 26.9810 \text{ Al}^{+}$, $m/z^{+} 43.9837 \text{ AlOH}^{+}$, $m/z^{+} 60.9865 \text{ AlO}_2\text{H}_2^{+}$, $m/z^{-} 42.9770 \text{ AlO}^{-}$, $m/z^{-} 58.9719 \text{ AlO}_2^{-}$, and $m/z^{-} 59.9797 \text{ AlO}_2\text{H}^{-}$ for prepared boehmite particles and commercial ones (Strange et al. 2022a; Strange et al. 2022b). The observed spectral agreement verifies the successful hydrothermal synthesis of boehmite.

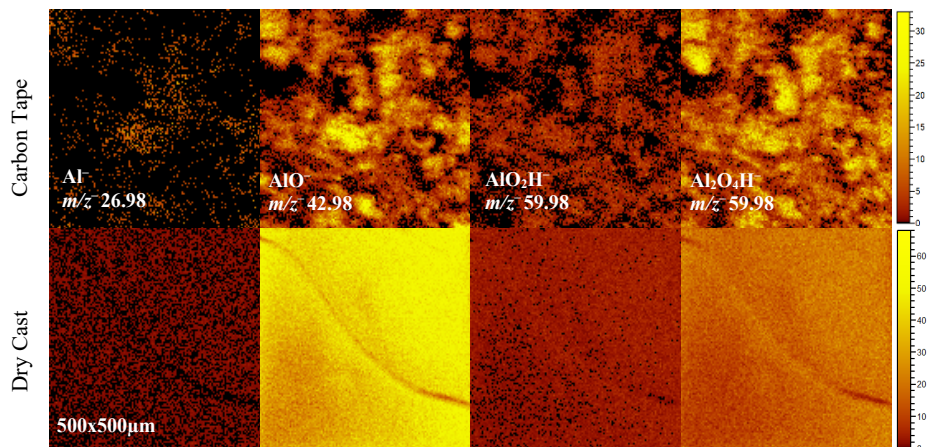


Figure 9.6. Negative SI images of Al^{-} , AlO^{-} , AlO_2H^{-} , and $\text{Al}_2\text{O}_4\text{H}^{-}$ in the boehmite samples prepared with carbon tape (a) and dry-casting (b), respectively.

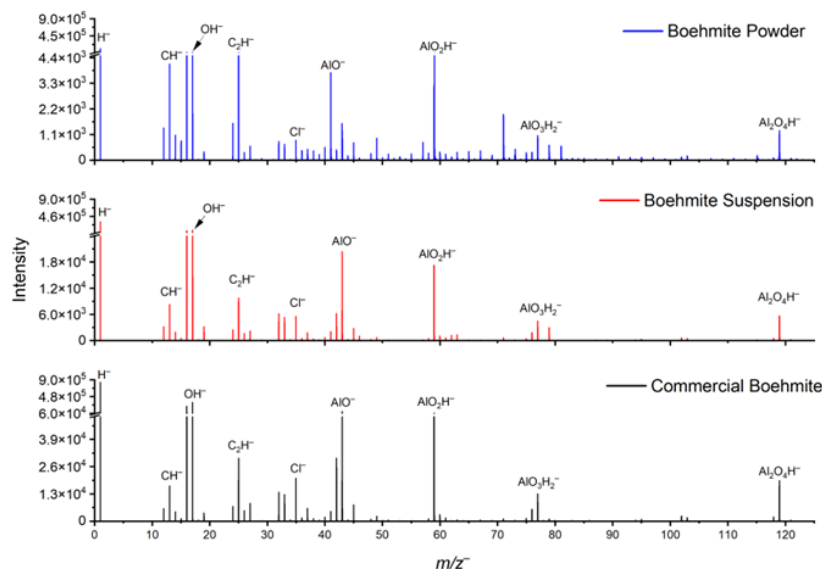


Figure 9.7. ToF-SIMS negative mass spectral comparison of synthesized boehmite samples prepared using dry powder (blue) and by a suspension (red) to commercial boehmite (black).

