Extraction of Rare Earth Elements from Chloride Media with Tetrabutyl Diglycolamide in 1-Octanol Modified Carbon Dioxide

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Abstract: Rare earth elements (REEs) are critical to our modern world. Recycling REEs from used products could help with potential supply issues. Extracting REEs from chloride media with tetrabutyl diglycolamide (TBDGA) in carbon dioxide could help recycle REEs with less waste than traditional solvents. Carbon dioxide as a solvent is inexpensive, inert, and reusable. Conditions for extraction of Eu from aqueous chloride media were optimized by varying moles percent of 1-octanol modifier, temperature, pressure, Eu concentration, TBDGA concentration, Cl^- concentration, and HCl concentration. These optimized conditions were tested on a Y, Ce, Eu, Tb simulant material, REEs containing NdFeB magnets, and lighting phosphor material. The optimized conditions were found to be 23 °C, 24.1 MPa, 0.5 mol% 1-octanol, with an excess of TBDGA. At these conditions $95 \pm 2\%$ Eu was extracted from 8 M (mol/m^3) HCl. Extraction from the mixed REE simulate material resulted in separation of Y, Eu, and Tb from the Ce which remained in the aqueous solution. The extraction on NdFeB magnet dissolved into 8 M HCl resulted in extraction of Pr, Nd, Dy, and Fe >97%. This results in a separation from B, Al, and Ni. Extraction from a trichromatic lighting phosphor leachate resulted in extraction of Y and Eu >93% and no extraction of Ba, Mg, and Al.

Keywords: rare earth elements; carbon dioxide; extraction; chloride media; phosphors; magnets; diglycolamide

1. Introduction

Rare earth elements (REEs), the 15 lanthanides plus scandium and yttrium, are important and essential for our modern world. Rare earth elements are used in micro-electronic devices (e.g., cell phones), magnets (used in wind turbines), lighting phosphors (e.g., fluorescent lighting; LEDs), solid-oxide fuel cells, catalysts, and advanced weapons systems [1–4]. Due to the widespread usage of the REEs there is high industrial demand, and the projected exports coming out of China cannot meet worldwide demand [5]. In 2017 China produced about 78% of the world supply of lanthanide ores and refined REE products [6]. China's current monopoly of REEs and REE-containing materials allows it to dictate supply and export quotas as well as market price. While there are REE deposits in regions other than China, opening a mine in the United States requires significant financial investment [7], a lengthy environmental assessment and permitting process (up to 10 years for the permitting process [8]), and additional time thereafter to actually develop the mine and produce product. One way to expand the supply of REEs is through urban mining. Urban mining is "the systematic reuse of anthropogenic material from urban areas" [9]. Urban mining can be used to recycle REEs from end-of-life products. Through recycling, supply chain vulnerabilities can be minimized by narrowing the gap between REE supply and REE demand.

Some REE recovery methods propose use of HCl for dissolution recovery of REEs from a variety of matrices including ores and e-waste. Soluble, leached REEs are removed from the acidic liquor using a ligand in a multi-stage solvent extraction process. The common ligands used in the REE mining industry are di-2-ethylhexyl-phosphoric acid (P204) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (P507) [10–12]. Traditional multi-stage solvent extraction results in organic solvent byproduct waste. Extraction and recovery of REEs from end-of-life products is very similar to recovery of REEs from ore, in that strong mineral acid usage to dissolve REEs from the various matrices is the most feasible approach as evidenced by the majority of reports in literature where end-of-life products are concerned [13–22].

In this study, solvent extraction using CO_2 as the main extracting solvent is examined. The purpose for exploring use of CO_2 is to replace the main organic solvent used in conventional solvent extraction processes (e.g., dodecane, hexane, Isopar, etc.) with a solvent that is less expensive, easier to recycle and recover, and which has considerably fewer negative environmental side-effects. Supercritical carbon dioxide is used in scaled industrial systems for a variety for industrial extraction purposes [23]. Carbon dioxide can be used for separations and extractions in a variety of physical forms. The gas can be heated and compressed into the supercritical fluid phase and used to extract metals, or the gas can be condensed into a dense liquid phase. Whereas many literature reports can be found for supercritical fluid metal extraction, few authors report on use of liquid CO_2 for metal extraction. An extraction processes using liquid CO_2 would consume less energy than a supercritical CO_2 process as it would require no heat while the pressure requirements would be similar for either system.

Metal ions are not soluble in CO_2. Thus, in order for solvent extraction of metal ions using CO_2 to occur the charge on the metal ion must be made neutral, the coordination requirements of the metal must be fulfilled, and the resulting metal-ligand complex must be CO_2 soluble. A variety of chelating compounds can be used to complex metals which result in extractable metal-ligand complexes using CO_2 in either a supercritical or a liquid phase. Advantages for using liquid CO_2 compared to use of supercritical CO_2 are primarily higher solvent density and lower process temperatures. Higher solvent density leads to higher metal-loading capacity into the liquid CO_2 solvent, and lower processing pressures when compared to supercritical CO_2. Lower processing temperatures equate to cost-savings and, thus, more economical processes.

Diglycolamides (DGAs) have attracted much study and attention recently for hydrometallurgical extraction and separation processes for actinides and the REEs. These ligands are composed of carbon, oxygen, and nitrogen, unlike traditional organophosphorus ligands such as tri-*n*-butyl phosphate (TBP) or the ligands used in the REE mining industry (P204 and P507). Diglycolamides are recyclable as well as completely incinerable. Those properties allow for decreased waste being generated with a separation process. N,N,N′,N′-tetrabutyl diglycolamide (TBDGA), Figure 1 is a DGA with shorter carbon chains than the more commonly researched diglycolamides such as tetraoctyl diglycolamide (TODGA). TBDGA has been shown to be effective at extraction of lanthanides from nitric acid media [24,25]. It has also been shown that TBDGA has potential for lanthanide extraction from hydrochloric acid media into a variety of organic solvents. such as 1-octanol, chloroform, *n*-octane, etc. [26,27].
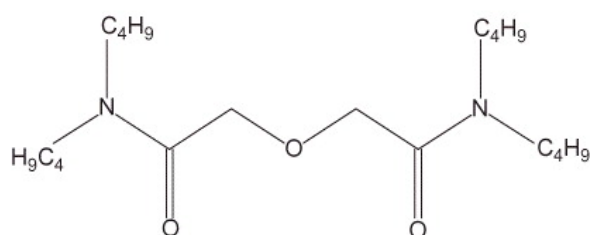

Figure 1. The chemical structure of N,N,N′,N′-tetrabutyl diglycolamide.

