

FINAL PROJECT REPORT

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DE-FG02-03ER46034: The Effect of Organic Ligands on the Sorption of Neodymium,
Gadolinium and Uranium onto Nontronite and Goethite

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Summary

The sorption of the rare earth elements (REE) Nd^{3+} and Gd^{3+} onto goethite in the presence of Suwannee River fulvic acid in 0.1 M NaCl solutions at 25 °C was investigated quantitatively. The experiments involved batch titrations whereby the concentrations of REE and/or fulvic acid remaining in solution were determined as a function of pH. In the absence of fulvic acid, removal of REE from solution is enhanced in the presence of goethite over the pH range from 6 to 8, compared to the unary system (REE only) in which precipitation of an amorphous hydroxide occurred at pH greater than or equal to 8. In the absence of REE, removal of fulvic acid from solution is enhanced in the presence of goethite in the pH range from 2 to 8 at least 9, compared to a unary (fulvic acid only) system. The presence of fulvic acid at concentrations from 10 to 50 ppm enhanced REE sorption onto goethite slightly at pH less than 7, but had no discernable effect at higher pH values. Fulvic acid at a concentration of 100 ppm exhibited a greater enhancement of REE sorption at $\text{pH} < 7$, but inhibited REE sorption slightly at $\text{pH} > 7$. Experiments investigating the effect of sorption of REE onto goethite by citrate were also performed. However, these studies were not completed owing to experimental difficulties. The results obtained in this study represent an important contribution to the ultimate goal of predicting the mobility of trivalent REE (and analogous trivalent actinides) in the presence of natural organic matter and goethite.

1. Original Project Objective

The main objective of our research was to investigate the sorption of Nd^{3+} , Gd^{3+} and UO_2^{2+} onto nontronite clay and goethite in the presence of oxalate, citrate, EDTA and humic acid. The study is intended to contribute to the prediction of the migration of radionuclides in the vadose zone.

2. Effect of Fulvic Acid on REE Sorption Onto Goethite

The sorption of Nd and Gd onto goethite was studied as a function of pH and FA concentration using a batch titration method at 25 °C and a fixed ionic strength of 0.1 mol kg^{-1} NaCl.

2.1. Methods

Microcrystalline precipitates of goethite ($\alpha\text{-FeOOH}$) were prepared according to the method of Atkinson et al. (1967). Solutions containing 50 grams of A.C.S certified ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) dissolved in 800 mL of deionized water (DI), and solutions containing 28.05 g of A.C.S certified potassium hydroxide (KOH) pellets dissolved in 200 mL of DI were mixed. Argon was continually pumped through the system in order to prevent CO_2 infiltration. The mixture was then placed in a water bath at 60°C for two days, with frequent agitation. The solution was washed with DI water continually over a period of three days. The precipitate was separated by vacuum-filtration using a Hardened Ashless Circles paper filter (90 mm diameter). The precipitate was placed in an oven at 80 °C for 24 hours. The precipitate was then ground up with an agate mortar and pestle and sieved using a #5 120- μm mesh screen. The ground goethite was placed in a 250 mL polypropylene bottle with a screw top and stored at room temperature. The BET surface area of the $\alpha\text{-FeOOH}$ was 69 m^2/g . The samples were analyzed by x-ray diffraction (XRD). The XRD revealed peaks that matched the published pattern for goethite.

The fulvic acid (FA) used in this study was Suwannee River fulvic acid (SRFA) obtained from the International Humic Substances Society (IHSS). This FA has been extensively characterized and is an accepted standard. The FA was used as received with no further treatment. The concentrations used in this study were 10, 20, 30, 50 and 100 ppm.

Stock solutions prepared from 1000 ppm Nd and 10,000 ppm Gd standard solutions containing 2% HNO_3 were used for all these experiments. These standards were obtained from Alfa Aesar, a Johnson Matthey Company.

For the calibration of the combination glass electrode used to record pH, standard solutions of 0.01 m, 0.001 m and 0.0001 m HCl and NaOH, all at a total, constant ionic strength of 0.1 m NaCl were prepared. Titrants of acid and base were prepared by diluting 1 N HCl and 1 N NaOH solutions to 0.1 molar. Fresh batches of all NaOH solutions were prepared approximately every three weeks.

