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Solubility of $Nd(OH)_3$ at high pH

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Neodymium hydroxide, $Nd(OH)_3$, solubility experiments were carried out in duplicate at room temperature over the pH interval of 10 to 13 for up to 670 days. The ionic radii of Nd(III) is similar to that of Pu(III) and Am(III), so that the former is an appropriate analog for the latter radionuclides. Average concentrations of Nd in solution approach a value of 2.0×10^{-7} mol/L and equilibrium concentrations show no dependence on solution pH. Compared to previous work, the data from this investigation form a continuum across pH-space, indicating agreement amongst data sets.

I. INTRODUCTION

Safe disposition of Transuranic (TRU) waste in a deep geologic repository is an essential lynchpin to the Department of Energy's (DOE) strategy to clean up waste produced during the nuclear weapons production era. Currently, TRU waste is being reposed in the Waste Isolation Pilot Plant (WIPP) located in southeast New Mexico ~2,150 feet below the surface in the Permian Salado formation. The Salado formation is made up mainly of halite and anhydrite and the chemical compositions of intergranular brines reflect equilibrium with these phases[1]. The possibility that brine may intrude into the repository and interact with waste cannot be dismissed and transport of radionuclides may occur as a result. Because of reactions between trapped O_2 and steel after repository closure, the fugacity of O_2 in the repository is expected to become very low, and the oxidation state of redox-sensitive radionuclide species will be correspondingly low. Although chemically reduced radionuclide compounds are typically less soluble than their higher oxidation state counterparts, geochemical modeling indicates that the solubility of Pu(III) is ~100× higher than that of Pu(IV) ($1.7 – 3.1 \times 10^{-7}$ M versus $0.58 – 2.5 \times 10^{-8}$ M, respectively)[2]. It is imperative then that transport of the two most problematic radioactive elements in TRU waste, Am(III) and Pu(III), be quantified for conditions germane to repositories in which brine solutions may be present.

Because the common isotopes of neodymium are non-radioactive and possess nearly equivalent ionic radii to reduced Am and Pu [112, 114 and 111.5 pm, coordination number = 6 for Nd(III), Pu(III) and Am(III), respectively][3], most of the research bearing on this problem has focused on $Nd(OH)_3$ solubility. Although numerous investigators[5-9] have reported the solubility of $Nd(OH)_3$, there is a lack of solubility data for conditions of high pH, temperature and ionic strength. We report solubility data for $Nd(OH)_3$ in experiments conducted over a pH interval (10 to 13) at room temperature. Additional solubility experiments will be carried out at higher temperatures (up to 180 °C), and results of these experiments will be reported later.

II. Material and Methods

II.A. Neodymium hydroxide synthesis and characterization

Neodymium hydroxide was synthesized using the method outlined by Wood et al.[9] In brief, ~1 gram of Nd_2O_3 powder (Alpha Aesar) was reacted with 6.67 grams of de-aerated water at a temperature of 200 °C for 14 days in Parr® vessels. The powders were dried for approximately 3 weeks in a controlled atmosphere glove box. An SEM image of the resulting material is shown in Fig. 1. The $Nd(OH)_3$ crystals appear to be small (up to ~500 nm in largest dimension). Analysis by XRD (Fig. 2) indicates that the material is highly crystalline $Nd(OH)_3$ with no evidence of other phases.

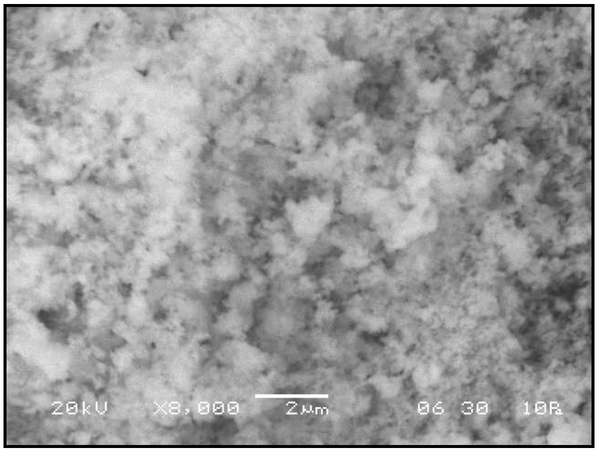

Figure 1. Scanning Electron Microscope image of the synthesized $Nd(OH)_3$ powder.

II.B. Experimental

All experiments were carried out in a controlled atmosphere glove box designed to exclude carbon dioxide. Approximately 0.25 g of synthesized $Nd(OH)_3$ powders were placed into 120 mL polypropylene bottles with 100 mL of a 0.010 molal de-aerated NaCl solution. The pH values of the solutions were adjusted to those of interest using high-purity 2.0 M NaOH prior to addition of $Nd(OH)_3$ powders. The final Na concentrations were between 0.01 and 0.17 molal. The solution pH values were 10, 11, 12 and 13±0.10.

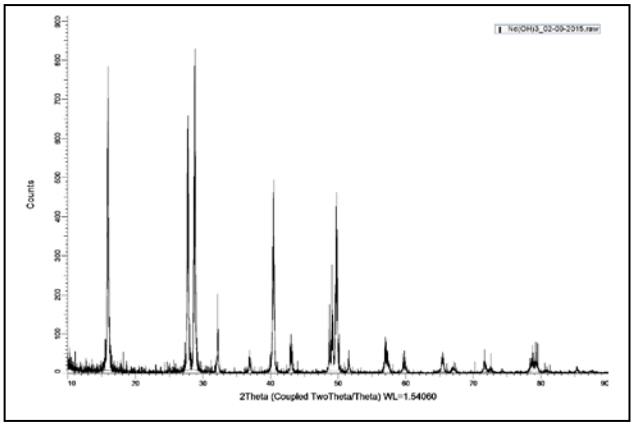

Figure 2. X-ray diffraction pattern of the synthesized $Nd(OH)_3$ powder.

