Measurement and Recovery of Rare Earth Elements from Hypersaline Fluids

Ph.D. proposal update

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4 November 2015

Abstract

The rare earth elements (REE) are a suite of 16 elements with coherent and predictable chemistries with ubiquitous utilization in modern technology. While not truly rare in average abundance, the lack of concentrated deposits and the challeneges of intra-group separations make these elements highly valuable and difficult to produce in mass. Large economic and environmental costs associated with primary REE extraction motive the development of alternative REE resources, such as concentrated brines. This thesis will focus on the occurrence of REE in hypersaline fluids and the separation of the REE from these fluids.

The REE hare currently produced exclusively through primary mining activities. However, these methods pose significant environmental risk and occur almost exclusively in China. A technology capable of exploiting alternative REE resources domestically would be environmentally, economically, and geopolitically important.

Geothermal fluids represent a promising target for validating REE extraction and recovery from complex aqueous systems. A typical geothermal power plant handles tens to hundreds of thousands of gallons per day per MWe of brine with known, elevated concentrations of the REE. However, significant challenges exist for the extraction of the REE given their dilute concentrations (as compared to the major constitutents of the brine) and, in turn, the large excesses of non-REE cations capable of competing for the reactive sites of an extraction technology.

The goals of this research will be to evaluate the feasibility of extracting and recovering the REE from saline fluids. The development of this technology will be supported through focused experimentation and development of analytical techniques along with consideration of previously published data and adaptation of existing recovery schemes.

The goals of the research will be achieved through four specific objectives. The first objective of this work will be to accumulate available water quality data with REE measurements from the literature and explore relationships among the REE as well as between the REE and other commonly measured, bulk analytes. The second objective will be to develop and validate an efficient liquid-liquid extraction for determination of REE in hypersaline brines. The third objective will be to study the effects of ligand functionality and geometry on the partitioning behavior of the REE from brines to functionalized adsorbents. The final objective will be to study the best performing adsorbent(s) in detail. Taken together, these objectives will be a contribution to the understanding of trace-metal geochemistry, particularly in high salinity systems, and an assessment of extraction and recovery strategies targeted at the REE in hypersaline fluids.

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1.0 Introduction

Modern technologies — including catalysts, high-strength alloys, high-efficiency phosphors, lasers, and magnets — are dependent upon the unique properties of the rare earth elements (REE) for their efficacy of operation. However, global REE material-flows are prone to complex environmental, technical, and geopolitical forces on both the supply- and demand side. Development of economically-viable technologies for the extraction of the REE and other critical materials from unconventional sources (such as geothermal fluids, oil and gas produced waters, or coal combustion residuals) has great potential value to: generate a consistent domestic supply of materials critical to green energy and defense technologies; valorize high-volume wastes or low-value industrial byproducts; and avoid environmental impacts from primary REE mining.

1.1 What are rare earth elements?

The REE constitute much of Group 3 of the periodic table, a group of 16 transition metals, including the lanthanide series (La to Lu, excluding Pm), Yttrium (Y) and Scandium (Sc). The "rare" moniker stems from their initial isolation from uncommon mineral phases in the 18th and 19th century [1], though the natural abundance of REE in the earth's crust range from 0.52 parts per million (ppm) to 41.5 ppm, in the same range as Pb or Sn and exceeding the natural, crustal abundance of Ag and Hg [2].

In the natural sciences, predictable thermodynamic differences between the REE make these elements uniquely capable tools for interpreting natural geologic and chemical processes [3, 4]. Rare earth lithogeochemistries have long been used to infer depositional environments of geologic strata [3, 5, 6]. Similarly, REE serve as benign analogs to the transuranic actinide series for nuclear waste disposal studies [7, 8]; as potential markers of regional authenticity for high value exported food products such as wine, pumpkin-seed oil, and olive oil [9–11]; and for studying mixing and metal cycling in the oceans [12, 13].

Many of the same properties that yield the unique and predictable geochemistry of the REE have lead to their use in more consumer products than nearly any other element group [1, 14]. In most applications, the performance of the REE is unmatched [15, 16], making substitution (with more readily available/environmentally benign elements) undesirable.

Based on atomic number, the REE are segregated into light and heavy REE (LREE and HREE, respectively) with the division occurring between Eu and Gd [1]; some studies further distinguish middle REE (MREE), though the specific elements are inconsistently defined between authors [17–19]. These "weight" distinctions allow for simplified description and

quantification of the inter-element relationships, typically ratios of normalized concentrations, which are exploited in REE analysis. Similarly, anomalies of certain REE — due to redox lability for Ce and Eu [20] and large anthropogenic emissions for Gd [21] — are used to interpret geochemical processes. Y and Sc exhibit similar properties to the lanthanides and are thus included in the suite of REE with Y being most similar to HREE and Sc being most similar to LREE in solution [20].