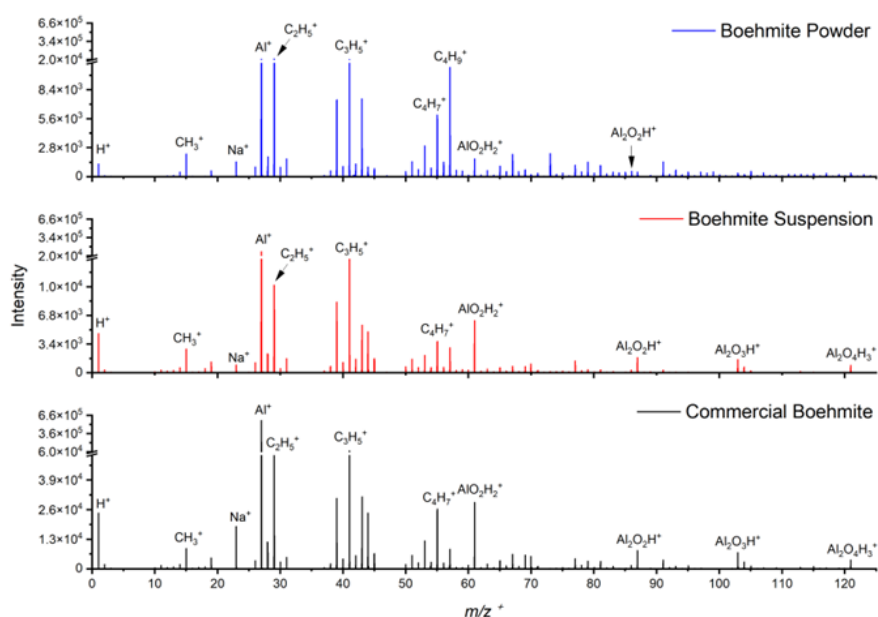


Figure 9.8. ToF-SIMS positive mass spectral comparison of synthesized boehmite samples prepared using dry powder (blue) and by a suspension (red) to commercial boehmite (black).

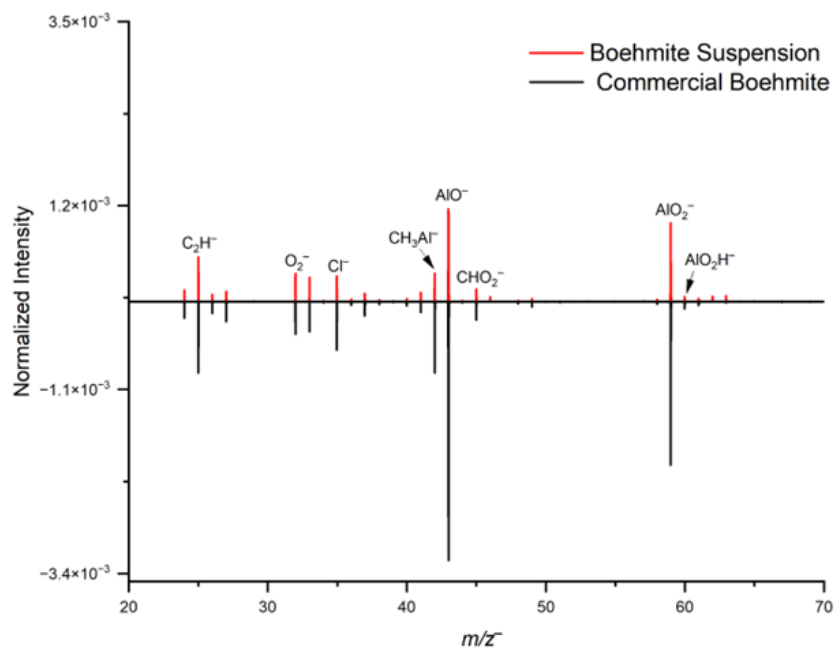


Figure 9.9. ToF-SIMS negative mass spectral comparison between the suspended synthesized boehmite (red) and the commercial boehmite (black).

