Extraction of Rare Earths
from a Nitrate Acid Solution

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Abstract

Objectives

This is a study looking at the equilibrium extraction of rare earth elements (mainly europium and praseodymium) from idealized process stream. The objectives of this study were to understand the extraction process of these rare earths in single ion solutions, then adding other ions into this solution, and observing how much of the metal ion was extracted during the extraction process. The other metal ions that were added to the aqueous solution was manganese. The first stage of the study was to find the optimal starting pH of the aqueous solution, and to make an isotherm to display where the optimal pH would be. The next stage was to compare the different elements' isotherms and run the experiments together to see if the other ions would interfere with the extraction of the rare earths.

Findings

The results from the experiments that were completed to equilibrium showed that the pH does affect how well the extraction process takes place. The optimal pH for extraction of europium from a nitric acid solution is between 1.3 and 2.5 pH, and the optimal pH for the extraction of praseodymium is similarly to that of europium and is between 1.3 and 2.5 pH. There was no affect seen with the addition of manganese to the solution during the extraction of europium within the optimal pH range.

Introduction

This study looked at solvent extraction, which is a form of ion exchange that extracts metal ion from the pregnant leach solution (aqueous phase) to an organic phase. In the organic phase, there are two different species mixed together, the extractant (the main kinds used today are phosphoric acid based alkyl phosphorus reagents [4]), and the diluent, which dissolves the extractant and is insoluble in water. In this study, the diluent was chosen to be kerosene because of its availability and use in the literature [3][4][9]. Some other common diluents used for rare earth extraction include octane, toluene, benzene, and xylene (there has been some noted differences between them in how well they extract [3]). The aqueous phase contains the metal ions and is generally an acidic solution. In this study, the metal ions are in a nitric acid solution.

Solvent extraction fits in with the whole leaching process as shown below in Figure 1. The aqueous phase in the initial portion of this study contains a single metal ion, usually europium, but sometimes praseodymium. In the later stages of this study, other metal ions were added to the aqueous solution to help simulate the pregnant leach solution that will be obtained during the actual leaching process. This is done because, during this actual leaching process, there is not going to be just one metal ion in the aqueous solution, there are going to be many ions. So at first, it is important to understand the mechanics of how each metal ion is extracted from the aqueous phase into the organic phase in order to understand how they might extract if more ions are in the solution. It can be seen from Figure 1 that there are other processes that happen before and after solvent extraction. This figure is meant to be an overview of where

solvent extraction fits during the process of leaching and is not necessarily representative of how rare earths are extracted.
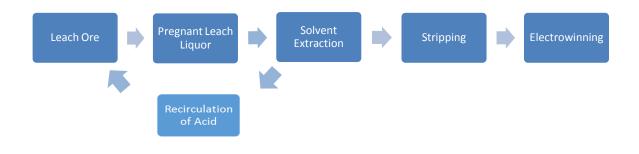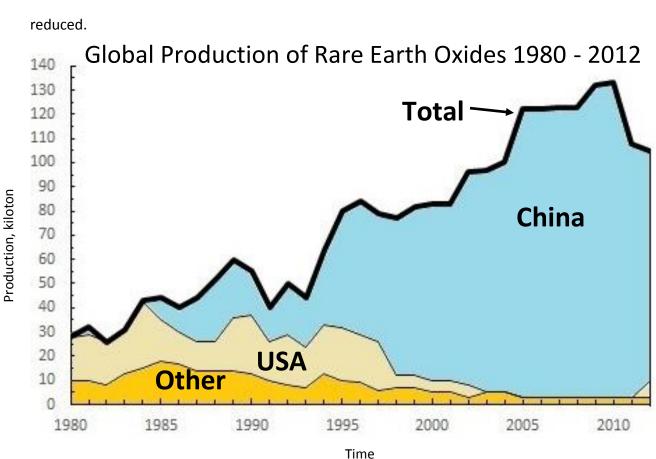

Figure 1
General overview of the leaching process. (Author's Work)

The objectives of this study are to understand the extraction of single rare earth metals and also to explore any possibilities of any common metal ion affecting the extraction of the rare earth metals.

Broader Impact

Rare earth elements are used in many modern technologies, so they have become very important resources. For instance, liquid-crystal displays and televisions use europium, permanent magnets have rare earth elements as their alloying elements and are used in portable disk drives and DVD drives, and catalytic converters use cerium[7]. According to Haxel at the Department of the Interior, "in 1999 and 2000, more than 90% of REE required by U.S. industry came from deposits in China."[7] A graph of this can be seen in Figure 2, which is shown below. The x-axis from left to right shows time moving forward. On the y-axis, which shows the

world production of rare earth oxides. It can be seen that the United States was producing

some of these rare earth elements until the 1980s after which the production has slowly been

reduced.

Global Production of Rare Earth Oxides 1980 - 2012

Figure 2
World production of rare earth elements. The data referenced after USGS's Mineral Commodity Summaries [2].