1.2   What is the context of this study?

The constantly increasing consumer products incorporating the REE, and the ensuing demand for these products, have established the REE as valuable global commodities. Domestic demand in 2012 was 11,300 tons, while the global demand was more than 113,000 tons [22]. Much of that demand is a result of a booming green energies market. In particular, the permanent magnets sector is expected to experience significant growth between 2013 and 2020. High-efficiency generators used in turbines and electric motors require strong and light permanent magnets. Currently, magnets using neodymium, praseodymium, and samarium (with dysprosium and terbium additives) are the strongest and lightest commercially available.

Even at the height of domestic REE production at Mountain Pass in CA (2012), the U.S. imported $520MM worth of REE compounds, with nearly 40% coming from China, in order to support a demand of 11,300 tons [23]. A booming green energies industry fueled, and continues to fuel, both domestic and global demand, where the REE provide superior performance and efficiency compared to alternative materials [14, 16]. Sustained growth in these technologies is dependent on diversifying REE sources given projected supply shortages in the medium- to long-term. Traditional mining of REE from ore deposits is unlikely to fulfill this demand for technical and economic reasons, especially in the US where traditional mining of REE is suspended. China, the world's leading source of REE and primary supplier of global demand for many years (Figure 1.1, has indicated partial control of exports, or punitive tariffs, in the near future. This emphasizes the need for REE separation and recovery from unconventional matrices, such as geothermal fluids or coal fly ash.

Global REE reserves are estimated at 130 million metric tons [24], much of which is located in low-concentration deposits or ocean-floor manganese nodules, which are both extremely expensive to mine with current methods. This limits the number of readily mineable REE deposits and, ultimately, our ability to increase REE supply [25, 26]. Aqueous media such as brines or produced waters from geothermal energy, conventional oil/gas, and shale gas extraction operations are potentially significant, but unexplored sources of REE.

Presently, REE extraction is accomplished by traditional mining (e.g. open-pit) followed by chemically-, and energy-intensive element separations, which incur a significant environmental burden (Figure 1.2; [27]). Even when present in ores at appreciable levels, REE are commonly commingled with radioactive thorium and uranium, which need to be safely separated and stored in addition to standard waste management associated with mining (e.g. tailings) [28, 29]. Stringent environmental regulations, time-intensive processes, and expensive permits complicate the opening of new, domestic mines because of these inherent risks. On this basis,
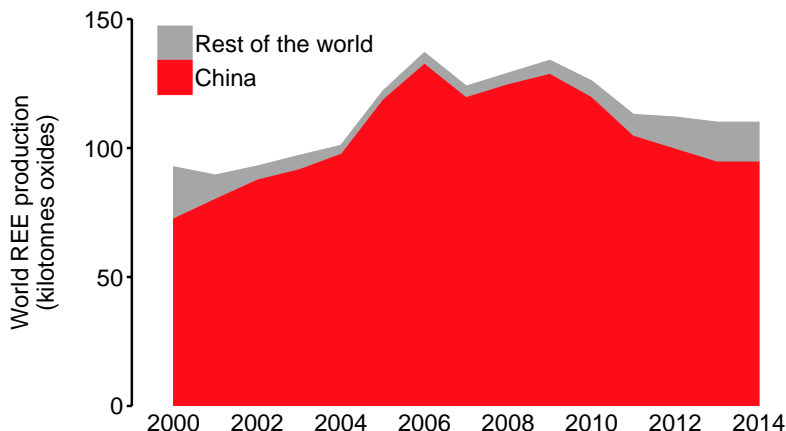
Figure 1.1: Global, primary REE production, 2000-2014. Data from U.S. Geological Survey [24].

projections expect that exploiting traditional REE sources to meet increasing demand will be a significant challenge. In 2012, China was responsible for more than 95% of the global REE supply [24]. China also had the largest demand for REE, at 66% of the total global demand [24]. The US was the next largest consumer, at 10–15% of the total demand. In 2011, China announced a 35% reduction in exports of REE, in an effort to meet their domestic needs [23]. This created large instability in the REE market as there were no other major sources for REE [26, 30, 31]. China is expected to continue reduction of exports, through either quotas or tariffs, as a mean to reduce stress on its REE reserves [22, 24].

