



The role of water in extraction and separation of rare earth elements in supercritical carbon dioxide



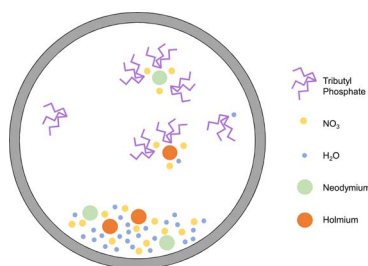
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GRAPHICAL ABSTRACT



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ABSTRACT

Rare earth elements can be complexed with tributyl phosphate, thus forming a metal-ligand complex which is soluble in supercritical CO₂. In this study, neodymium and holmium nitrate were extracted into supercritical CO₂ with varying amounts of tributyl phosphate (from 8 to 80 mM) and water (from 0 to 200 mM). Temperature was held at 60 °C and pressure ranged from 17 to 28 MPa. UV–vis spectroscopy was used to measure supercritical metal concentrations, and near-IR spectroscopy was used to measure water concentrations. It was found that holmium is preferentially extracted over neodymium, with the greatest separation occurring when the molar ratio of tributyl phosphate to lanthanides was approximately 1–2, and when no water was added. Affinity constants were fit to the data. The results suggest that a soluble Ho(NO₃)₃·2TBP·H₂O complex accounts for the preferential extraction of holmium, especially at lower water and tributyl phosphate concentrations.

1. Background

1.1. Motivation

Rare earth elements (REEs) consist of the 15 lanthanides, scandium, and yttrium. REEs are used in a variety of applications including electronics, magnets, catalysts, glass, and solid-state lighting. Many of these applications are critical for strategic technologies, including REE permanent magnets for electric vehicles, phosphors for energy-efficient lighting, and catalysts for automotive emission reduction [1,2]. To

address the United States' dependence on imported REEs, the Department of Energy is seeking to develop domestic sources using a multi-part strategy, including developing improved separation processes to isolate individual REEs from each other [1].

REEs are conventionally separated using solvent extraction. In this process, an aqueous solution is brought into contact with a nonpolar phase containing organic extractants, which form metal-ligand complexes with the REEs and pull them into the nonpolar phase. This is generally done in a series of mixer-settlers, which consist of a mixing stage to form an equilibrium metal distribution between the two

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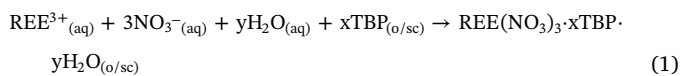
phases, followed by a settling stage where the phases coalesce and separate. The REEs are then stripped with an aqueous stream, also usually in a series of mixer-settlers [2,3].

Conventional solvent extraction can be used to separate REEs from gangue elements to form a mixed REE product. Alternatively, solvent extraction can generate relatively pure individual REE products by exploiting differences in binding affinity due to the decreasing ionic radius across the lanthanide series [4]. However, because these binding affinity differences are very minor, only slight separation of adjacent lanthanides can be achieved [3]. As a result, hundreds of mixer-settler stages are sometimes required in order to produce multiple single-metal products [2]. Another disadvantage of solvent extraction is the high acid concentrations which are sometimes required in the strip solution depending on the type of extractant employed; 4–5 M HCl was used for europium production at Mountain Pass, for example [4]. This results in high acid consumption with associated costs and environmental impacts [2,5,6]. Clearly alternative separation and purification methods for REEs with lower costs and environmental effects would be attractive for commercial use. The use of selective extraction in supercritical fluids may offer a cleaner and more sustainable option than conventional solvent extraction.

1.2. Supercritical extraction

Several researchers have explored the use of supercritical extraction to separate various REEs from each other. In one version of this process, a solid or solution phase containing REEs is brought into contact with supercritical carbon dioxide containing a dissolved extractant. The extractant combines with the salt to form a metal-ligand complex, which then dissolves into the supercritical phase. Advantages over conventional solvent extraction could potentially include faster reaction rates due to the high diffusivity and low viscosity of supercritical CO₂, enhanced separation by tuning solvation properties of the CO₂ via pressure or temperature adjustment, and potential reduction of acid required for stripping.

Many different extractants have been used for supercritical extraction of lanthanides including tributyl phosphite [7], tributyl phosphine oxide [7], di-2-ethylhexyl-phosphoric acid [8], and various beta diketones [7,9–11]. The tributyl phosphate (TBP) system has received particular attention in recent years. TBP is a neutral extractant sometimes used in solvent extraction of REEs from nitrate solutions. It functions by replacing coordinated water molecules surrounding a metal salt, thus rendering it soluble in the organic (or supercritical) phase.