Potentiometric titrations were carried out in a 500mL jacketed glass reaction vessel. The temperature was held constant at 25 °C (± 0.1 °C) with a Thermo Haake™ DC 10 circulating water bath. A Kd Scientific™ syringe pump using two positive displacement pumps delivered the desired titrant (acid or base) into the reaction vessel. The reaction vessel was fitted with a Denver Instrument™ Model 215 glass pH electrode and polyurethane tubing to maintain a positive-pressure argon atmosphere. A Teflon-coated magnetic stir-bar was used inside the reaction vessel. The vessel was positioned on top of a Corning™ stir plate. Argon was continually passed through a tube filled with Ascarite and then into the reaction vessel to exclude CO₂ during the run.

Prior to every potentiometric titration run, the glass pH electrode was calibrated with the aforementioned standards. Approximately 0.2 g of goethite were placed in the reaction vessel with 200 g of 5 ppm Gd or Nd stock solution. The stock solution maintained a 0.1 m ionic strength using 0.09 m NaCl as a background electrolyte and 0.01m HCl. Titrants of 0.1M HCl or NaOH were delivered into the reaction vessel to adjust pH.

The time to attain equilibrium (i.e., attainment of a relatively constant pH) varied depending upon the concentrations of FA (longer periods of time were required for higher FA concentrations), but typically it did not exceed 20 minutes per titrant addition. The pH was considered to have stabilized when the change in pH was less than 2 mV/min. Upon attainment of equilibrium, samples were extracted from the vessel via a BD 5ml polypropylene syringe for analysis of Nd or Gd via inductively coupled plasma-atomic emission spectroscopy and a 10ml syringe for UV-vis spectroscopic analysis of FA. These samples were forced through a 0.2 μ m Millex GN Millipore nylon membrane filter and stored until analysis.

A forward titration typically commenced with a solution with an initial pH of approximately 2.5, which was increased by adding increments of a solution of 0.1 M NaOH. The solution was titrated to a pH of approximately 11.5. Typically, immediately following the forward titration, a reverse titration would take place. The reverse titration would result in an incremental decrease in pH to approximately 2 using 0.1 M HCl as a titrant. Typical aliquots of acid or base added in each titration step ranged between 0.1 and 2 mL. Samples were taken at approximately 30 mV intervals in order to obtain roughly 2 samples per pH unit. Typical forward and reverse titrations took between 10 and 14 hours total.

2.2. Results and Discussion

All the experimental investigations for this study were carried out in a similar fashion. Five separate types of titration experiments were performed. These may be classified in the following manner:

- 1) Blank or unary neodymium, gadolinium or fulvic acid systems. These runs involved only neodymium, gadolinium or fulvic acid in a 0.1 m NaCl background solution, and typically involved forward titration (i.e., increasing pH) only.
- 2) Binary neodymium and fulvic acid in a 0.1 m NaCl background solution. Typically, these runs involved both forward and reverse (i.e., decreasing pH) titrations.

- 3) Binary neodymium and goethite in a 0.1 m NaCl background solution. These runs involved both forward and reverse titrations.
- 4) Binary fulvic acid and goethite in a 0.1 m NaCl background solution. These runs involved both forward and reverse titrations.
- 5) Ternary REE (neodymium and gadolinium, respectively), fulvic acid and goethite in a 0.1 m NaCl background solution. These runs involved both forward and reverse titrations.

The main focus of this project was of course investigation of the ternary REE-FA-goethite system. However, investigation of the constituent unary and binary systems is a prerequisite to understanding the more complicated ternary interactions.

Unary runs containing only Nd or Gd in 0.1 m NaCl showed that nearly 100% of the initial REE remained in solution over a pH range from 2 to 8 (Fig. 1). Above pH 8 the REE concentrations drop to near zero. There was no significant difference in the behavior of Nd and Gd. The drop in concentration above pH 8 is almost certainly a result of the precipitation of amorphous REE hydroxide. This interpretation is consistent with available solubility data.