Primary mining effectively constitutes 100% of the REE production worldwide [24, 32], but interest in recovery of REE from end-of-life stocks (EOL), from unconventional resources, and from REE-containing industrial wastes has expanded rapidly in recent years [33]. High volumes of REE are deployed in permanent magnets, while high-value REE are used in phosphors [31], making these products two primary targets for recycling from EOL products along with metal hydride batteries [32, 34]. REE are applied in many other products, but the REE content is dissipated in-use or rendered unrecyclable by current designs [15]. Ferrous shredder waste (where magnets could accumulate) is a promising potential resource for REE and other critical materials. However, Bandara et al. [35] propose that recycling of ferrous shredder-waste would need to exceed 50% in order to dampen Nd price volatility from recycling alone. The conclusion from these forecasts is the need for novel, alternative feedstocks [35].

1.3   What are the goals of this study?

This research seeks to address the potential for REE extraction and recovery from dilute aqueous sources. This work is motivated by the desire to diversify REE sources, promote development of low-carbon energy sources, valorize industrial byproducts, and avoid the environmental disruption associated with primary REE mining. A combination of a literature analysis, analytical method development, controlled experimentation, and statistical and geochemical modeling will be used to address these goals.
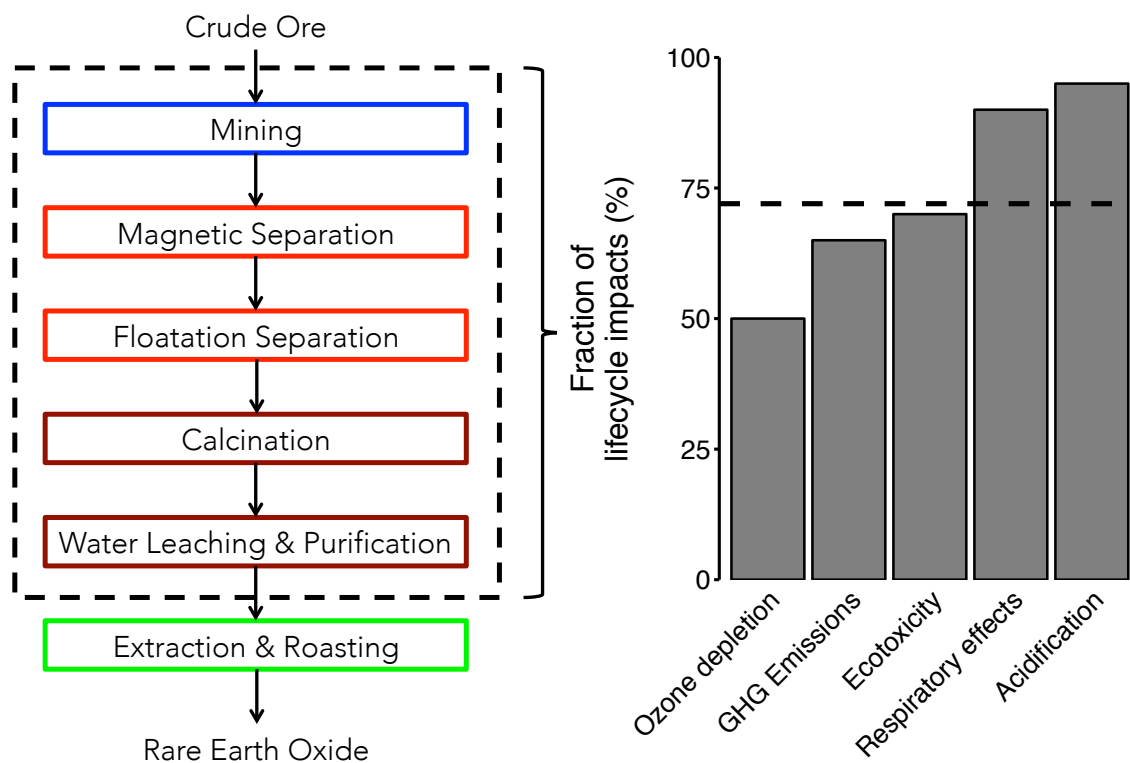
Figure 1.2: Traditional REE production flowsheet (left) and the associated fraction of lifecycle environmental impacts for the boxed boundary (right) using data from Zaimes et al. [27]. Only selected impact categories are shown, however the dashed line (72%) indicates the overall average across ten categories.

The three, specific objectives of this work and the related questions they were developed to answer are as follows:

1. Determine REE abundance and trends in natural waters.

   - What is the natural variability of REE in aqueous media?