TBP has a greater binding affinity to heavier REEs, due to the stronger binding forces associated with their smaller atomic radii [3,4,12], but its selectivity is low relative to other extractants [3,4]. Studies have shown that heavier REEs are preferentially extracted by TBP in supercritical systems [13–15]. Most recently, a study by Zhu et al. showed preferential extraction of holmium over neodymium at temperatures of 45–60 °C and pressures of 14–19 MPa (Nd and Pr were shown to separate very little) [15]. It has been suggested that this preferential extraction of heavier REEs is due to a combination of the TBP binding affinity effect and differences in the supercritical solubility of the various metal-ligand complexes. For example, Nd forms a CO₂-soluble complex with 3 or 4 TBP molecules, while Ho forms a soluble complex with 2, 3, or 4 TBP molecules [13,14]. Supercritical CO₂ with TBP has been used to extract REEs from aqueous nitrate solutions [16,17] and from solid nitrate salts [13,14,18]. In general, a more water-rich environment will result in less extraction. This is because of 1) the reduction in REE activity from dilution and 2) the ability of water to form complexes with TBP and thus reduce the TBP available for REE

extraction [19]. Because water concentrations have not been measured in the supercritical phase during REE extraction, the effect of water on extraction and separation of REEs has not been quantified.

1.3. Goal and scope

In this work, neodymium and holmium nitrate were extracted using TBP in supercritical CO₂. Absorption spectroscopy in the visible range was used to quantify extraction of Nd and Ho, as demonstrated in previous studies [10,13,15]. A novel element of this work is the use of near-IR spectroscopy [20] to measure water extraction in conjunction with lanthanide extraction. A range of TBP concentrations, a range of water concentrations, and a range of pressures were explored to observe the effect on Nd/Ho extraction and separation. This work builds upon previous studies by:

- Demonstrating improved separation of Nd and Ho relative to previous work [15]
- Quantifying for the first time the effect of water on the extraction process via spectroscopic measurements in the near-IR range
- Fitting a set of affinity constants for Nd, Ho, and water extraction in agreement with the observed data

2. Materials and methods

2.1. Materials

Neodymium nitrate (Nd(NO₃)₃·6H₂O), holmium nitrate (Ho(NO₃)₃·5H₂O), and tri-n-butyl phosphate (TBP, 97%) were purchased from Sigma-Aldrich (St. Louis, MO). The TBP was dried with molecular sieves (mSorb 3A 8 × 12, Delta Adsorbents, Roselle, IL) prior to use. Karl Fisher titration indicated that the water concentration in the dried TBP was 170 ppm. A bone-dry liquid carbon dioxide tank with a siphon was purchased from Airgas (Radnor, PA).

The extraction system is shown in Fig. 1. All tubing and valves were purchased from High Pressure Equipment Company (Erie, PA). The CO₂ delivery system consisted of a CO₂ pump (Teledyne Isco model 260D, Teledyne ISCO, Lincoln, NE) equipped with a cooling jacket used to cool the CO₂ to 10 °C. A reactor with an internal volume of approximately 50 mL (3.05 cm inner diameter and 7.1 cm length) was used for the extraction experiments (Thar Technologies, Pittsburgh, PA). Sapphire windows capped each end (Thar Technologies, Pittsburgh, PA), and the seal was formed using fluoropolymer encapsulated Viton gaskets (McMaster Carr, Elmhurst, IL). Temperature was monitored via a 1/8" thermocouple immersed in the supercritical phase, and the pressure was monitored with a pressure transducer from Omega (Stamford, CT).

The cell was positioned in the sample compartment of a Shimadzu UV3600 spectrophotometer. A holder was used to position the cell such that the beam shone through the two sapphire windows, intersecting only the supercritical phase of the cell. A magnetic stir plate underneath the sample holder was used to agitate the cell.

2.2. Procedure

Each experiment began by loading the cell with the lanthanide nitrate salts, TBP, and water if applicable. Care was taken to ensure that the sapphire windows remained clean and free of solids or droplets. The cell was heated to 60 °C and pressurized with CO₂ to the required pressure. The cell was then allowed to stir for 30 min. Previous studies have shown that 30 min of stirring is sufficient to reach equilibrium concentrations of metal complexes in supercritical CO₂ [7,10,21,22]. This was confirmed by measuring spectra at regular intervals; it was found that 30 min was sufficient to reach steady state.

The spectrophotometer was used to measure the absorbance spectra of the supercritical phase using a sampling interval of 1 nm. Baseline spectra were taken every few hours to correct for any atmospheric

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