Unary runs containing only FA in 0.1 m NaCl (Fig. 2) show that FA appears to be lost almost completely (~ 90%) from solution at the lowest pH (2). Between pH 2 and 6 the amount of FA in solution increases steadily and then plateaus at about 75% of the original concentration from pH 6 to 11.5. The loss of FA at low pH could be a result of adsorption to the walls of the glass reaction vessel, or coagulation of FA molecules to a size larger than can pass through the 0.2 μm filter.

Plots of REE concentration vs. pH for binary Nd(Gd)-goethite runs show a similar shape to those of unary REE runs, except that the REE concentrations in the former begin to decrease at 2 pH units lower than in the latter (Fig. 3). Thus, the presence of goethite enhances the removal of REE from solution between pH 6 and 8. This is attributable to sorption of REE onto goethite surfaces. The plot of REE concentration vs. pH resembles closely a classic cation adsorption edge plot, in which aqueous cations do not adsorb onto a mineral surface that is positively charged at low pH, but become increasingly adsorbed as pH increases and the mineral surface becomes increasingly negatively charged.

In the binary REE-FA experiments, plots of the concentration of REE vs. pH are similar to those in the unary REE experiments up to approximately pH 6 (Fig. 4). The REE concentration does not change much between pH 2 and 6. Between pH 6 and 8, the concentration of REE appears to be slightly less when FA is present. Unlike in the unary system, the concentration of REE in the binary system reaches a minimum at pH 9 of roughly 30-40% of the initial REE concentration, and then increases slightly before leveling off between pH 10 and 11.5 at a value of 40-60% of the original concentration. Plots of FA concentration vs. pH for this same set of runs also show a local minimum in FA concentration at pH ~ 9 (Fig. 5). Thus, the presence of FA appears to increase the solubility of Nd hydroxide in the basic pH range, but at the same time, the presence of Nd appears to decrease the solubility of FA over this same range.

Binary experiments involving FA and goethite exhibited comparatively poor reproducibility from run to run (Fig. 6). Like the unary FA runs, FA concentration was low at low pH and increased with increasing pH. However, unlike the unary FA runs, FA

was almost completely removed from solution from pH = 2 to pH = 6-9 (depending on the run). Above pH = 6-9, the concentration of FA gradually increased with further increases in pH, but even at the highest pH measured (11.5), not all the original FA returned to solution. The plots of FA concentration vs. pH somewhat resemble classic adsorption edge plots for anions, except that the adsorption edge is not as sharp. Comparison of the FA-goethite runs with the unary FA runs shows clearly that the presence of goethite results in greater removal of FA from solution over the entire range of pH studied. These findings suggest that FA is strongly adsorbed to goethite at low to neutral pH, but becomes desorbed as pH increases, probably because both FA and goethite become increasingly negatively charged with increasing pH.

Ternary experiments showed that addition of FA at concentrations between 10 and 50 ppm to the REE-goethite system caused a shift in the adsorption edge to lower pH and raised slightly the degree of adsorption at acidic pH, but otherwise did not change the shape of the plots of REE concentration vs. pH (Fig. 7). Between 0 and 10 ppm FA, the adsorption edge shifted to lower pH by roughly 0.5 units. However, within the scatter in the data, there did not appear to be much of a difference in the adsorption edges at FA concentrations between 10 and 50 ppm. On the other hand, addition of 100 ppm FA caused a rather more profound change in the shape of the adsorption edge. At pH less than ~ 6, in the presence of 100 ppm FA the adsorption edge was shifted about 1.5 pH units lower than the adsorption edge in 0 ppm FA solution, and ~ 1 pH unit lower than for solutions with 10-50 ppm FA. Moreover, the adsorption edge for the 100 ppm FA run crosses that for the 0 ppm FA runs at about pH 7, and some REE remains in solution from pH 7 to at least pH 10, unlike the case at lower FA concentrations where Nd is effectively completely removed at pH > 7. These results suggest that at low pH (< 7), FA enhances adsorption of REE, probably via formation of a ternary surface complex. However, the effect of FA is not linear at concentrations between 10 and 50 ppm, and the degree of enhancement over this range is relatively small. It appears that a major change occurs between 50 and 100 ppm, whereby at low pH there is a rather substantial enhancement of sorption of REE, but at high pH there is a subtle inhibition of sorption/precipitation, the latter probably due to the formation of strong aqueous REE-FA complexes that enhance solubility.