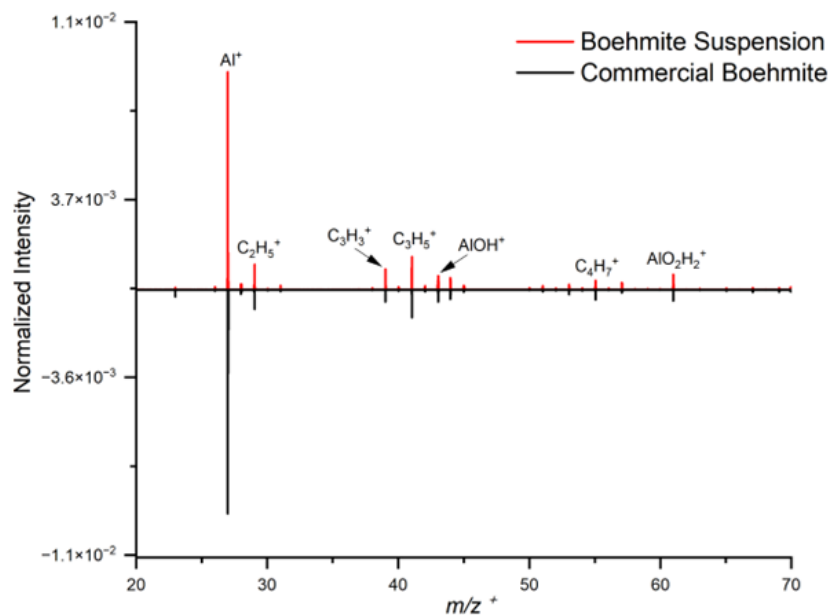


Figure 9.10. ToF-SIMS positive mass spectral comparison between the suspended synthesized boehmite (red) and the commercial boehmite (black).

9.3.4. XRD

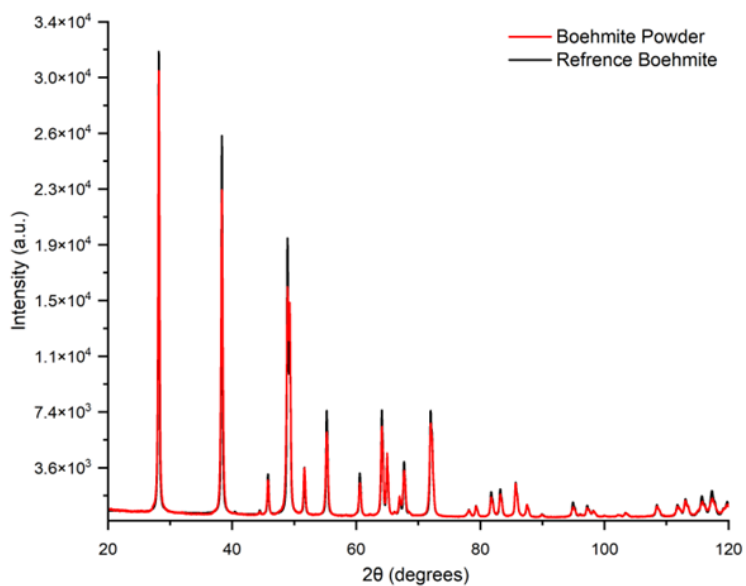


Figure 9.11. XRD comparison of powdered boehmite (red), and reference boehmite (black).

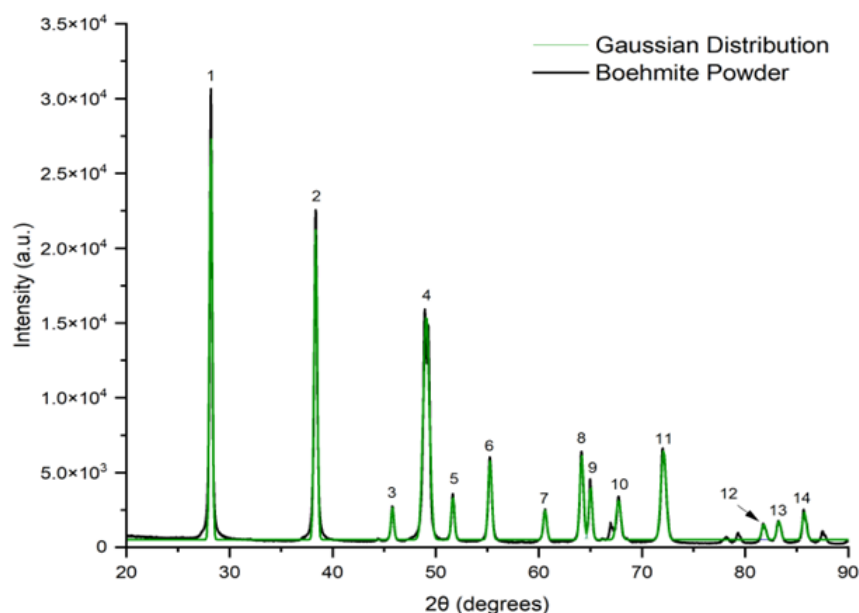


Figure 9.12. XRD comparison of Gaussian distribution fit (green) and powdered boehmite (black).