   - What quantitative methods exist for considering below detection limit values?

   - What is known about REE occurrence in brines?

   - What relationships between REE and bulk solution properties are important for REE fate and transport?

2. Develop efficient liquid-liquid extraction technique for separation of REE from hypersaline brines.

   - How are REE measured in aqueous samples?

   - Will these techniques work for hypersaline, chemically complex brines?

   - What are the limits of effectiveness for an LLE technique (with respect to brine composition)?

3. Study the effects of ligand functionality and geometry on the partitioning behavior of the REE from brines to functionalized adsorbents

   - What ligands have high, aqueous-phase affinity for the REE?

   - How does surface attachment affect the affinity of these ligands for the REE?

   - What are the best performing ligands for REE recovery?

   - How do these ligands perform under a range of aqueous conditions?

The specific objectives of this work were developed to address gaps in the literature to date while building on the existing REE and functionalized adsorbent knowledge base. These objectives are meant to address application specific (i.e. REE recovery from geothermal brines) uncertainty as well as foster a more fundamental understanding of the REE systematics. The methods proposed to address these objectives are detailed in §2.1-2.3.

2.0 Research plan

Four specific objectives were developed for this work, combining literature review, data analysis, analytical technique development, focused experimentation, and modeling:

- Determine REE abundance and trends in natural waters.

- Develop efficient liquid-liquid extraction technique for separation of REE from hypersaline brines

- Study the effects of ligand functionality and geometry on the partitioning behavior of the REE from brines to functionalized adsorbents

These individual tasks are described subsequently in §2.1–2.3.

2.1 Determine REE abundance and trends in natural waters

In this objective, a compilation and analysis of data from numerous independent studies of REE in natural waters was performed. The compiled data were used to develop a consistent database of REE concentrations and their associated major solute chemistry and to explore interelement relationships, examine trends in REE abundance, and test hypotheses related to REE abundance as functions of major solution chemistry parameters. The tasks within this objective were: (1) to ascertain an expected range of dissolved REE concentrations in waters of variable chemistries, (2) to derive unbiased estimates of REE distributions, and (3) to investigate trends in REE abundance in groundwater in relation to other available chemical parameters (e.g. pH, ionic strength, and major solution species). Results of this work have been published and described in detail in Noack et al. [36].

The major findings of this work were that the REE are found in natural waters across ten orders of magnitude of concentrations, that pH appears to be the only variable at the "macro" scale of this study which significantly influences abundance, and that, while limited data exist for REE in brines, the REE composition of brines is potentially unique. These results have implications on the remainder of this project. First, the natural variability and lack of data of REE in brines necessitates development of robust, reliable analytical techniques for such waters as well as the application of this technique to hypersaline brine samples. Second, the lack of consistent predictors of REE abundance requires focused experimentation of REE source and sink behavior in the environments of interest.

2.2 Develop a liquid-liquid extraction technique for separation and concentration of REE from brines

In this objective, REE separation and preconcentration from highly saline brines using a liquid-liquid method was studied. A significant limitation of published methodologies for REE quantification in aqueous samples is the lack of validation of the methods in systems with high salinity and dissolved metals. A common ligand used for REE complexation and extraction, bis(2-ethylhexyl) phosphate (HDEHP), was studied in a heptane diluent. The tasks of this objective were to: (1) demonstrate feasibility of REE recovery from small volumes of hypersaline brines by LLE, (2) optimize LLE methodology for high salinity and metals content, and (3) validate method for synthetic brines of varying complexity. Results of this work have been published and described in detail in Noack et al. [37].

The major finding of this work was that the REE are measurable at environmentally relevant concentrations in hypersaline solutions with high accuracy using small volumes of samples. Moreover, the method is robust to variability in salt, dissolved organic carbon, and competing metal concentrations. This method can be confidently applied to the analysis of natural samples in the future for calibration of engineered recovery systems.

2.3 Study REE partitioning to novel functionalized adsorbents from saline solutions

In this objective, novel functionalized adsorbents were studied for the extraction and recovery of REE from geothermal fluids. Geothermal fluids represent a promising alternative REE source given their known, elevated REE concentrations [38, 39] and the large volumes in which they are handled daily ($\sim 100,000$ gal/MWe/day) [40]. Extraction of the REE from these chemically complex fluids may be possible using high-capacity, REE-selective adsorbents in a fixed bed (or another configuration). Experimentation and modeling as part of this objective will focus on the batch reactivities of two ligands known to have high REE affinity (phosphono-acetic acid, PAA, and Diethylenetriaminepentaacetic acid?, DTPA, which is grafted onto the surface as either an acid form or a dianhydride), which have been attached to an aminated silica gel support. This work will be completed in collaboration with Kedar Perkins (Dept. Chem.) and Jon Callura (CEE), and will serve as the basis for an ongoing study of REE extraction from geothermal fluids.