Although fewer binary and ternary runs were performed for Gd than for Nd, it was apparent in all cases that the differences between these two REE were approximately the same or less than the degree of run-to-run reproducibility. In both the binary Nd(Gd)-goethite and ternary Nd(Gd)-FA-goethite systems, there was a significant hysteresis between forward and reverse titrations. On the reverse titration, not all Nd(Gd) desorbed from the goethite in the acid region over the time scale of the experiment (hours).

Attempts thus far to model the sorption of REE/FA onto goethite in terms of surface complexes were only successful for the binary REE-goethite system. Satisfactory results could not be obtained for the binary FA-goethite or the ternary systems. The lack of success in fitting a surface complexation model to systems involving FA may be largely due to inadequate thermodynamic models for FA itself, for the interaction of FA and REE in aqueous solution, the interaction of FA with the goethite surface, or a combination of these. On the other hand, it was quite possible to describe the behavior of the binary Nd-goethite system using the modified diffuse double-layer (DDL) model of Dzombak and Morel (1990). A blind modeling approach similar to the one described by

Richter et al. (2005) was employed, in which all the parameters required for the modeling were either taken from previous experimental studies or were estimated. For details see Armstrong (2005).

3. Effect of citrate on REE adsorption onto goethite

A similar set of batch titration experiments were attempted for the Nd-citrate-goethite system. The procedures were nearly identical to those for the study involving FA, except that FA was replaced by citrate, and citrate was to be quantified using ion chromatography (Dionex ICS-3000). After considerable work, an analytical protocol was developed for citrate using an isocratic elution with a 40 mM NaOH eluent, a Dionex AS 11 column, and electrolytically suppressed conductivity detection. With this protocol, it was possible to obtain an excellent calibration curve using 1, 5, 10 and 50 ppm citrate standards. Because the experimental solutions would have had a large excess of chloride over citrate owing to the use of a 0.1 M NaCl background electrolyte, and the chloride would have saturated the column and interfered with the determination of citrate, we employed silver pretreatment cartridges from Dionex. These cartridges removed the bulk of the chloride prior to injection on the column. A series of tests showed that citrate was not removed to any significant extent by the pretreatment cartridges.

Armed with this analytical protocol for citrate, we proceeded to conduct experiments on the Nd-citrate binary. Experiments with 5 ppm Nd and either 10 or 20 ppm citrate in 0.1 M NaCl were conducted. However, in these binary systems, little or no citrate could be detected over the entire pH range of the experiment. Possible reasons for this observation are: 1) citrate may have adsorbed onto the glass walls of the experimental apparatus over the entire pH range; 2) Nd and citrate may have formed an insoluble precipitate over the entire pH range, and this precipitate was removed by filtration; or 3) Nd and citrate may have formed a strong, inert aqueous complex that was not dissociated in the ion chromatograph and was not retained by the column. We do not believe that explanation 1) is likely to be valid in our case. First, it would be highly unusual behavior for an anion such as citrate to adsorb to the glass walls over the entire pH range. Second, the citrate standards were prepared in glass volumetric flasks and there was no evidence of complete citrate loss in those standards, even at citrate concentrations lower than those employed in the experiments. Hypothesis 2) possibly could be tested by varying the concentrations of Nd and citrate. As these two concentrations are lowered below the solubility product for the putative Nd-citrate precipitate, it should be possible to detect citrate at least at some pH values. However, if the solubility product were so small that citrate concentrations would have to be below the detection limit of the method to avoid precipitation, then this test would not be feasible. Hypothesis 3) could be tested by adding an excess of a ligand known to be a strong complexer of Nd, such as EDTA, which would bind the Nd and free citrate so that it could be detected by ion chromatography. Success of this method requires that the added ligand NOT interfere itself with the IC determination of citrate. These tests were planned and partially carried out, but a lack of stability of personnel and ultimately a lack of time, prevented a full investigation.

4. Conclusions

This study has demonstrated that, at fulvic acid concentrations likely to occur in most natural settings, a slight enhancement of the sorption of Nd and Gd onto goethite will occur over the pH range of 2-7. Unusually high concentrations of fulvic acid (greater than or equal to 100 ppm) result in significant enhancement of adsorption at low pH (<7) and slight inhibition of sorption at high pH (>7). Therefore, the major conclusion of the study is that the presence of fulvic acid alone will not increase the mobility of Nd and Gd, and by analogy, trivalent actinides, as long as goethite is present.