The XRD data collected from the synthesized particles shown in **Figure 9.11** was compared to reference patterns available in the COD, specifically entry 9012253, which corresponds to boehmite synthesized under similar hydrothermal conditions.³⁵ The strong agreement between the two data sets is indicated by a low weighted profile R-factor (RWP) of 15 and all characteristic peaks present in the synthesized boehmite sample. This result confirms that the dominant crystal structure of the material is orthorhombic.

An analysis of crystal size from XRD data was performed using Gaussian peak fitting and the Scherrer equation. Gaussian fitting was conducted with OriginPro's Peak Analyzer to determine the Full Width at Half Maximum (FWHM) of each peak. The resulting FWHM values were then applied to the Scherrer equation to obtain a rough estimate of crystal size. An analysis of crystal size with XRD data was performed using Gaussian peak fitting (Eqn. (7.1)) and the Scherrer equation (Eqn. (9.2)) (Patterson 1939). The Gaussian fitting shown in **Figure 9.12** was conducted with OriginPro's Peak Analyzer to determine the full width at half maximum (FWHM) of each peak as follows,

$$y = y_0 + \frac{A}{\beta \sqrt{\frac{\pi}{4 \ln(2)}}} \exp\left(-\frac{4 \ln(2)(x-x_c)^2}{\beta^2}\right) \quad \text{Eqn. (9.1)}$$

where y is intensity, y_0 is the initial intensity of the Gaussian curve, A is area under the Gaussian curve, x is the diffraction angle, x_c is the diffraction angle at the peaks center, and β is the

FWHM. The resulting FWHM values were then applied to the Scherrer equation (Eqn. (9.2)) to obtain a rough estimate of crystal size,

$$D = \frac{K\lambda}{\beta \cos(\theta)} \quad \text{Eqn. (9.2)}$$

where D is the mean size of the crystalline domains is, K is the Scherrer coefficient, λ is the X-ray wavelength, and θ is half of the diffraction angle (Yang et al., 2011). The Scherrer equation is only suitable for obtaining an accurate estimate of crystal sizes below 100 – 200 nm range and the FWHM and diffraction angle data must be in radians (Holzwarth & Gibson 2011). Crystalline size calculations were performed in Excel® utilizing a Scherrer coefficient of 0.9 and wavelength of 1.54056 Å. The results from the calculations estimated the crystal size to be between 12 – 28 nm. Compared to the SEM and TEM analysis, the estimate found with FWHM is lower than particles observed in the SEM images. Boehmite crystallite size obtained from diffraction data only accounts for undisturbed crystal lattices in individual crystals.⁴ For example, SEM and TEM images show individual nanoparticles which consist of one or more crystallites, indicating that the size measured by SEM and TEM is expected to be higher than that determined by XRD.

9.4. Conclusion

Successful hydrothermal synthesis of boehmite was confirmed via ToF-SIMS and XRD characterization. SEM and TEM data allow for the imaging of individual particle sizes and crystal structure. ToF-SIMS analysis of the synthesized particles confirms that the chemical profiles align with the commercial boehmite. XRD analysis confirms the presence of an orthorhombic crystal structure, representative of boehmite.