2.3.1 Material characterization

A key component of understanding the reactivities of our adsorbents is the thorough characterization of the materials. Multiple techniques will be used to characterize the functionalized adsorbents including thermogravimetric analysis (TGA), acid-base titrations, electrophoretic mobility measurements, and X-ray photoelectron spectroscopy. Figure 2.1 illustrates the results of TGA for the unfunctionalized, 3-aminopropyl silica gel (AP-SiO2) as well as the DTPA-functionalized resin. For each sample, the concentration of sites was detemined to

be 1 mmol/g, which agrees with the specification provided by the AP-SiO2 manufacturer. Figure 2.2 illustrates the conversion of the basic surface amines of the unfunctionalized material to an acidic form as a result of the functionalization scheme (addition of carboxyl groups).
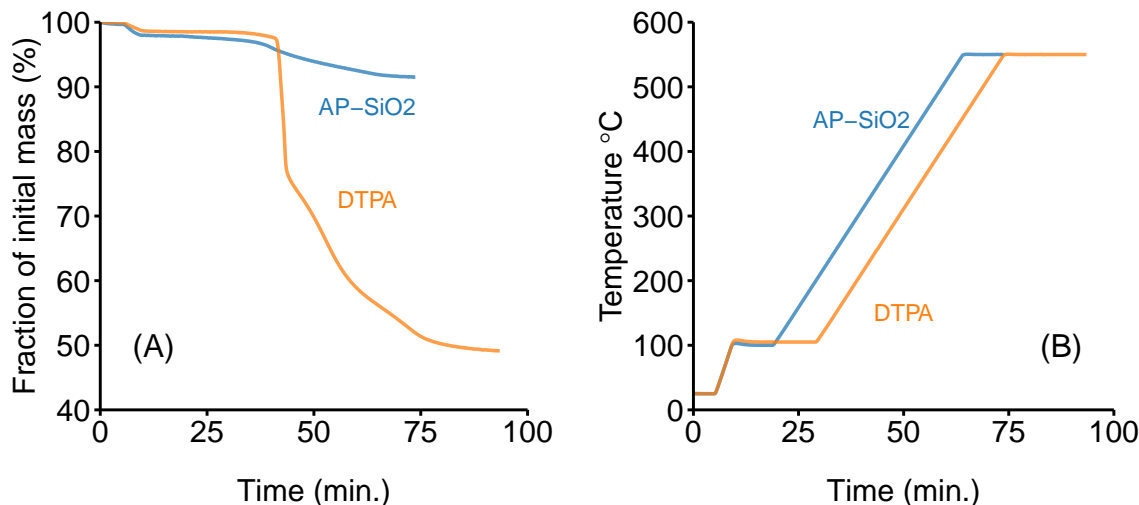

Figure 2.1: Thermogravimetric analysis (TGA) of starting material (AP-SiO2) and DTPA-functionalized adsorbent. (A) Mass loss vs. time for two solids tested. Using the molecular weights of each surface group, the site concentration is calculated to be 1 mmol/g for each solid. (B) Temperature ramp programs used for TGA.

2.3.2 Adsorption edges

Adsorption edges will be used to study the pH dependency of the adsorbent performance. Some preliminary data for anhydrous-DTPA is shown for 0.5 M and 3.0 M NaCl using Nd, Gd, and Ho as characteristic REE in Figure 2.3. From these results, we see peculiar behavior where the REE are bound significantly at low pH, but do not adsorb at mid-range/circum neutral pH as would be expected based on carboxyl-functionality ("expected" model behavior for DTPA shown in Figure 2.4). Additional testing is underway to determine the sources of this deviation. Adsorption edges will be generated for all functionalized materials (PAA and both DTPA forms).

