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EXPERIMENTAL DETERMINATION OF SOLUBILITY OF NEODYMIUM HYDROXIDE IN HIGH IONIC STRENGTH SOLUTIONS AT 298.15 K UNDER WELL-CONSTRAINED CONDITIONS: COMPARISON WITH MODEL PREDICTIONS

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Introduction

Nd(III) is a good non-radioactive analog for actinides in +III oxidation state (An(III))[1]. Therefore, Nd(III) has been studied extensively for the investigation of the chemical behaviors of An(III)[1]. In the review performed by Baes and Mesmer [2], the authors reviewed solubility experiments on $Nd(OH)_3$(s) prior to 1976. Since then, there have been several solubility experimental studies of $Nd(OH)_3$(s) in literature [e.g., 3-7]. However, few solubility studies were conducted in high ionic strength solutions that are applicable to nuclear waste disposal in salt formation environments [5]. In this presentation, we report the experimental results from our long-term solubility studies on $Nd(OH)_3$(cr) under well constrained conditions in high ionic strength solutions relevant to salt formation environments. The purpose of this work is for model validation tests.

Experimental Methods

Our long-term solubility experiments equilibrium was approached from undersaturation at 298.15 K, using high-purity crystalline $Nd(OH)_3$(cr) synthesized according to the procedure described by Wood et al. [6]. As detailed in Wood et al. [6], many other synthesis methods suffer from various shortcomings, which would result in difficulty/uncertainty interpreting solubility data. Therefore, starting with well-defined high-purity material is of fundamental importance to the success of solubility experiments. In synthesis of $Nd(OH)_3$(cr), high purity Nd_2O_3 was first loaded into Paar® reaction vessels with deaerated DI water, and then the reaction vessels were sealed in a glovebox under a positive pressure of an inert gas. The reaction vessels were then removed from the glovebox and placed into a muffle furnace. $Nd(OH)_3$(cr) was synthesized by reacting the high purity Nd_2O_3 with the deaerated DI water at 473.15 K in Paar® reaction vessels for a period of two weeks. Following the synthesis step, the reaction vessels were then transferred back into the glovebox, and were opened for drying in an atmosphere of inert gas. This synthesis method assures the complete conversion of Nd_2O_3 to $Nd(OH)_3$(cr), as demonstrated by XRD and SEM-EDS characterizations (Figures 1 and 2). Note, the deaerated DI water used in the synthesis was prepared by vigorously bubbling high purity Ar or N_2 gas through the DI water for a minimum of 30 minutes in the glovebox. This deaeration process was intended to remove any dissolved CO_2 and therefore ensure the synthesis process was not contaminated by carbonate.

Supporting Data

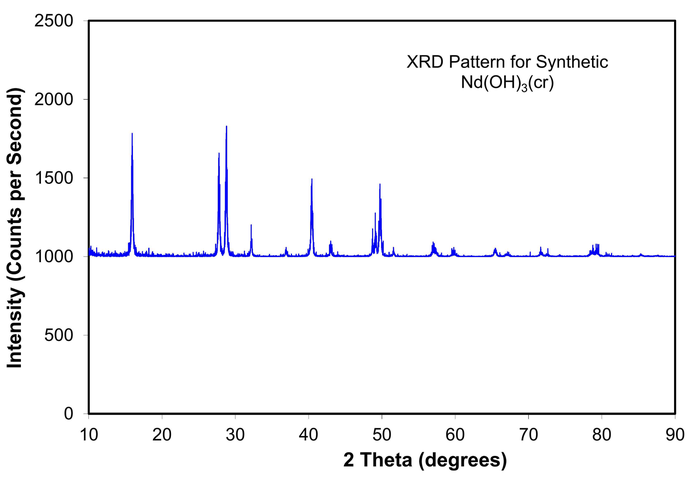

Figure 1. XRD pattern of the synthetic $Nd(OH)_3$(cr) used in the long-term experiments in this study.

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Experimental Methods (Continued)

In our solubility experiments, approximately 0.3 grams of $Nd(OH)_3$(cr) were placed into serum bottles and 100 mL of supporting solutions with the desired ionic strength, were added to the serum bottles in the glovebox, and the filled serum bottles were sealed with clip caps. The supporting solutions consisted of 4.4 and 5.0 mol•kg^{-1} NaCl solutions where mol•kg^{-1} refers to concentration on molal scale, i.e., moles per 1000 g of water. All supporting solutions were prepared from reagent grade chemicals from Fisher Scientific, or its associated vendors, and deaerated DI water. In our solubility experiments, hydrogen ion concentrations (i.e., pmH, hydrogen ion concentrations on molal scale) were not adjusted, rather the pmH was controlled by the dissolution of $Nd(OH)_3$(cr), as the pmH range, buffered by the dissolution of $Nd(OH)_3$(cr) in high ionic strength solutions, had not been determined in previous studies.