Preliminary investigations of the Nd-citrate-goethite system suggest that, at the concentrations of Nd and citrate employed in the study, either an insoluble Nd-citrate precipitate or a relatively inert aqueous Nd-citrate complex forms. Further study is required to determine the likely effect of citrate on REE/actinide mobility in the presence of citrate.

An important piece of future work would be to repeat the fulvic acid experiments in the presence of CO₂. Work on the CO₂-free system was an important initial step in unraveling the full effect of organic ligands on REE adsorption onto goethite. However, because CO₂ is ubiquitous in the natural environment, it will be important to determine how fulvic acid affects this adsorption in the presence of CO₂.

5. References

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- Atkinson, R. J., Posner, A.J. and Quirk, J.P. (1967) Adsorption of Potential—Determining ions at the Ferric Oxide—Aqueous Electrolyte Interface. *J. Phys. Chem.*, 71, pp. 550–558.
- Dzombak, D.A. and Morel, F.M.M. (1990) Surface Complexation Modeling: Hydrous Ferric Oxide. John Wiley & Sons Inc. New York, New York.
- Richter, A., Brendler, B., and Nebelung, C. (2005) Blind prediction of Cu(II) sorption onto goethite: Current capabilities of diffuse double layer model. *Geochimica et Cosmochimica Acta*, 69. pp. 2725-2734.

6. Figures

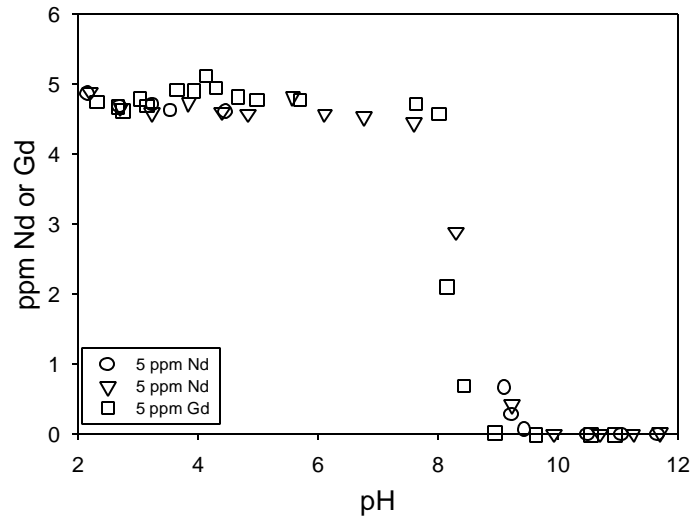


Figure 1: Plot of Nd (Gd) concentration vs. pH for the unary (no goethite or FA) system. The initial Nd (Gd) concentration for each run is given in the legend. Note close correspondence between Nd replicates, and between Nd and Gd. Concentration drops precipitously at pH ~ 8.

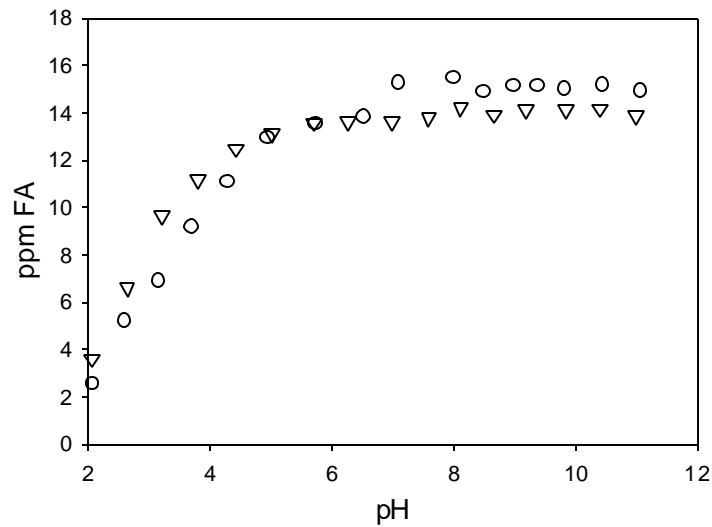


Figure 2: Plot of fulvic acid (FA) concentration vs. pH for the unary (no goethite or REE) system. The initial FA concentration for both runs was 20 ppm. Correspondence among runs is not quite as good as for REE unary systems, probably because the analytical method for FA is not as precise as that for REE.