10. *In Situ* SEM Imaging of Particles in Slurry Conditions

This task will provide critical information about particle size distribution and aggregation that can be used to constrain a constitutive relationship for the rheological properties of waste slurry. Such information will be needed for modeling particle settling, consolidation, and salt crust movement in waste pretreatment. Particle size and aggregation affect the dissolution of boehmite, which is assumed to be the rate-limiting step in the aluminum dissolution process (Peterson et al. 2018). Particle size and aggregation also control the rheological properties of waste slurry in waste processing (Yu et al. 2019). Boehmite has been a good model system to understand the dispersity and rheological properties of the waste slurry that depends on surface and solution chemistry, although its platelet-like shape imposes a challenge for *in situ* measurements and modeling. *In situ* liquid scanning electron microscopy (SEM) offers the advantage of imaging particles in the liquid medium directly, providing more insights on systems by observing particle dispersity compared to the conventional SEM analysis of static particle shape, size, and morphology in a dry vacuum environment. We performed *in situ* liquid SEM and image analysis to study hard crust formation, particle aggregation, and settling behavior of Al-bearing phases under the conditions that closely match Hanford Tank Waste using the SALVI device.

10.1. SALVI fabrication

SALVI is a microfluidic reactor device with vacuum compatibility (Yang et al. 2011a; Yang et al. 2011b). The fabrication process of SALVI is entirely conducted in a cleanroom environment. The microfluidic channel structure was fabricated with SU-8 molding and PDMS prototyping. This process creates a microchannel of 200 μm wide $\times$ 150 μm depth $\times$ 5 mm long enclosed in a PDMS block. The PDMS piece was cut out from the SU-8 mold and plasma bonded to the 100 nm thick silicon nitride (SiN) membrane (Norcada, Edmonton, AB, Canada, $1.5 \times 1.5 \text{ mm}^2$ in area). Two ports were used as inlet and outlet of the microfluidic channel (Supelco, Bellefonte, PA, USA, 15 cm long, 1.58 mm O.D. $\times$ 0.5 mm I.D.). A set of PEEK union is used for sealing up the tubing which makes it a closed loop system. The fabricated SALVI device was graphite coated for 15 nm thick to reduce surface charging during the *in situ* liquid SEM analysis.³⁴

10.2. Sample preparation

We utilized commercial boehmite (AlOH60 Nabaltec, Schwandorf, Germany), commercial synthetic boehmite (ACTILOX 200SM, Nabaltec, Schwandorf, Germany), and in-house synthesized nano-boehmite (see section 4). Boehmite particles were suspended into DI water with a concentration of 10 $\mu\text{g/mL}$. The liquid mixtures were vortexed for 1min and sonicated for 5min before loading into a SALVI device.

10.3. Instrument information

In situ SEM imaging of boehmite particles in DI water was performed using plasma focused ion beam (PFIB) - SEM (Thermos Scientific Helios 5 Hydra UX Dual Beam Multiple Ion Plasma FIB/SEM, USA) at ORNL CNMS. A series of apertures of 1 μm in diameter were milled using the focused ion beam and they are spread 100 μm apart each other. The Xe ion beam energy was 30 kV and the current was 1 nA with a 900 ms dwell time. The inner diameter of the aperture was roughly 1 μm diameter after milling. The working distance was 4.1 mm. The stage was 52° tilted to accommodate the PFIB angle. After milling, secondary electron (SE) images were taken in the aperture area using the following settings: 5 kV electron beam energy, 50,000 times magnification, and 0.1 nA beam current.