2.3.3 Uptake kinetics

The surface complexation/adsorption kinetics of these adsorbents is a critical design parameter for fixed bed deployment. These uptake kinetics will be studied in batch for all adsorbents. Figure 2.5 illustrates that not only are there kinetic limitations to the adsorption (evidenced by the significant increase from 3 hours to 3 days of contact time), but that it is also element dependent, potentially based on ionic size (r_{3+}: Nd>Gd>Ho) as the thermodynamic affinities display a reverse trend [42]. Kinetic tests will utilize higher REE concentrations, so
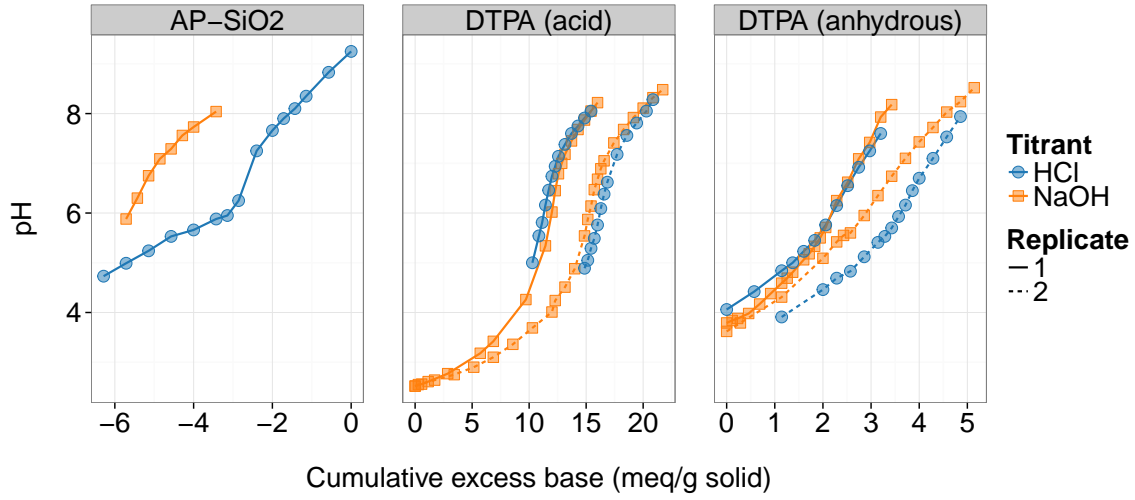
Figure 2.2: Titration curves for the raw, un-functionalized support (3-aminopropyl silica gel, 3-AP Si) and for two forms of the functionalized resins (DTPA (acid) and DTPA (anhydrous)). Titrations were performed in 5 g solid L^{-1} suspensions in a 0.5 M NaCl electrolyte. Solid and dotted lines indicate replicate titrations. Note that the x-axes for each panel are unequal while the y-axes are uniform.
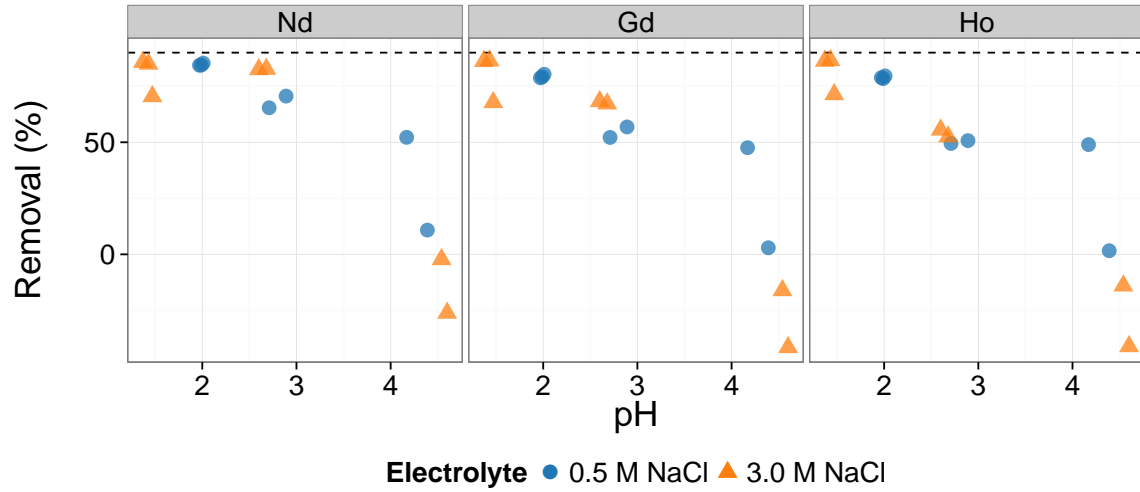
Figure 2.3: REE removal ($1 - C_f/C_i$; $C_i = 100$ ppb each REE) from saline solutions as a function of pH for two different electrolyte concentrations using 10 g/L anhydrous-DTPA functionalized silica gels. Contact time was 3 hours. Dashed line indicates 90% removal. Large negative removals shown are likely a result of pipette error when diluting 3 M NaCl samples for analysis, but based on reagent purities (no detectable REE contamination) these can be effectively be treated as zero.
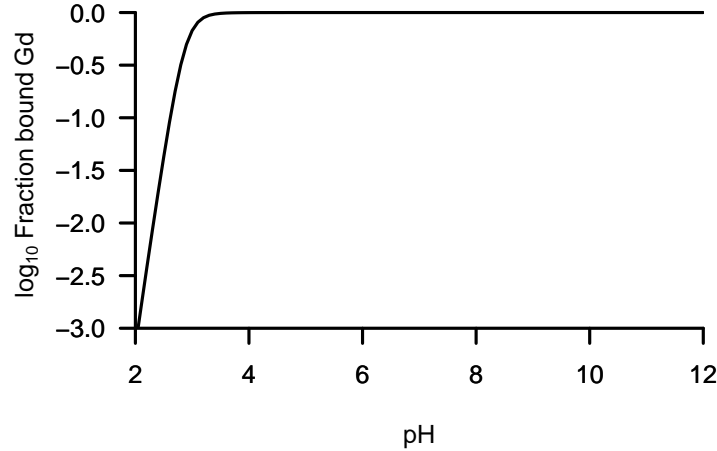
Figure 2.4: Predicted adsorption isotherm for DTPA-functionalized resin, using aqueous thermodynamic data in lieu of a surface complexation model. Model considered the following species of Gd: Gd^{3+}, $GdOH^{2+}$, $Gd(OH)_2^+$, $Gd(OH)_3^0$, $GdCl^{2+}$, $Gd(DTPA)^{2-}$, and $Gd(HDTPA)^-$. Association constants for these species are taken from Lee and Byrne [41] for the hydrolysis products, Millero [8] for the chloride complex, and Grimes and Nash [42] for the DTPA species (which also include the acid-dissociation constants for DTPA). Calculation conditions were $[Gd]_{tot} = 100$ ppb, $[DTPA]_{tot} = 10$ mM, 0.5 M NaCl.