TBDGA has been studied for extraction of REEs in CO_2 previously. Tian et al. have studied the extraction of REEs with a TBDGA/HNO_3 adduct in supercritical CO_2 [28]. They found that TBDGA/HNO_3 adduct could not extract Nd or Eu. However, when acetone was introduced to the CO_2 as a modifier about 85% and 90% of Nd (III) and Eu (III), respectively, were extracted in a dynamic extraction. Using acetone as a diluent modifier makes the diluent more polar, allowing for more polar metal-ligand complexes to have increased solubility in CO_2. While this indicates the TBDGA-Ln-Cl species is polar, the complex is charge neutral [26,29]. The complex formation is shown in Equation (1):

$$Ln^{3+}_{(aq)} + nTBDGA_{(o)} + 3Cl^-_{(aq)} \leftrightarrow Ln(TBDGA)_nCl_{3(o)}, \tag{1}$$

Extraction of REEs from HCl with TBDGA in CO_2 has not previously been studied, and no reports of the extraction of metals with a liquid CO_2 system have been published. This paper examines and optimizes this extraction for pressure, temperature, mole percent 1-octanol as a modifier, varying TBDGA concentration, and varying metal concentration. Data from this research will be beneficial to the development of a more environmentally friendly, more efficient method of extracting REEs from end-of-life products.

2. Materials and Methods

The following reagents from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO, USA) were used as-received: Europium (III) chloride hexahydrate (99.9%), 1-octanol ($\geq$99%), hydrochloric acid (ACS grade), nitric acid (trace-select grade), and hydrogen peroxide (trace-select grade), tri-chromatic phosphor powder. Methanol (ACS grade) was used as received from Fisher Scientific (Fisher Scientific, Hampton, NH, USA). Liquid carbon dioxide was used as received from Norco Inc. (Boise, ID, USA). N,N,N$'$,N$'$-tetrabutyl diglycolamide (95%) was used as-received from Tractus Chemical (Tractus Chemical, London, England). All water used was purified to a resistivity of at least 18 MΩ-cm.

All extractions were performed in the system shown in Figure 2. The system downstream of the pumps was constructed of Hastelloy C276 with the exception of the pressure transducer and the over-pressure relief valve. All pumps were controlled with a Teledyne ISCO D-Series controller (Teledyne, Lincoln, NE, USA). Both CO_2 pumps were Teledyne ISCO model 500 HP syringe pumps and the ligand pump was a Teledyne ISCO model 260 D syringe pump. The pressure transducer was a HEISE digital pressure gauge (Ashcroft Inc., Stratford, CT, USA). All valves were purchased from Autoclave Engineers (Erie, PA, USA) and all tubing was received from VICI Valco Instruments Co. Inc. (Houston, TX, USA). The equilibrium reaction cell was 54.35 mL and the sample cell was 64.47 mL. Both cells were machined at Idaho National Laboratory from Hastelloy bar stock. The trap solution was ~20 mL of 1-octanol. The temperature of the cells was determined with a TRD thermocouple. For all extractions at 23 $\pm$ 2 °C the cells were kept uninsulated at room temperature and were not heated or cooled. For all extractions >23 °C the cells were insulated and the temperature was controlled using a process control assembly comprised of Omega Engineering PID controllers, variacs, and Omega Engineering cartridge heaters (Omega Engineering, Norwalk, CT, USA). For extractions at 2 $\pm$ 2 °C an ice bath was used to cool the cells. After all extractions, a methanol flush was performed by filling the cells with methanol and running 24.1 MPa CO_2 through the system until no methanol remained in the cells.

The basic extraction procedure was as followed: 10 mL of an aqueous solution containing europium (III) chloride was pipetted into the sample cell with the upstream tube dipped into the liquid. The solution was stirred continuously with a stir bar. The reaction cell and equilibrium cell were kept at a specific temperature. Liquid CO_2 (10 °C) was pumped into the system, shown in Figure 2, and the system was kept at a constant pressure. A micro-metering needle valve, heated to ~100 °C, was used to keep the CO_2 flowrate at about 5.0 mL/min at the pump. Once the CO_2 flow rate was constant a 1-octanol solution containing TBDGA was pumped into the system for 60 min. After 60 min the flow of 1-octanol and TBDGA was stopped. The CO_2 continued to flush the system for 90 min. After 90 min

the flow of CO_2 was stopped, and the system was depressurized. The contents remaining in the cell were collected and a water rinse of the cell was collected with the original sample. Extractions were performed in duplicate.
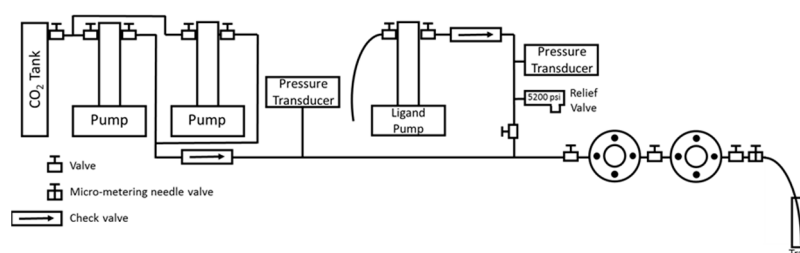
Figure 2. Diagram of the system used for CO_2 extractions.

All samples were digested due to organics remaining in the cell. This digestion followed the EPA method 3052: Microwave Assisted Acid Digestion of Siliceous and Organically-based Matrices. Some changes were made to the procedure to adapt it for current use. The samples were shaken before 0.500 mL was removed and put into a Teflon tube. To the sample 9.0 mL of concentrated nitric acid was added slowly. Drop-wise, 1.0 mL of hydrogen peroxide was added. A pre-reaction step was performed to avoid excessive pressure buildup while microwaving the samples. The sample was heated in a hot water bath at approximately 90 °C for 30 min. Every 5 min 0.5 mL of hydrogen peroxide was added to the samples drop-wise. The samples were then loaded into a MARS CEM Microwave (CEM, Mathews, NC, USA). The pre-programed setting 3052H-HP500 was used. After digestion the sample was removed and the tubes were rinsed three times with 10% HNO_3. The rinse was collected. The samples and rinses were diluted to 25.0 mL in a class A volumetric flask. This process was performed in triplicate. All sample analyses were performed on an Agilent model 7900 ICP-MS (Agilent, Santa Clara, CA, USA).