10.4. Optimizing *in situ* liquid SEM

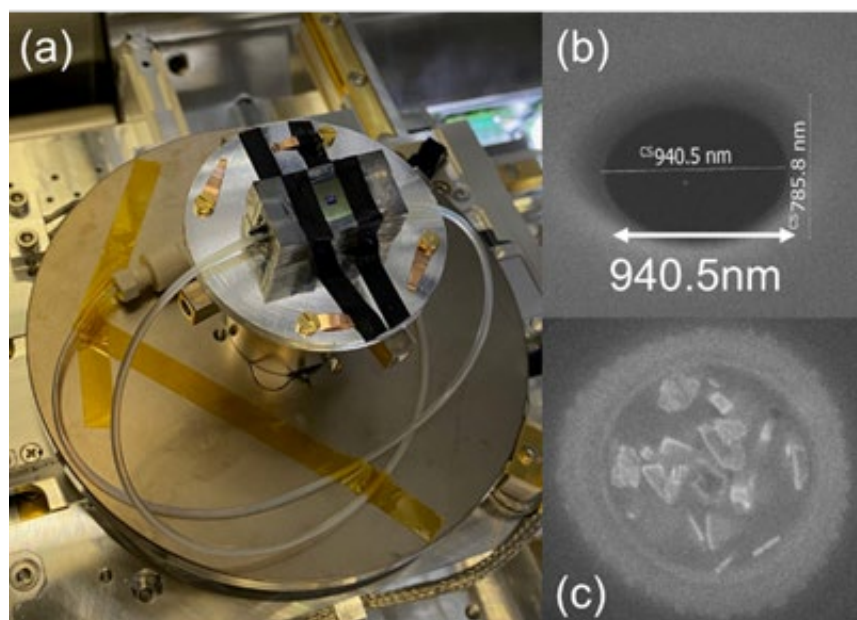


Figure 10.1. *In situ* liquid SEM imaging: (a) a liquid loaded SALVI device mounted on the PFIB-SEM sample chamber, (b) PFIB milled aperture on the SiN membrane, and (c) an SE image of boehmite particles (200SM) in the aperture.

During an *in situ* liquid SEM experiment, graphite coated empty SALVI devices were first placed onto the SEM sample holder with carbon double tapes to prepare for milling apertures (**Figure 10.1a**). Using the PFIB, 17 apertures, each 1 μm in diameter, were milled in the middle of microchannel side SiN membrane (**Figure 10.1b**). After obtaining milled apertures, the SALVI cell was pulled out of the main chamber and boehmite particles in DI water were injected using a syringe. Then, the loaded SALVI cell was set to return to high vacuum.

SE images were taken on top of each aperture to identify individual boehmite particles and measure their size (**Figure 10.1c**). The particle measuring tool from the PFIB-SEM software was used to determine particle sizes. To determine the optimal setting to perform *in situ* liquid

SEM using the PFIB-SEM, we initially utilized commercial boehmite AOH60 and 200SM particles in DI water samples. After identifying optimal settings, *in situ* liquid SEM sessions were conducted using the in-house synthesized nano-boehmite particles suspended in DI water.

10.5. *In situ* liquid SEM of commercial boehmite particles

The optimization of *in situ* liquid SEM was performed using commercial boehmite AOH60 and 200SM. Approximately 30 secondary electron (SE) images of apertures with particles were captured to identify particles and their size distributions for AOH60 and 200SM, respectively. **Figure 10.2** shows images of apertures of the boehmite particle sample. As seen in **Figure 10.2a**, slight leaking from the aperture may occur during SE imaging acquisition due to the beam effect. However, it was minor enough to allow observation of particles inside of milled apertures. The pressure increase during sample injection after the milling apertures may also be a cause of the slight wetting of the aperture perimeters, which can be resolved by precisely controlling sample injection using a pump in the future. The liquid volume underneath the aperture may circulate with higher electron beam energy (10kV); this can be reduced by using lower beam energies (i.e., 1 – 5 kV).

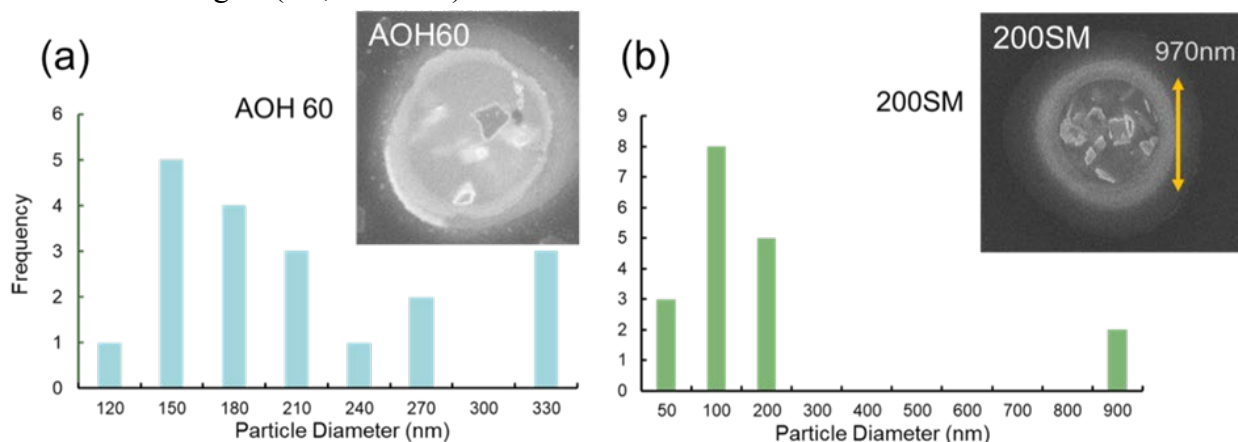


Figure 10.2. Particle size distribution based on SE imaging of (a) AOH60 (n=19) and (b) 200SM (n=18).

