

Measurement and Recovery of Rare Earth Elements from Hypersaline Fluids

Ph.D. proposal

Clinton W. Noack

Department of Civil and Environmental Engineering
Carnegie Mellon University
Pittsburgh, PA 15213

Ph.D. Committee and affiliations

Professor Athanasios Karamalidis (co-advisor), CEE

Professor David Dzombak (co-advisor), CEE

Dr. J. Alexandra Hakala, NETL-Pittsburgh

Professor Mitchell Small, CEE

Professor Newell Washburn, Chemistry

23 October 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 challenges 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 motivate 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 development of the Marcellus shale for natural gas provides an excellent case study for the use of REE in source identification and apportionment. Both the character (i.e. elevated salinity, dissolved heavy metals, naturally occurring radioactive material) and volume (millions of liters per drilled well) of waste brines associated with the oil and gas extractive industry provide sufficient motivation for investigation of advanced monitoring tools for protection of freshwater resources. Similarly, the wide variety of contaminant sources (i.e. having the potential to degrade high quality waters) in Southwestern Pennsylvania — including conventional oil and gas wastewater, abandoned mine drainage, varied industrial wastes, municipal waste, and agricultural run-off — further promote the search for analytes which would allow for discrimination among potential sources.

The REE have previously been used to hypothesize groundwater mixing and sources of salinity in steady-state systems. However, these methods have either lacked mathematical rigor (i.e. are qualitative and typically based on visual inspection of REE profiles) or have failed to consider variability in source signatures while assuming conservative behavior (i.e. deterministic).

The goals of this research will be to evaluate the feasibility of using REE as tracers of saline groundwaters, and to determine the appropriate mathematical and statistical models for interpreting REE data for environmental forensics. The development of these models will be supported through focused experimentation and development of analytical techniques along with consideration of previously published data and adaptation of existing source apportionment models.

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.

Contents

Abstract	ii
List of Tables	v
List of Figures	vi
1 Introduction	1
1.1 What are rare earth elements?	1
1.2 What is the context of this study?	2
1.3 What are the goals of this study?	4
2 Research plan	5
2.1 Determine REE abundance and trends in natural waters	5
2.2 Develop a liquid-liquid extraction technique for separation and concentration of REE from brines	6
2.3 Study REE partitioning to novel functionalized adsorbents from saline solutions	6

List of Tables

List of Figures

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.

Rare earth elements (REE) constitute a group of chemically similar metals in the lanthanide series (atomic numbers 57–71), as well as yttrium and scandium, which are essential components of modern technologies from magnets to batteries. Their extensive use as chemical catalysts, in metallurgy and alloys, glass polishing and other sectors of manufacturing make them an absolute necessity for advanced technologies and materials [1]. However,

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,⁷ 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.⁸

In the natural sciences, predictable thermodynamic differences between the REE make these elements uniquely capable tools for interpreting natural geologic and chemical processes.^{9, 10} Rare earth lithogeochemistries have long been used to infer depositional environments of geologic strata.^{9, 11, 12} Similarly, REE serve as benign analogs to the transuranic actinide series for nuclear waste disposal studies;^{13, 14} as potential markers of regional authenticity for high value exported food products such as wine, pumpkin-seed oil, and olive oil;¹⁵⁻¹⁷ and for studying mixing and metal cycling in the oceans.^{18, 19}

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;⁷ some studies further distinguish middle REE (MREE), though the specific elements are inconsistently defined between authors.²⁰⁻²² 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 Eu²³ and large anthropogenic emissions for Gd²⁴ — 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.²³

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 [2]. 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 [?]. 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. 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 U.S. demand for many years, 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 coal fly ash. Recovering REE from unconventional resources is of national security and economic importance.

Although the REE supply is expected to remain even with demand for the next 5-7 years, a supply shortage is expected in the longer term, as demand for technologies using REE increases [REF]. Therefore, sustained growth in these technologies is dependent upon the diversification of REE sources to meet demand. Traditional mining practices used for extraction and enrichment of REE from ores are unlikely to fulfill this demand for technical and economic reasons. This emphasizes the need for REE separation and recovery from unconventional matrices.