2.1. Phase Equilibrium of 1-Octanol at Room Temperature Liquid CO_2

Three milliliters of 1-octanol was added to a 54.35 mL Hastelloy C-276 reaction cell with a sapphire view window at approximately 23 °C. $CO_{2(l)}$ was delivered into the cell. The pressure at which there visibly was only one phase in the cell was recorded. This was repeated for 4, 8, 12, and 16 mL of 1-octanol in duplicate

2.2. Extraction of Eu from 8 M HCl Varying Mole Percent 1-Octanol

The extraction procedure outlined above was followed. The sample was 1000 mg/kg europium in 8 M (mol/m^3) HCl. The pressure was kept constant at 34.5 MPa, and the temperature for the equilibrium and extraction cell was 23 °C. The mole ratio of TBDGA to Eu was kept at 5:1. The mole percent of 1-octanol ranged from 0.5 to 3 mol%. The TBDGA concentration and the flow rate of the 1-octanol TBDGA solution for each mole percent studied are shown in Table 1.

Table 1. Mole percent solution and flowrates for the varying mole percent *1*-octanol.

Mole Percent 1-Octanol in CO_2	Concentration TBDGA in 1-Octanol Solution (M)	Flow Rate of the 1-Octanol TBDGA Solution (mL/min)
0.5	0.072	0.077
1	0.036	0.153
2	0.018	0.307
3	0.012	0.460

2.3. Extraction of Eu from 8 M HCl Varying Temperature

The extraction procedure above was followed with the temperature of the equilibrium and reaction cell being varied from 2 to 50 °C. The sample was 1000 mg/kg Eu in 8 M HCl. The pressure was kept constant at 34.1 MPa. The mole percent 1-octanol was 2%, and the 2% 1-octanol and TBDGA solution conditions are shown in Table 1. The temperature tested were 2, 23, 40, and 50 °C.

2.4. Extraction of Eu in 8 M HCl Varying Pressure

The extraction procedure above was followed, but the pressure was varied from 13.8 MPa to 34.5 MPa. The sample was 1000 mg/kg Eu in 8 M HCl. The temperature was kept constant at 23 °C, and the percent mole 1-octanol was 2%. The conditions of the TBDGA in 1-octanol solution are shown in Table 1. Pressures tested were 13.8, 20.7, 24.1, 27.6, and 34.5 MPa.

2.5. Extraction with Varying Eu Concentration

The extraction procedure above was followed, but the Eu concentration in the sample was varied from 1000 to 50,000 mg/kg in 8 M HCl. The pressure and temperature were kept constant at 34.5 MPa and 23 °C, respectively. The mole percentage of 1-octanol was 2%. The conditions of the TBDGA in 1-octanol solution are shown in Table 2. The mole ratio Eu:TBDGA and the Eu concentration in each sample tested are shown in Table 2.

Table 2. Eu solutions, Eu:TBDGA mole ratio.

Eu:TBDGA Mole Ratio	Eu Solution in 8 M HCl (mg/kg)
0.2	1000
1	5000
5	25,000
10	50,000

2.6. Extraction of Eu from 8 M HCl with Varying TBDGA Concentration

The extraction procedure above was followed, but the TBDGA concentration was varied from 1000 mg/kg to 50,000 mg/kg in 8 M HCl. The pressure and temperature were kept constant at 34.5 MPa and 23 °C respectively. The mole percentage 1-octanol was 2%. The flow rate of the 1-octanol/TBDGA mixture was 0.3067 mL/min. The mole ratio TBDGA:Eu and the TBDGA concentration for each test are shown in Table 3.

Table 3. TBDGA solutions, Eu:TBDGA mole ratio.

TBDGA:Eu Mole Ratio	Concentration TBDGA in 1-Octanol (M)
1	0.00281
0.4	0.00701
0.2	0.0140
0.1	0.0281

2.7. Extraction of Eu from Varying HCl Concentration and Cl$^-$ Concentration Solutions

The extraction procedure above was followed, but the HCl concentration and Cl$^-$ concentration of the solution were varied. All samples contained 1000 mg/kg Eu. The pressure and temperature were kept constant at 34.5 MPa and 23 °C respectively. The mole percentage 1-octanol was 0.5%. The conditions of the TBDGA in 1-octanol solution are shown in Table 3. The solutions tested were: 5 M NaCl/0.01 M HCl, 5, 6, 7, 8, 10, and 11 M HCl.

2.8. Extraction on Phosphor Leachate

The standard extraction procedure from above was followed with the following specifics. A phosphor REE simulant material was created with of 250 mg/kg each Y (III), Ce (IV), Eu (III), and Tb (III) in 8 M HCl. A phosphor leachate was made by dissolving 1.0 g trichromatic phosphor in 8 M HCl. ICP-MS and ICP-OES was used to determine the concentration of materials in the phosphor solution. Extraction of these solutions were performed with 0.072 M TBDGA in 1-octanol with a flow rate of 0.077 mL/min (0.5 mol% 1-octanol), 23 °C, 34.1 MPa, 5 mL/min in $CO_{2(l)}$.

2.9. Extraction on Magnet Leachate

A neodymium iron boron magnet solution was made by dissolving 1.0 g ground roasted magnet into 50.0 mL 8 M HCl. This reaction is exothermic and bubbling occurs. The HCl should be added to the magnet slowly. This solution was then diluted 1:5 for the extraction experiments. ICP-MS was used to determine the metal concentrations in solution. Extraction on these solutions were performed the same as on the phosphor leachate solutions.