The measured mean particle size of dissolved AOH60 particles was 215 nm while 200SM was 231 nm. The median size of the dissolved AOH60 was 189 nm and 200SM was 153 nm. The size range of AOH 60 was 117 nm – 347 nm and 200SM was 30 nm – 959 nm. The nominal D50 of AOH60 is ~ 900 nm and 200SM ~ 350 nm. The preliminary results from *in situ* liquid SEM imaging suggest coagulation of the smaller 200SM particles and more dispersion of the AOH60 at the natural pH under low particle loadings. Additional experiments are warranted to obtain a more holistic understanding of the particle size distributions and particle stabilities under a wide range of pH and ionic strength conditions.

10.6. *In situ* liquid SEM of synthesized nano-boehmite

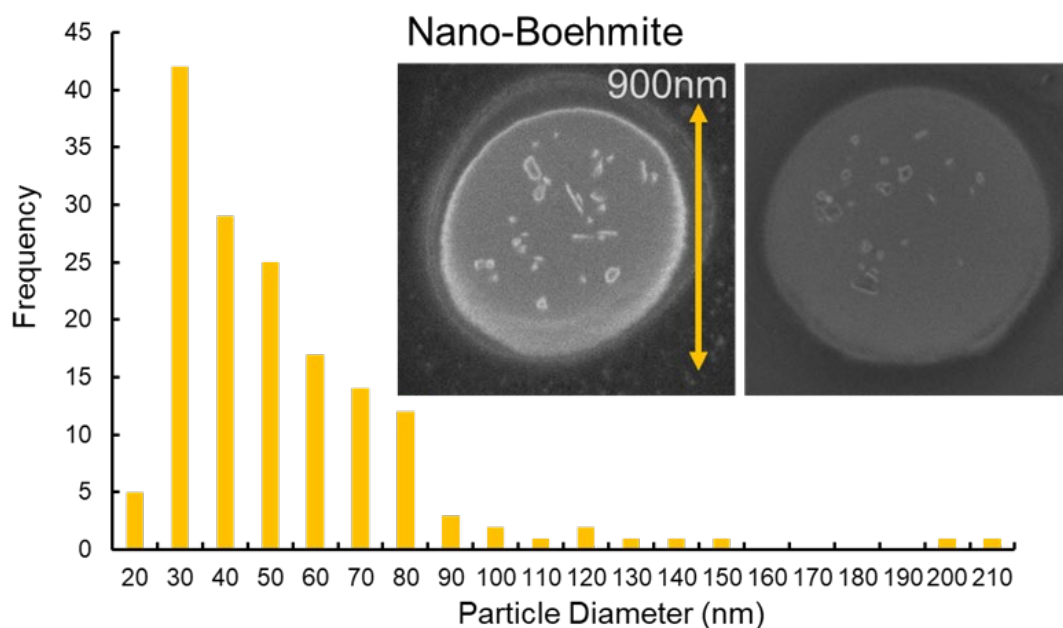


Figure 10.3. Particle size distribution based on SE imaging of nano-boehmite (n=157).

Two *in situ* SEM sessions were performed with optimized settings to collect SE images of nano-boehmite particle images. Several SE images (35 ea.) of apertures with particles were captured to determine particle sizes and their size distributions. **Figure 10.3** shows images of two apertures containing nano-boehmite particles. The measured mean size of nano-boehmite particles was 57 nm. The median size was 50 nm. The size range of nano-boehmite was 21 nm – 212 nm. The particle size difference between AOH60 and nano-boehmite will be further investigated considering characteristic chemical compositions from *in situ* liquid ToF-SIMS spectral analysis of AlOH60 and nano-boehmite to determine the effect of particle phase change and dissolution of aluminum-containing salts in the liquid state.

10.7 References

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