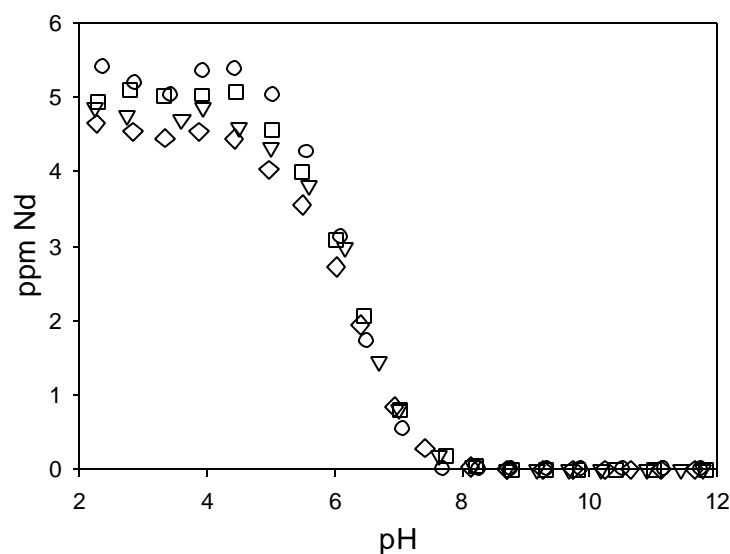


Figure 3: Plot of Nd concentration vs. pH for the Nd-goethite binary system (no FA) system. The initial Nd concentration is 5 ppm in all cases. Data are shown for four different replicate experiments. The data are somewhat scattered in the low-pH region but are fairly reproducible at $\text{pH} > 5$. Note that, compared to Fig. 1, the drop in Nd concentration occurs at approximately 2 units lower in pH, indicating that the presence of goethite enhances Nd removal from solution at $\text{pH} = 4\text{--}8$.

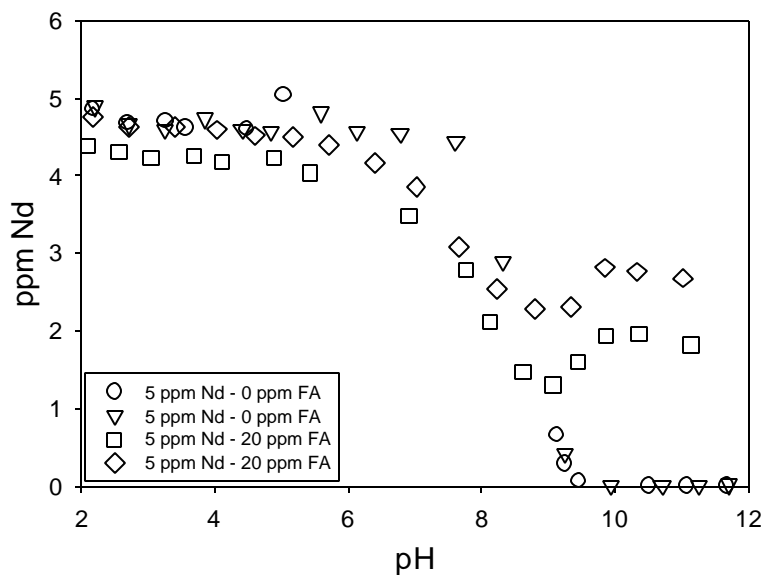


Figure 4: Plot of Nd concentration vs. pH for the Nd-FA binary system (no goethite) with 5 ppm Nd and 20 ppm FA. For comparison, data from two unary Nd-only runs are also shown.