3. Results and Discussion

No Eu was extracted from 8 M HCl with TBDGA in CO_2. Similar results were seen by Tian et al. with a nitric acid/TBDGA adduct [28]. Tian et al. used acetone as a modifier and saw improved extraction of Nd/TBDGA and Eu/TBDGA complexes. Both acetone and methanol modifiers were used in this study, but minimal Eu/TBDGA extraction was observed with both of those modifiers. While acetone and methanol are common modifiers for CO_2 extractions on solid materials, they both have low partition-coefficients between the aqueous phase and the CO_2 phase [22]. Therefore, as expected, neither acetone nor methanol work well as modifiers when aqueous solutions are used with CO_2 as the extracting solvent. 1-octanol is a well-known diluent that has commonly been used for liquid-liquid solvent extraction. It has been specifically studied as a diluent for the extraction of lanthanides from HCl solutions with TBDGA [29]. In this study, improved extraction of Eu/TBDGA complexes was observed with 1-octanol as a co-solvent when compared against other modifiers previously studied [26]. CO_2 modified with 1-octanol was used for all extractions conducted in this paper for the intended purpose of modifying the polarity of the CO_2 and improving Eu/TBDGA complex solubility.
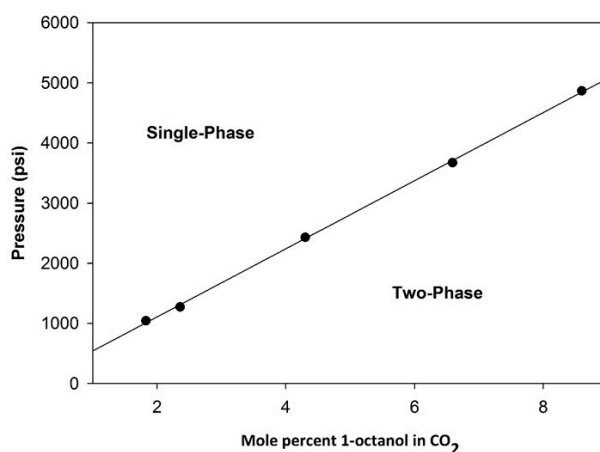
3.1. Phase Equilibria of 1-Octanol in CO_2

The phase equilibria of 1-octanol in $CO_{2(l)}$ at 23 °C was determined by standard visual practices. As the $CO_{2(l)}$ was introduced into the cell the pressure increased. As the pressure increased the liquid 1-octanol phase mixed with CO_2, expanded, appeared to become less viscous, broke into smaller droplets, and then formed a single, homogenous phase. The liquid droplets of 1-octanol could visually be seen to dissolve into the $CO_{2(l)}$ as pressure increased. At about 8.96 MPa the density of the 1-octanol and the $CO_{2(l)}$ were approximately equal. As the pressure increased the density of $CO_{2(l)}$ increased to be greater than the density of the 1-octanol. The pressure at which a single, homogenous phase appeared was determined. Each stage is shown in Figure 3. Figure 4 provides a graphic depiction of the phase equilibria given as the mole percent 1-octanol varies from about 1.8 to 8.6 mol%. The graphical region above the phase line indicates pressures at which the 1-octanol/$CO_{2(l)}$ system is single phase; the region below the line indicates pressures at which the system is comprised of two liquid phases.
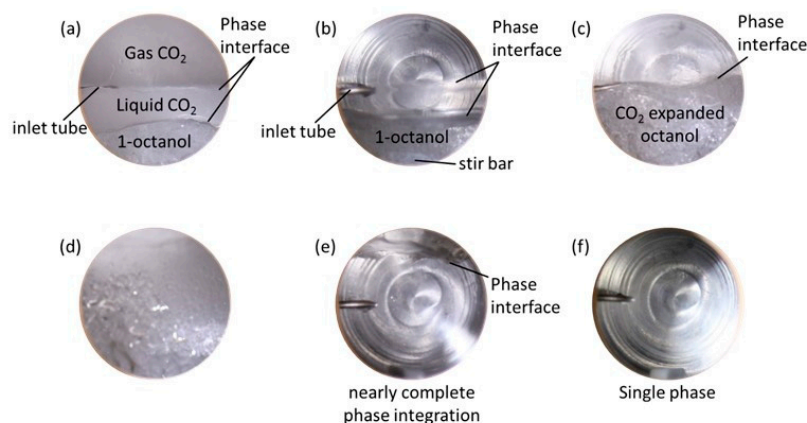
Figure 3. Phase equilibria of 1-octanol with CO_2 as the pressure increased at 23 °C. (**a**) 1-octanol with liquid CO_2 being added to the cell. A gas phase CO_2 layer formed above the liquid phase CO_2. (**b**) 1-octanol with liquid and gas CO_2 phases above it. (**c**) 1-octanol was expanded by the CO_2 with liquid CO_2 above it. (**d**) The density of the 1-octanol and the CO_2 are both 824 kg/m^3 at 8.96 MPa. The 1-octanol formed droplets in the CO_2. (**e**) The liquid CO_2 was denser than the 1-octanol, and the 1-octanol was the top phase at greater than 8.96 MPa. (**f**) The 1-octanol and the liquid CO_2 are single-phase.

Figure 4. Phase equilibria of 1-octanol with liquid $CO_{2(l)}$ at 23 °C.