that small aliquots can be removed from each reactor and diluted for measurement without significantly altering the solid-liquid ratio. Because reactor pH cannot be measured *in situ*, it will only be recorded before REE addition and at the end of contact time. Suspensions will be pre-equilibrated with appropriate acid or base doses prior to REE dosing to minimize pH changes during reaction.

2.3.4   Constant pH isotherms

Constant pH isotherms will provide useful data regarding the REE affinity (K_{LF}) of the functionalized materials as well as the effective capacity (q_{max}). Roosen et al. [43] functionalized a silica–chitosan hybrid support with DTPA and found that the isotherm data were well fit by a Langmuir-Freundlich model (Eq. 2.1).

$$q_e = q_{max} \left(\frac{(K_{LF}C_e)^n}{1 + (K_{LF}C_e)^n} \right) \tag{2.1}$$

Solid suspensions, pre-equilibrated with acid or bases doses, will be mixed with varied REE doses for a contact time determined from kinetic experiments.

2.3.5   Tests of REE-selectivity

In the complex aqueous systems of interest, the REE will compose a trace component of the bulk solutes. Therefore, it is important to understand the effects of competitive cations
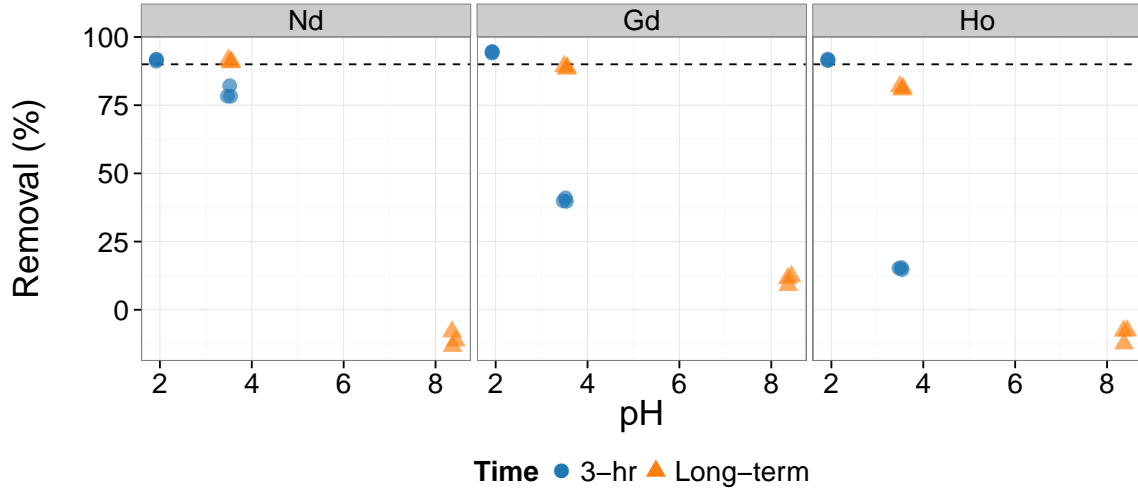
**Figure 2.5:** REE removal ($1 - C_f/C_i$; $C_i = 100$ ppb each REE) from 0.5 M NaCl as a function of pH for two different contact times using 10 g/L anhydrous-DTPA functionalized silica gels. Contact times were 3 hours and 3 days. Dashed line indicates 90% removal.