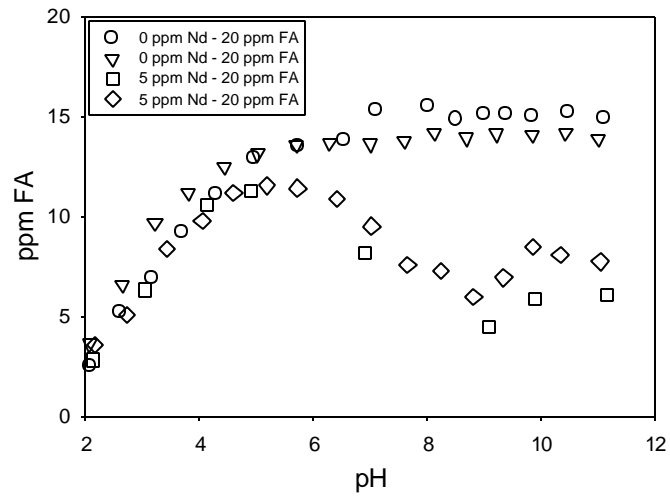


Figure 5: Plot of FA concentration vs. pH for the Nd-FA binary system (no goethite) with 5 ppm Nd and 20 ppm FA. For comparison, data from two unary FA-only runs are also shown.

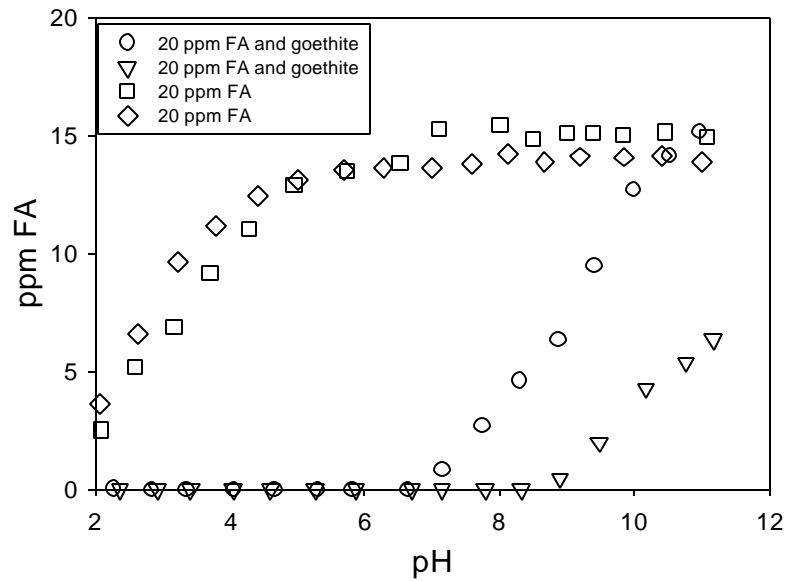


Figure 6: Plot of FA concentration vs. pH for the FA-goethite binary system (no REE) with 20 ppm FA. For comparison, data from two unary FA-only runs are also shown.

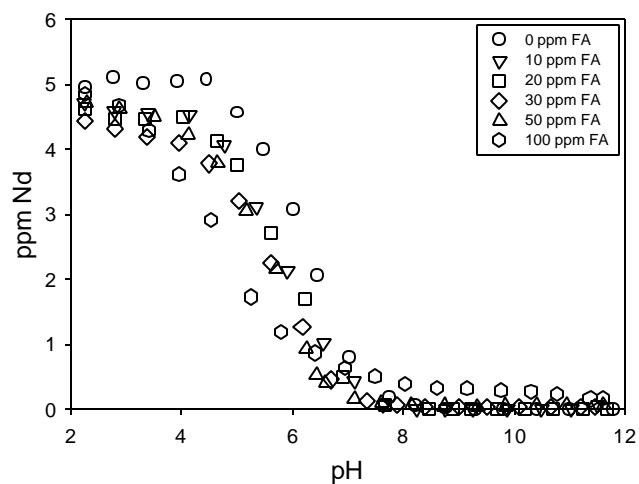


Figure 7: Plot of Nd concentration vs. pH for different concentrations of FA in the presence of goethite. The initial Nd concentration was 5 ppm in all experiments shown. The initial FA concentration for each run is given in the legend. Note the enhancement of Nd sorption due to FA at $\text{pH} < 7$, and the slight inhibition of Nd adsorption at $\text{pH} > 7$ and an FA concentration of 100 ppm.