3.2. Effect of 1-Octanol Concentration on Eu Extraction Efficiency from Aqueous HCl Solution
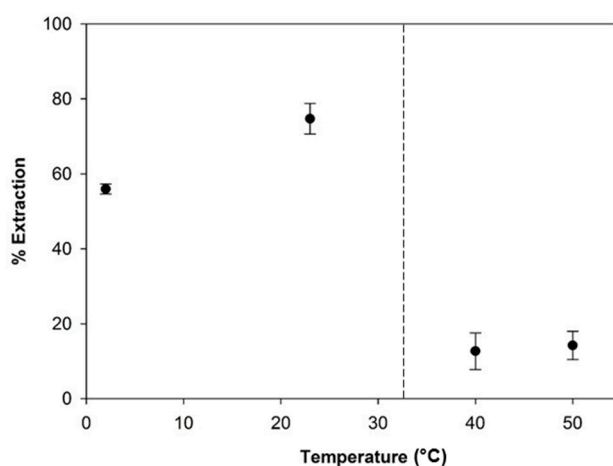
The percent extraction of Eu from 8 M HCl with TBDGA in $CO_{2(l)}$ as a function of 1-octanol concentration are shown in Figure 5. As the mole percent 1-octanol in CO_2 increased from 0.5 mol% to 3.0 mol% the extraction efficiency of the Eu-TBDGA complex into CO_2 decreased. As the mole percent 1-octanol increased it becomes visually apparent that 1-octanol partitions into the aqueous HCl phase and is not removed with the CO_2, both during the extraction and during the follow on 90 min CO_2 flush cycle. As the experiment progressed the amount of organic (unbound TBDGA, Eu-TBDGA complex, and 1-octanol) partitioned into the aqueous HCl phase increased. This indicates the limit of the CO_2 solvent's ability to extract 1-octanol/TBDGA out from the aqueous HCl phase occurs at fairly low levels of 1-octanol/TBDGA dissolved into CO_2. At 34.5 MPa and 1 mol% 1-octanol the aqueous HCl solution in the cell was cloudy and contained visible unextracted organic, even after a 90 min flush. The TBDGA-Eu complex appeared to preferentially partition to the 1-octanol phase in the cell versus the $CO_{2(l)}$ phase.
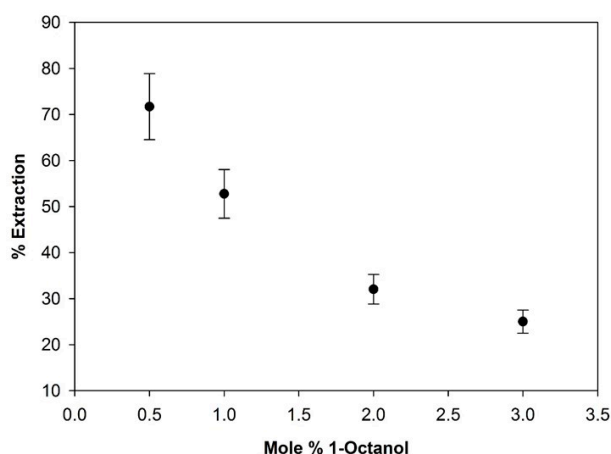
Figure 5. The percent extraction of Eu from 10 mL 1000 mg/kg Eu in 8 M HCl with TBDGA in 1-octanol at 23 °C and 34.5 MPa in $CO_{2(l)}$. The mol% of 1-octanol was varied by the flow rate as listed in Table 1.

3.3. The Effect of Temperature on 1-Octanol/TBDGA-Mediated Extraction of Eu from HCl Solution

The percent extraction of Eu from 8 M HCl using TBDGA in 1-octanol modified CO_2 as a function of temperature ranged from 2 to 50 °C is shown in Figure 6. From 2 to 23 °C there is an increase in extraction efficiency. The increase is attributed to solubility differences of 1-octanol into CO_2 vs. solubility of 1-octanol into 8 M HCl at those temperatures and is not a function of complex stability or reaction kinetics. After 60 min of extraction at 2 °C it was noted there was organic remaining partitioned to the aqueous phase. That organic remained even after the 90 min CO_2 flush. At 23 °C there was very little organic partitioned to the aqueous phase. When the extraction temperature was increased to >40 °C there is a significant drop in extraction; transitioning from 75% Eu extracted at 23 °C to approximately 13% Eu extracted at 40 °C. At temperatures higher than 50 °C there was little to no organic remaining in the aqueous phase, but due to thermodynamic instability of the Eu-TBDGA metal-ligand complex very little Eu was extracted out of the HCl. It was previously shown that the complexation between TBDGA and lanthanides is exothermic in chloride media [26,29].
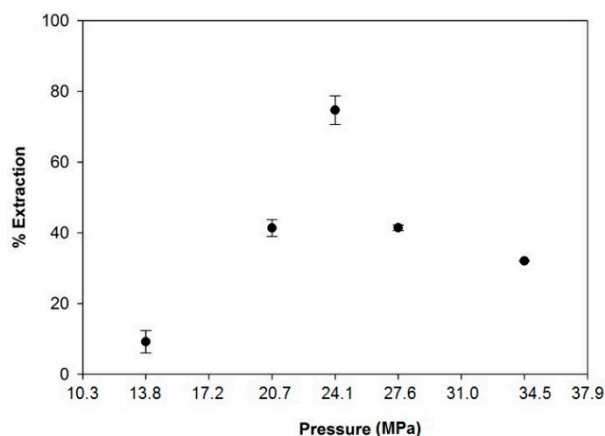

Figure 6. The percent extraction of Eu from a 1000 mg/kg in 8 M HCl solution with TBDGA in CO_2 modified with 2 mol% 1-octanol as the temperature is varied from 2 °C–50 °C at 34.5 MPa. At temperatures less than 31 °C CO_2 is a liquid, and above 31 °C the CO_2 is in the supercritical phase. This point is shown with a dotted line.

### 3.4. The Effect of Pressure on Eu Extraction from HCl Media Using 1-Octanol/TBDGA in CO_2

The effects of varying the pressure was studied. Data showing percent extraction of Eu from 8 M HCL using the 1-octanol/TBDGA system in $CO_{2(l)}$ as the pressure varied from 13.8 to 34.5 MPa at approximately 23 °C are given in Figure 7. As the pressure increased from 2000 to 34.1 MPa the percent extraction of Eu also increased. As the pressure increased from 24.1 to 34.5 MPa the percent extraction of Eu decreased. There is a maximum in the extraction at 24.1 MPa with a percent Eu extraction of 75%. Although there is higher solubility of 1-octanol at higher pressures, as shown in Figure 4, less organic is remaining in the cell at 24.1 MPa than at 34.5 MPa. It is hypothesized that this behavior is attributed to the increased solubility of water into CO_2 at higher pressures. King et al. [30] showed that as the pressure increased the solubility of water into the CO_2 also increases. As the solubility of H_2O in the $CO_{2(l)}$ increased the solubility of 1-octanol and the TBDGA-Eu complex in the $CO_{2(l)}$ decreased. The effect of water is investigated in a later section of this paper. This would lead to lower recovery of Eu at higher pressures. However, there may be an increase until 24.1 MPa due to the extraction requiring a high solubility of *1*-octanol in the $CO_{2(l)}$.

Figure 7. The percent extraction of Eu from 1000 mg/kg Eu 8 M HCl solution with TBDGA in $CO_{2(l)}$ modified with 2 mol% 1-octanol as a function of pressure (13.8–34.5 MPa) at 23 °C.