Solution samples were periodically withdrawn from the experiments to determine if the system had reached equilibrium. Before each sampling, pH readings were taken for each experiment. In each sampling, about 3 mL of solution samples were taken from each experiment, and the solution samples were filtered through a 0.2 mm filter, and transferred into pre-weighed 10 mL Grade A volumetric flasks. After filtration, masses of each solution sample were determined with a balance precise to the fourth decimal place. Samples were then immediately acidified with 0.5 mL of the Optima® Grade HNO_3 from Fisher Scientific, and diluted to 10 mL with DI water. Prior to chemical analyses for Nd using the PerkinElmer NexION 300D ICP-MS, and for Na using the PerkinElmer Optima 3300 Dual View (DV) ICP-AES, aliquots from the afore-mentioned acidified samples were further diluted to an appropriate ionic strength.

Results and Discussions

The measured pH readings were converted to hydrogen ion concentrations on molar scale (i.e., pcH) based on the correction factors determined in reference [8], and pcH's were converted to pmH's according to the equations in reference [9]. The final measurements for this study included sodium, neodymium, chloride, and hydrogen ion molal concentration data.

The results from our long-term solubility experiments indicate that the pmH range (~9.6 — ~9.7) exhibited by the dissolution of $Nd(OH)_3$(cr) is similar to that controlled by the dissolution of brucite in high ionic strength solutions [10]. The measured solubility of $Nd(OH)_3$(cr) in 4.4 and 5.0 mol•kg^{-1} NaCl solutions, were compared with the model-predicted solubilities of $Am(OH)_3$(s). In the model prediction, solubility values in equilibrium with $Am(OH)_3$(s) in the above solutions are predicted by using the Waste Isolation Pilot Plant (WIPP) thermodynamic model [11-15]. The comparison demonstrated that the model-predicted values were in good agreement with the measured $Nd(OH)_3$(cr) solubility data (Figure 3).

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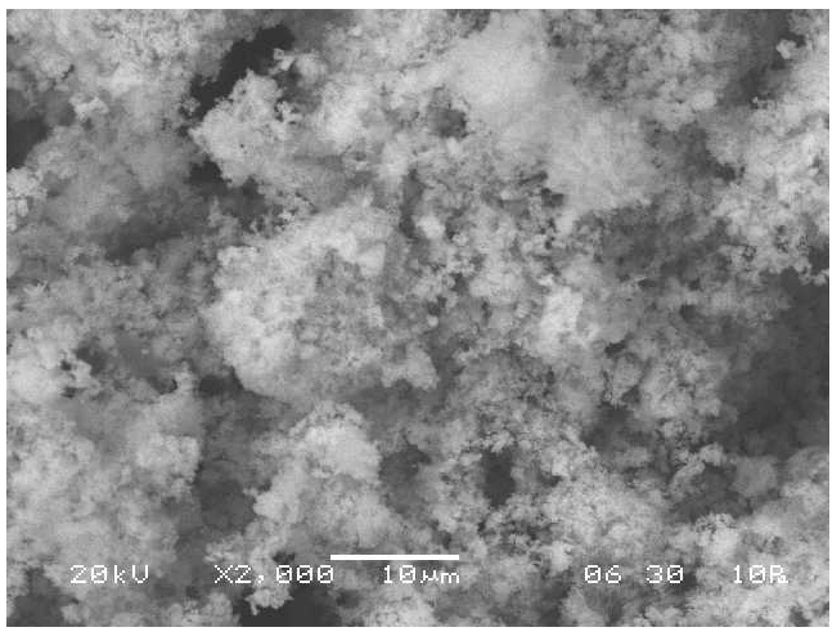

Figure 2. SEM picture of the synthetic $Nd(OH)_3$(cr) used in the long-term experiments in this study.

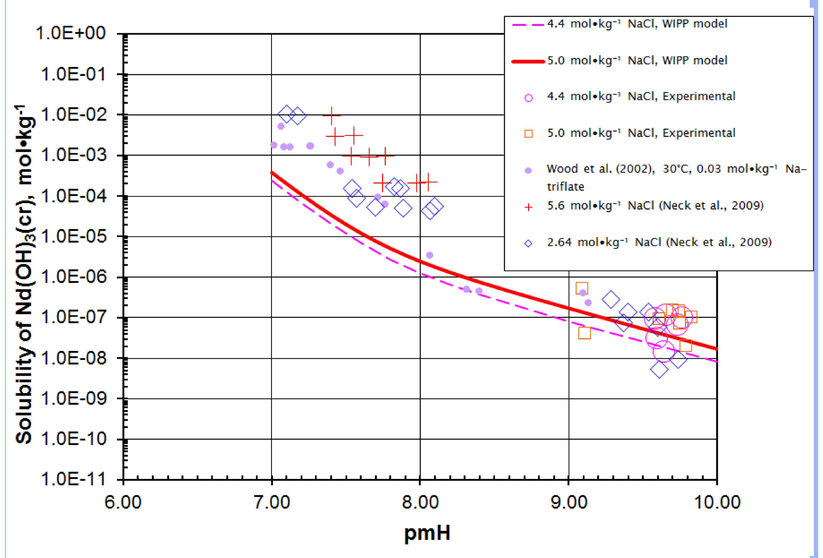

Figure 3. A plot showing solubilities of $Nd(OH)_3$(cr) as a function of hydrogen ion concentrations. Notice that the synthesis method of Neck et al. (2009) is different from that used in Wood et al. (2009) and in this study.

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