on REE uptake by our functionalized materials. Based on atomic radii, calcium (which is abundant in geothermal fluids) may be a potent competitor given the large mass action advantage of higher concentration. Figure 2.6 shows that for a 3 : 1 Ca:Gd ratio, no significant decrease of Gd adsorption is observed. Future competition tests will focus on more relevant solute concentrations, determined based on literature review of geothermal fluids [e.g. 44], as well as other metals.

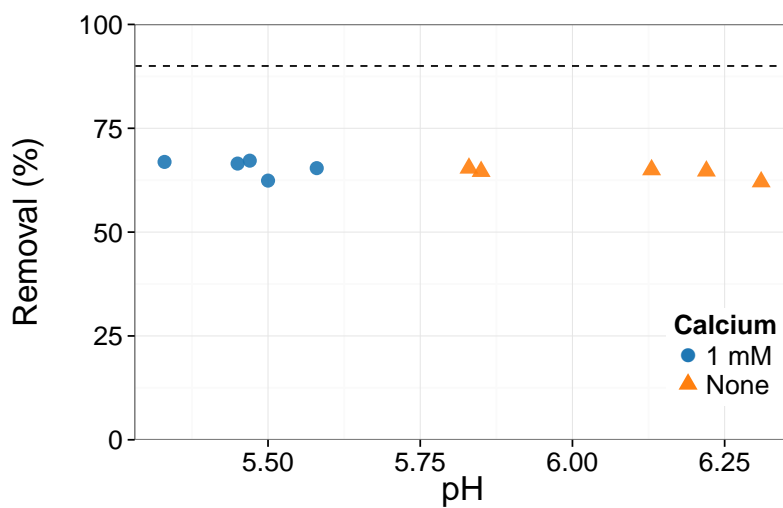**Figure 2.6:** Gd removal $(1-C_f/C_i; Ci = 300\ \text{µM Gd})$ from 0.5 M NaCl solutions as a function of pH with and without Ca dosing using 10 g/L anhydrous-DTPA functionalized silica gels. Contact time was 3 hours. Dashed line indicates 90% removal.

3.0 Major contributions and broader impacts

At the conclusion of this research, we expect to have contributed significant knowledge to the field of REE geochemistry, in particular, as it applies to saline fluids. While the context of this work primarily relates to geothermal waters, the potential for extraction of REE from aqueous media is far reaching. Other large-scale engineering processes such as carbon capture, utilization, and storage (CCUS), desalination waste-brine management, or oil and gas production handle large volumes of highly saline waters that may contain valuable quantities of REE. Moreover, highly selective adsorbents would represent a significant improvement compared to the relatively non-specific ligands utilized in solvent extractions during traditional REE production schemes.

More specifically, each objective of this research is expected to improve understanding of REE geochemistry. In Objective 1, the compilation and analysis of literature data highlighted the enormous variability in dissolved REE concentrations, while identifying the lack of knowledge regarding the controls on REE abundance and the occurrence of REE in hypersaline solutions. Objective 2 will provide a robust and rigorously validated technique for filling in this gap, allowing for reliable determination of the REE in brines, without requiring large sample volumes. Finally, Objective 3 provides systematic study of the effects of surface attachment of ligands, with known aqueous REE affinity, for use in an extraction and recovery scheme. As yet, economically viable alternatives to traditional REE extraction are almost non-existent. This work represents the early stages of developing a technology with the potential to generate a consistent domestic supply of materials critical to green energy and defense technologies; valorize high-volume wastes or low-value industrial byproducts; and avoid environmental impacts from primary REE mining..

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