3.5. The Effect of Initial Eu Concentration in the HCl Phase on Extraction Efficiency

In this series of dynamic extraction experiments the concentration of Eu initially present in the 8 M HCl is varied from 1000 to 50,000 mg/kg. Percent Eu extraction as a function of Eu:TBDGA mole ratio is shown in Figure 8. At high starting concentrations of Eu in the HCl phase the molar ratio of Eu to incoming TBDGA ligand is ~10:1; there is 10× more Eu than there is ligand. In that condition nearly all of the ligand is being pulled from the incoming solvent and complexing the large pool of excess Eu present in the HCl phase. As such, very little complete, charge-neutral, CO_2-soluble TBDGA-Eu complexes are being made in the 60 min run, resulting in low extraction efficiency. At a Eu:TBDGA mole ratio of 0.2 (i.e., 5× more TBDGA than Eu) the extraction efficiency is at its highest for the given conditions. These results indicate that regardless of the starting concentration of Eu in the aqueous phase an optimum ratio of TBDGA to metal is required for the formation of complete metal-ligand complexes which leads to efficient extraction.
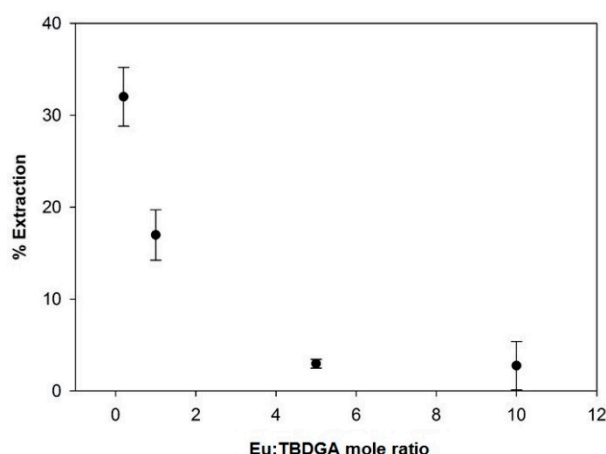
Figure 8. The percent extraction Eu from 8 M HCl with TBDGA in $CO_{2(l)}$ modified with 2 mol% 1-octanol at 34.5 MPa and 23 °C where the starting Eu concentration in the HCl phase is varied from 1000 to 50,000 mg/kg.

3.6. Effect of TBDGA Concentration on Eu Extraction Efficiency from 8 M HCl

Next, the Eu was kept constant, but the TBDGA concentration was varied. Data in Figure 9 show that as the molar ratio of Eu:TBDGA goes from 0.1 to 1 (i.e., ligand-rich conditions to equal molar amounts of ligand to metal) the Eu extraction efficiency drops significantly. As TBDGA ligand enters the HCl phase it complexes with Eu and forms TBDGA-Eu complexes. As intact complexes are made which are charge-neutral those complexes are CO_2 soluble and dissolve into the CO_2 phase and are swept out of the contact vessel. A larger amount of TBDGA would, therefore, result in more CO_2-soluble complexes.
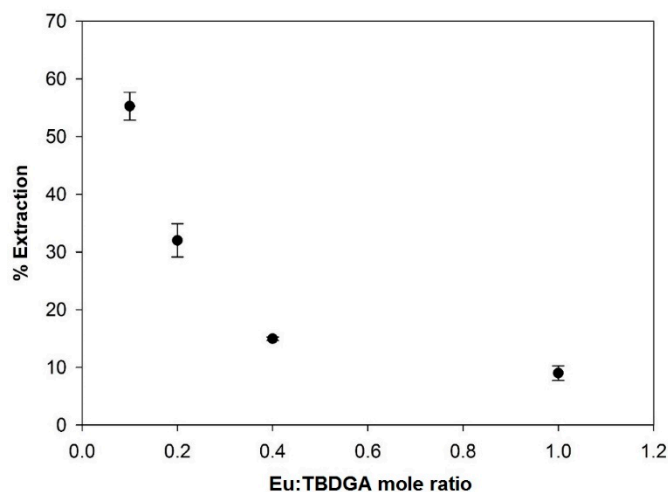
Figure 9. The percent extraction of Eu from a 1000 mg/kg 8 M HCl solution with varied TBDGA concentration in $CO_{2(l)}$ modified with 2 mol% 1-octanol at 34.5 MPa and 23 °C. The TBDGA concentration is listed in Table 3.

3.7. Effect of Varying HCl Concentration and Cl^- Concentration on Eu Extraction Efficiency from Chloride Solution

Although previous extractions were performed from 8 M HCl, varying the HCl concentration or extracting from NaCl could impact the extraction efficiency as was observed with the 1-octanol system. The effect of HCl concentration and Cl^- concentration on the extraction of Eu was studied at the optimum conditions of 23 °C, 24.1 MPa, and 0.5 mol% 1-octanol. The HCl concentration was varied from 5 M to 11 M, and the maximum NaCl concentration achievable of 5 M was studied. NaCl was

studied as it previously showed higher REE extraction from NaCl solutions than from equivalent HCl concentration solutions with TBDGA in 1-octanol [28]. Results for percent extraction of Eu from each HCl concentration and NaCl concentration solution studied in this work is given in Table 4. When varying the HCl concentration no extraction of Eu is observed from 5 M HCl through 7 M HCl. When the HCl concentration reaches ≥8 M the percent extraction of Eu reaches levels ≥95%. When extracting from ≤7M Cl⁻ concentration the flow rate of the $CO_{2(l)}$ significantly fluctuated from ~0 mL/min to ~10 mL/min with an average of ~5 mL/min. whereas, with ≥8 M HCl concentration few flow rate fluctuations were experienced and flow rate was maintained at about 5.0 mL/min ± 0.3 mL/min throughout the extraction. This is from dissolution of water into the $CO_{2(l)}$ phase, and transport of water downstream. At the point where the pressurized liquid would expand (the micro-metering valve orifice) the cooling of expansion would freeze the water in the line causing a flow obstruction. At 25 °C and 20.2 MPa, King et al. [30] observed that the solubility of water in $CO_{2(l)}$ was 0.378 mol%. Based on their observed trends, at 24.1 MPa and 23 °C the solubility of water in $CO_{2(l)}$ would be approximately 0.379 mol%. With 1-octanol being added as a modifier and shifting the polarity of the $CO_{2(l)}$ toward being more polar it can be expected that the solubility of H_2O would be greater than with pure $CO_{2(l)}$. As the HCl concentration or NaCl concentration decreased the concentration of water increased which allowed for greater solubility into $CO_{2(l)}$. The solubility of H_2O into the $CO_{2(l)}$ caused the extraction of Eu to significantly decrease.