Long-term experiments (>670 days) were sampled every 4 months to determine concentrations of Nd by ICP-MS methods. Each sampling consisted of a 5 mL aliquot of solution and great care was taken to use only glassware in the processing of the samples, because our own internal study concluded that Nd sorbs strongly onto typical laboratory plastic ware. Samples were filtered through a 0.2 µm membrane to remove small particles. Dilution factors were typically between 2- and 100-fold. The calibration curve for the two measured isotopes of neodymium (^{142,144}Nd) was over a 100-fold interval (0.010 to 10 ppb). An ^{115}In internal standard was also used ensure accuracy. Recovery of the ^{115}In standard was considered successful if the analysis was within 20% of input, but typically recovery was better than 95%. Concentrations of Nd determined on the two isotopes were within 5% of each other, so concentrations of the two isotopes were averaged for the final value. Sample pH was determined at each sampling using a pH probe calibrated on three NIST-traceable standards (7, 10 and 13). In addition, initial Na and Cl concentrations were determined by ICP-OES and IC methods, respectively.

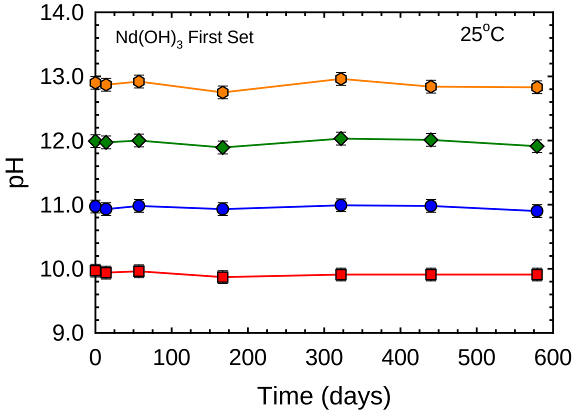

Figure 3. Plot of solution pH versus time for the first set of $Nd(OH)_3$ solubility experiments at room temperature.

III. Results

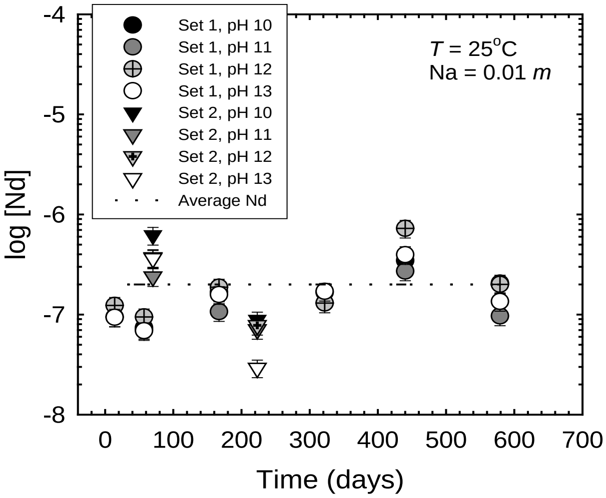

Figure 4. Plot of the $\log_{10}$ Nd concentration versus time for the solubility experiments at room temperature. The average Nd concentration from all experiments is displayed as the dashed line. Concentrations of Na are 0.01 to 0.17 m.

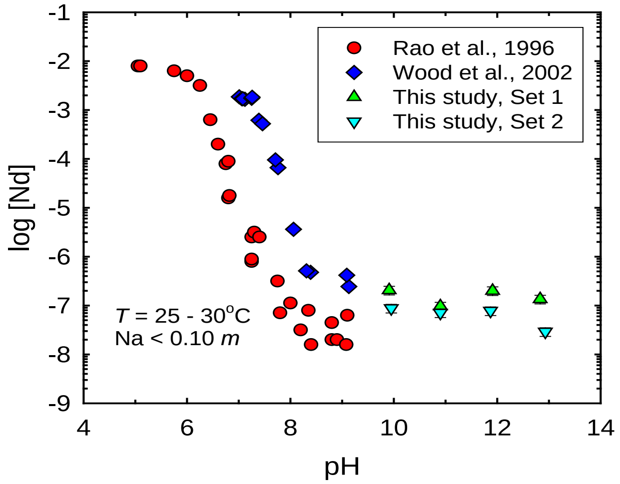

Figure 5. Plot of $\log_{10}$ Nd versus pH for data from Rao et al. [5] (red circles), Wood et al. [9] (blue diamonds) and this study (Set 1, triangles; Set 2, inverted triangles).

Fig. 3 is a plot of solution pH with time, showing that the pH of the solution was constant within experimental uncertainty (±0.10), except for the pH 13 experiment, in which the pH decreased ~0.2 pH-units over time. Fig. 4 is a plot of the concentration of Nd with time. The concentrations of Nd over the duration of the experiments were constant, indicating that equilibrium was established. Fig. 5 is a plot of log Nd concentration versus pH for our experiments and those of previous investigators [5,9]. Two important points can be drawn from the data. First, the concentrations of Nd from our experiments form a continuum of data from those of previous investigations. Collectively, these data indicate that our investigation is in accord with previous work. Second, there appears to be no dependence of the solubility on solution pH over the pH interval 10 to 13. These data appear to exclude the possibility of a $Nd(OH)_4^-$ complex, at least over this pH interval.

IV. CONCLUSIONS

Room-temperature solubility experiments carried out over a pH interval from 10 to 13 indicate no dependence of solubility on pH. Our data extends the range of previous data past pH 9 and, collectively, the sum of the data forms a complete continuum over a wide pH interval.

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