Global REE reserves are estimated at 130 million metric tons [1], 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 [3, 4]. 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 environ-

mental burden [5]. Even when present in ores at appreciable levels, REE are commonly comingled 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) [REF]. Stringent environmental regulations, time-intensive processes, and expensive permits complicate the opening of new, domestic mines because of these inherent risks. On this basis, 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 [REF]. China also had the largest demand for REE, at 66% of the total global demand [REF]. The US was the next largest consumer, at 15% of the total demand. In 2011, China announced a 35% reduction in exports of REE, in an effort to meet their domestic needs [REF]. This created large instability in the REE market as there were no other major sources for REE. China is expected to continue reduction of exports, through either quotas or tariffs, as a mean to reduce stress on its REE reserves [1, 2].

Primary mining effectively constitutes 100% of the REE production worldwide [4, 16], 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 [17]. High volumes of REE are deployed in permanent magnets, while high-value REE are used in phosphors [15], making these products two primary targets for recycling from EOL products along with metal hydride batteries [4, 7]. REE are applied in many other products, but the REE content is dissipated in-use or rendered unrecyclable by current designs [13]. Ionic liquids, which are becoming increasingly popular for “green” separations [18], have been shown to selectively leach REE from $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors with facile REE recovery by acid stripping or direct oxalate precipitation [19].

Similar approaches may be deployed for recycling scrap magnets, namely complete or selective dissolution of the magnet, followed by extraction of the REE from the resulting digestate. After dissolution of scrap NdFeB magnets in 6 M HNO_3 , Kim, Daejin et al. [20] employed membrane assisted solvent extraction to effectively separate the Nd (as well as Pr and Dy) from the Fe and B bulk. However, Bandara et al. [21] propose that recycling of ferrous shredder-waste (where magnets could accumulate) 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 [21].

Supply- and demand-side issues have renewed interest in critical material mining from seawater and other aqueous sources [9]. Several ongoing projects, funded by the Department of Energy Office of Energy Efficiency and Renewable Energy, are focused on the extraction and recovery of the REE (and other critical materials) from geothermal brines [22]. The team for this proposal is performing one of these projects, focused on development and use of functionalized adsorbents for REE extraction and recovery. These projects all aim to selectively capture the REE from a concentrated solution, while rejecting the bulk electrolytes as well as other, less valuable metals.

1.3 What are the goals of this study?

This research seeks to address the fundamental question of REE utility as aquatic geochemical forensic tools. This work is motivated by the desire to improve the ability to detect fluid mixing and determine sources of mixing components for protection of freshwater resources. A combination of a literature analysis, analytical method development, natural sample analysis, controlled experimentation, and statistical and geochemical modeling will be used to address these goals.

The four, 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?

The specific objectives of this work were developed to address gaps in the literature to date while building on the existing REE and natural tracer knowledge base. These objectives are meant to address application specific (i.e. shale gas development) uncertainty as well as foster a more fundamental understanding of the REE systematics. The methods proposed to address these objectives are detailed in §2.1-2.4.

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 §2.1–2.4.

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.⁵⁰ which is included in Appendix A.1.

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.⁵⁰ which is included in Appendix A.2.

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

References

- [1] U.S. Geological Survey. Mineral commodity summaries 2015. Report, U.S. Geological Survey, 2015.
- [2] Frost & Sullivan. Supply/demand dynamics of rare earth elements. Report, December 2013.
- [3] RL Moss, E Tzimas, H Kara, P Willis, and J Kooroshy. Critical metals in strategic energy technologies. Technical report, European Commission Joint Research Centre Institute for Energy and Transport, 2011.
- [4] Elisa Alonso, Andrew M Sherman, Timothy J Wallington, Mark P Everson, Frank R Field, Richard Roth, and Randolph E Kirchain. Evaluating rare earth element availability: A case with revolutionary demand from clean technologies. *Environmental science & technology*, 46(6):3406–3414, 2012.
- [5] George G. Zaines, Berlyn J. Hubler, Shuo Wang, and Vikas Khanna. Environmental life cycle perspective on rare earth oxide production. *ACS Sustainable Chemistry & Engineering*, 3(2):237–244, 2015.