Table 4. The percent extraction of Eu from various HCl and NaCl aqueous solutions with 0.5 mole percent 1-octanol, 24.1 MPa, 23 °C, and 5× TBDGA:Eu by mole.

Aqueous Solution	Percent Extraction
5 M NaCl, 0.01 M HCl	0% E
5 M HCl	0% E
6 M HCl	0% E
7 M HCl	0% E
8 M HCl	95 ± 2% E
10 M HCl	97 ± 2% E
11 M HCl	99 ± 3% E

3.8. Comparison of Extraction into 1-Octanol Modified CO_2 vs. 1-Octanol

The 1-octanol modified $CO_{2(l)}$ can be compared to the pure 1-octanol system studied in Case et al. [28]. A comparison of the reagents used and the percent extraction achieved in each system in summarized in Table 5. Both systems were extracting ionic Eu from 8 M HCl at 23 °C. For the $CO_{2(l)}$ system the pressure was kept at 24.1 MPa. In the $CO_{2(l)}$ system to achieve 95% extraction Eu a mole ratio Eu:TBDGA of 0.20 is required, and to achieve a 94% extraction Eu in the 1-octanol system a Eu:TBDGA of ~8.0 × 10⁻⁵ is necessary. The $CO_{2(l)}$ system used 54% less 1-octanol than the 1-octanol system to achieve similar percent extractions. When the Eu:TBDGA mole ratio is increased to 0.2 in the 1-octanol the extraction of Eu is reduced to 42%. The $CO_{2(l)}$ system is more efficient at utilizing less reagent (1-octanol and TBDGA) for extracting Eu. However, the 1-octanol system avoids using pressurized $CO_{2(l)}$.

Table 5. Comparison of extraction with TBDGA in 1-octanol to TBDGA in 1-octanol modified $CO_{2(l)}$. In parenthesis the percent extraction at an equal moles TBDGA:Eu as in the $CO_{2(l)}$ is stated.

| Identifier	1-Octanol	CO₂ Modified with 1-Octanol
Percent Extracted Eu	94% (42%)	95%
Moles Eu:Moles TBDGA	~8.0 × 10⁻⁵ (~0.2)	~0.20
mL 1-octanol:mL aqueous	1.0	0.462

3.9. Solubility of Ho-TBDGA in 1-Octanol-Modified CO$_2$

Solubility of the TBDGA/Ho complex was measured to determine if water was impacting the solubility of the TBDGA-REE complex into the CO$_{2(l)}$ modified with 1-octanol. The TBDGA/Ho complex was observed in three CO$_{2(l)}$ systems: water saturated single-phase system, water saturated two-phase system with a dry CO$_{2(l)}$ phase over, and dry 1-octanol. This was performed on Ho-TBDGA with UV-visible spectroscopy of the upper CO$_{2(l)}$ phase at 24.1 MPa, 23 °C, 0.5 mol% 1-octanol. The Ho-TBDGA complex was used due to Ho having a higher molar extinction coefficient than Eu. For this experiment, the molar extinction coefficient was determined from the integrated vibrionic band from 529 nm to 555 nm. This is shown in Equation (2) which is a modification of Beer's Law. Where *A* is the absorption, λ is the wavelength, *ε* is the extinction coefficient, and *b* is the cell path length, and *c* is the concentration of Ho:

$$\int_{\lambda_{555}}^{\lambda_{529}} A \, d\lambda = \varepsilon b c, \tag{2}$$

The UV–VIS spectra of a dry system, a single-phase water saturated system, and a two-phase water saturated system are shown in Figure 10. The peak area for the wet systems is less than the peak area for the dry systems. This indicates that the solubility of water in CO$_{2(l)}$ has an deleterious effect on the solubility of a REE-TBDGA complex in CO$_{2(l)}$.
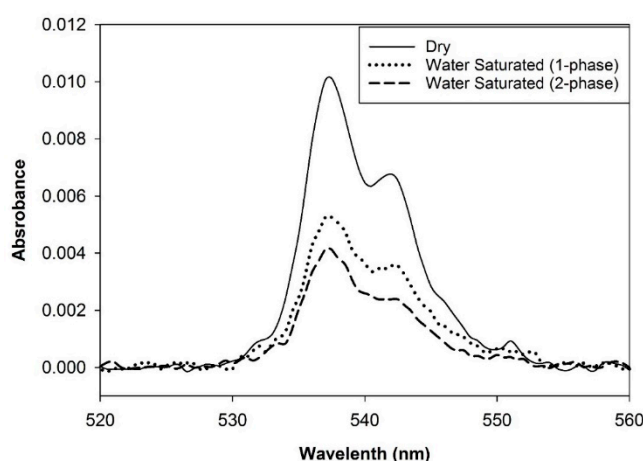
Figure 10. UV–VIS spectra from 520 nm to 560 nm of Ho-TBDGA complex in 0.5 mole percent 1-octanol modified CO$_{2(l)}$ at 23 °C and 24.1 MPa. By integrating the area under the peak the Ho concentration was determined. The integrated molar extinction coefficient or the peak from 529 nm to 554.5 is 26.6 A·nm·M^{-1}·cm^{-1}. The dry system (a solid black line) has a Ho concentration in the CO$_{2(l)}$ of 2.57 mM. The water saturated CO$_{2(l)}$ 1-phase wet system (dotted black line) had 4 μL of water added, and the Ho concentration in the CO$_{2(l)}$ was determined to be 1.45 mM. The 2-phase wet system (dashed black line) had 100 μL of water added, and the Ho concentration in the CO$_{2(l)}$ of 1.04 mM.
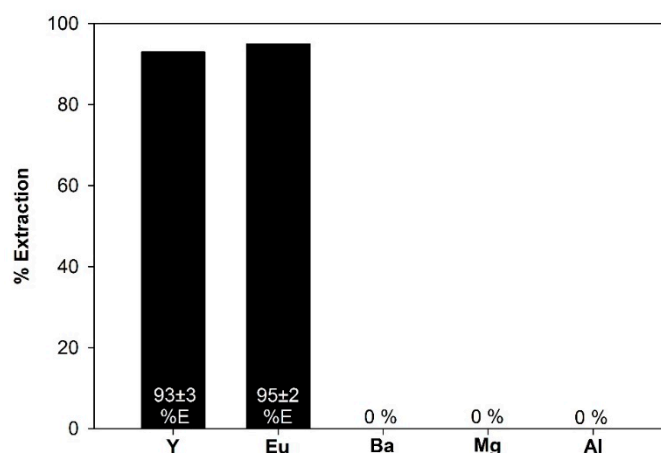
3.10. Extraction from Phosphor Material Leachate

