

Screening the Effects of Ligand Chemistry and Geometry on Rare Earth Element Partitioning From Saline Solutions to Functionalized Adsorbents

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ABSTRACT

The goal of the project is to prepare adsorbents, solid supports functionalized with organic ligands, for separation and recovery of lanthanides from chemically complex geothermal fluids of geothermal power plants. The project involves initial development and testing of low-cost, reusable functionalized adsorbents for selective recovery of critical elements from geothermal fluids in multistep processes, with pre-concentration of rare earth elements (REE) on the resin and recovery by acid elution. Ligands with known ability to bond selectively with REE in aqueous solution are examined. Tests with simulated low-temperature geothermal waters under simulated extraction process conditions are conducted. Results of material characterization and uptake experiments are presented.

Introduction

The rare earth elements (REE) are commonly defined to include the naturally occurring lanthanides (Lanthanum (La) to Lutetium (Lu), excluding Promethium (Pm)) as well as Yttrium (Y) and Scandium (Sc), which are lighter, but chemically similar elements. Prized for their unique properties, the REE are widely applied in both consumer and industrial technologies from electronics displays and batteries to high-strength lasers and magnets.¹ However, global supplies of these materials are undiversified (with up to 95% of global demand being met by Chinese production), primarily because mineable ores are limited in number and geography.² Efforts to diversify the REE supply have focused on reopening old projects, such as the Mountain Pass mine in California, USA, or developing lower grade resources.

This work is focused on diversifying REE resources by examining hypersaline brines as an alternative source. The challenges associated with recovering REE from complex aqueous media relate to the fact that existing separation technologies for REE are not adequately selective or involve many chemical steps, which increases the overall cost of the process. Solid-phase extraction (SPE) of REE from aqueous matrices has desirable advantages relative to other separation techniques, such as liquid-liquid separation or co-precipitation, because consumption of reagents is limited, the separations can be performed rapidly with few process steps, and SPE can be scaled-up more easily.

We are screening functionalized adsorbents for their potential use in selective extraction of REE from simulated brines. Numerous ligands have been developed that complex strongly with the REE in solution, making them attractive candidates for surface functionalization, but their properties for solid phase extraction of the REE are unknown. We explore the relative efficacy for REE extraction of ligands that possess comparable functional groups but unique geometries (e.g. mono- vs. polydentate) as well as ligands with similar geometries but unique functional groups. Results are presented for characterization of the functionalized adsorbents (and synthesis procedure) as well as uptake experiments from synthetic brine solutions of variable composition.

Methods and Materials

Prospective ligands were acquired from various commercial suppliers and bound to solid supports. Sorption site concentration and attachment efficiency were determined using a fluorescence-based assay. Changes to the surface chemistry of the adsorbents were further studied by x-ray photoelectron spectroscopy (XPS) and rapid acid-base titrations of aqueous suspensions.

Uptake experiments were performed in synthetic brine solutions prepared using high purity salts. Experimentation focused on a 0.5 M NaCl background electrolyte with varying amounts of REE (using Neodymium (Nd) and Gadolinium (Gd) as model elements) and competing divalent cations (Ca and Zn).^{3,4} Adsorption edges (i.e. recovery as a function of pH with other conditions fixed) were collected for varying solution chemistries and sorbent-to-sorbate ratios in batch reactors with 3 hours reaction time. From these data, distribution coefficients were derived. In all experiments, the sorbed fraction of the REE was determined by mass balance, measuring only the supernatant concentration by ICP-MS. Control experiments (without solids) were performed at a range of REE concentrations and pH values to rule out wall-effects and/or precipitation.

Description of Results

Solid support characterization provided by the manufacturer indicated approximately 0.7 mmol sites/g of unmodified material. Based on XPS and fluorescence results, we estimated the density of sites and the attachment efficiency for all functionalized adsorbents. Titration studies showed a shift from basic surface chemistry (owing to the amine groups) to an acidic chemistry, confirming the attachment of chelating groups.

Observed percent recoveries from synthetic brines in uptake experiments indicated that the most promising ligands were poly-dentate with carboxyl-functionality. Screening conditions spanned a range of concentrations for competing ions expected in geothermal waters,⁴ and the upper range of REE concentrations found in natural waters.³ Higher than average REE concentrations were employed to increase precision of uptake calculations. Further experimentation is required to validate these preliminary results over a range of electrolyte conditions. Finally, significant uptake was observed for the best performing ligands throughout a pH range relevant to geothermal fluids.

REE uptake was robust in the presence of competitive, divalent cations (Ca), indicating good selectivity of the ligands screened so far. Addition testing with Zn and other potentially competitive divalent cations is planned.

Plans for Future Experimentation

Testing to date has focused on determining the batch (pseudo-) equilibrium behavior of the functionalized adsorbents at room temperature and in a constant background electrolyte. Successful implementation of this technology at scale requires understanding of the effects of temperature of extraction efficiency and kinetics. Experiments in batch will include tests at temperatures more relevant to geothermal fluids, Materials have been produced using a larger support size and will be tested. In addition, real brine samples are being acquired for testing through collaborative DOE efforts.

References

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