Extraction from a simulant mixture of REEs found in phosphors was examined. The percent extraction for the REEs is shown in Figure 11. The extraction efficiency is similar to what was observed in the liquid-liquid 1-octanol system (Figure 2 in Case et al. [29]). Cerium did not extract well at 8.27%, and the other REEs did extract >84% with Tb > Eu > Y. Cerium is low due to its larger ionic radius. These results are similar to what was observed in the 1-octanol/TBDGA extraction studied in Case et al. [29]. The percent extraction for Eu was lower than the previous extractions when only a single-element with optimized conditions were conducted. There is an effect from the competition with the other REEs for the TBDGA complex to form.
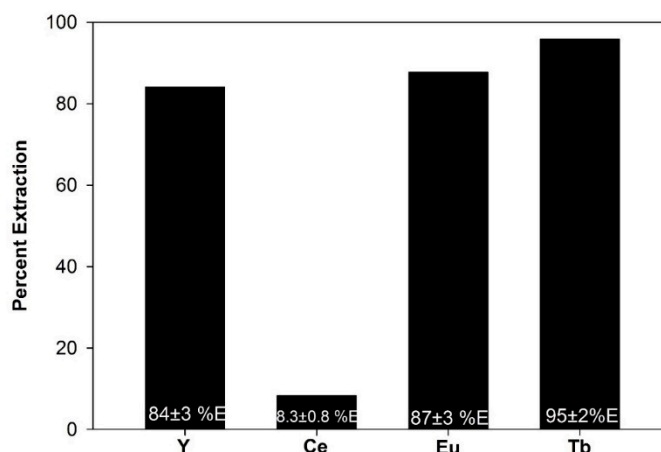
Figure 11. Extraction of 250 mg/kg each Y (III), Ce (IV), Eu (III), and Tb (III) in 8 M HCl with 0.072 M TBDGA in 1-octanol, 0.5 mol% 1-octanol, 23 °C, 5 mL/min, 24.1 MPa.

Next, extraction was performed on the phosphor leachate. Extraction from the phosphor leachate with TBDGA in 0.5 mole percent 1-octanol in $CO_{2(l)}$ at room temperature and 24.1 MPa was performed. The percent extraction is shown in Figure 12. Due to the Ce and Tb not leaching into the HCl at quantifiable concentrations by ICP-MS there is no extraction shown. The Y and Eu are very effectively separated from the Ba, Mg, and Al that did leach into the HCl. The percent extraction of Eu at 95% was similar to what was observed previously in Table 4. In this extraction compared to the phosphor REE simulant extraction, Figure 11, the Y and Eu percent extraction was higher than observed in the simulant material. There was less competition from the Tb, or one of the other elements in the leachate had a synergistic effect on the extraction.

Figure 12. Extraction from phosphor leachate in 8 M HCl with 0.072 M TBDGA in 1-octanol, 0.5 mol% 1-octanol, 23 °C, 5 mL/min, 24.1 MPa.

3.11. Extraction from Magnet Material Leachate

The extraction of metals from NdFeB (NIB) magnet dissolution in 5 M NaCl and 8 M HCl with TBDGA in 1-octanol modified $CO_{2(l)}$ was performed. The percent extraction of each metal is shown in Figure 13. The REEs and Fe were extracted at >97% from 8 M HCl. As the mass of the REEs increase there is an increase in the extraction efficiency, Dy > Nd > Pr. This was also observed in a liquid-liquid 1-octanol TBDGA extraction system studied by Case et al. [29]. TBDGA in 1-octanol modified $CO_{2(l)}$ is effective at extracting the REEs; however, >95% Fe is also extracted. Further steps would need to be taken to avoid the co-extraction of Fe with the REEs.
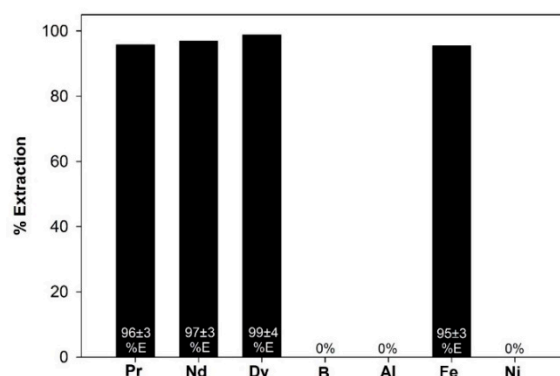
Figure 13. Extraction from neodymium iron boron magnet materials with 0.5 mol% 1-octanol in $CO_{2(l)}$, 0.072 M TBDGA in 1-octanol TBDGA:M by mole, 23 °C, 24.1 MPa, and a flow rate of 5.0 ± 0.5 mL/min.

4. Conclusions

When extracting Eu from 8 M HCl with TBDGA in 1-octanol certain conditions will optimize the extraction. When temperature is varied the highest percent extraction is observed at 23 °C. By varying the pressure a peak is seen in the percent extraction at 24.1 MPa. The percent extraction increased as the ratio of TBDGA:Eu increased. As the mole percent 1-octanol used to modify the system is decreased the percent extraction is increased; the highest percent extraction was observed at 0.5 mole percent 1-octanol. By optimizing this extraction of Eu from 8 M HCl with 0.5 mole percent 1-octanol approximately 95 ± 2% Eu can be extracted when using a Eu:TBDGA mole ratio of 0.2, and keeping the system at 24.1 MPa and 23 °C. Yttrium and Eu can be effectively extracted and separated from other elements from phosphor HCl leachate with TBDGA in 1-octanol modified $CO_{2(l)}$. Praseodymium, Nd, Dy, and Fe are extracted >97% from NIB magnet HCl dissolution with TBDGA in 1-octanol modified $CO_{2(l)}$.

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