This is a concern because, without domestic sources of rare earths, the U.S. is reliant upon

external sources. Therefore, the production of the applications that commonly use the rare

earth metals could be affected. This could not only affect the U.S. consumers but also the

United States military. Many common applications of these rare earths include electronics,

magnets, emission controls, optics, and ceramics [7]. Shown in Table 1, is the percent of end use

of the rare earths. There has been a decline in the use of these rare earths for catalytic fluid

cracking of petroleum, but there has also been an increase use of these elements in other applications [6]. The permanent magnets that use two percent of the rare earths are most likely used in computers.

Table 1
End Uses of Rare Earth Elements. Abridged from source [2]

End Uses	Percentage
Automotive catalytic converters	32
Metallurgical additives and alloys	21
Glass polishing and ceramics	14
Petroleum refining catalysts	8
Permanent magnets	2
Other	23

Figure 3 contains a graph showing the supply risk compared with the impact of the restriction of these elements. This figure comes from the Committee on Critical Mineral Impacts of the U.S. Economy, Committee and Earth Resources, and the National Research Council. On the x-axis in Figure 3 is the supply risk going from one, which is low, to four, which is high. The rare earth were placed in the four category because of the U.S. is reliant upon imports for continue production of produces using rare earths [6]. The percent break down of imports are as follows: China 76 percent; France, 9 percent; Japan, 4 percent; Russia, 3 percent [6]. Because such a high percent of the imports come from one country, this could lead to a potential shortage in the availability of these rare earths. On the y-axis in Figure 3 shows the impact of the supply restriction. If the restriction of the rare earths were to occur, this shows how much the restriction would impact the U.S. economy based on specific applications for which rare earths are used. The primary end uses are emission controls, magnets, and electronics.
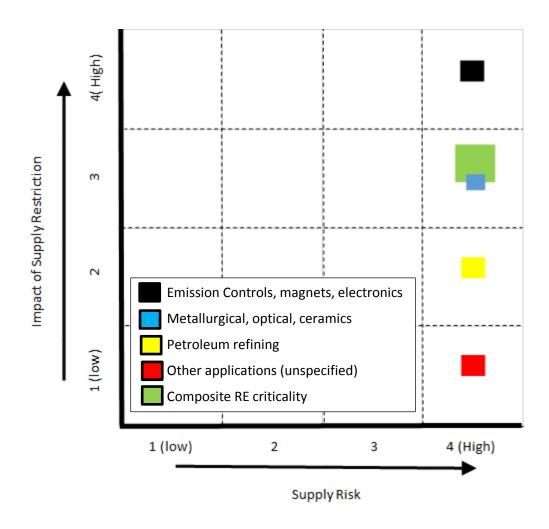
Figure 3
This figure shows how the supply risk versus the impact of supply restrictions are very high. Image redrawn from source [2]

Procedure

Materials

Preparation of Organic Solution. The organic solution contains two components, the diluent and the extractant. The extractant used in the study was bis(2-ethylhexyl) phosphoric acid (DEHPA) obtained from SNF Flomin. The diluent used was kerosene obtained from a local store and has no dye or other additives added to it. Unless otherwise stated, the following procedure was used: 3.3 mL DEHPA and 6.7 mL of kerosene are added to a separatory funnel and hand shaken for five minutes to ensure the DEHPA is fully dissolved in the kerosene. This combination of DEHPA and kerosene is commonly used in the literature, and the effects of using different ratios of each will be discussed later in this paper.

Preparation of Rare Earth Solution. Stock solutions of the rare earth elements were obtained from Buck Scientific, and contained 1000 parts per million (ppm) rare earth metal ions in 7 % nitric acid. These stock solutions were diluted with de-ionized water to 100 ppm for use in extraction experiments. The starting pH of the solution was measured and then adjusted to the desired pH with sodium hydroxide, if the pH needs to be increase and, if the pH needs to be lowered, the solution was created by using 7% nitric acid in the place of de-ionized water.

Extraction Procedures

This study focused on the equilibrium of solutions when the organic and the aqueous are mixed in a separatory funnel. Shown in Figure 4, an experiment can be seen in a separatory funnel after the extraction process. The tests are ten minutes long, done in two-minute intervals in order to release the pressure that was built up during the extraction, so the solution can come to equilibrium. Making sure the solution comes to equilibrium is important because when this point is reached, the reactants are being consumed and produced at the same rate, so there is no net transfer of the metal ions into the organic solution. During this mixing of the solution, the two phases the form an emulsion which gives the reaction more surface area so that the reaction time can be sped up. After the mixing process is complete, the solution is allowed to sit for twenty minutes so the two phases can separate completely. The aqueous solution is removed from the separatory funnel through the bottom and this sample's pH recorded. Regardless of the method used for analysis of the extraction whether it's atomic absorption spectroscopy (AAS) or the use of inductively coupled plasma (ICP), the samples taken from the separatory funnel are diluted with 7% nitric acid to such that the initial concentration would be 5 ppm which is a dilution of 20:1 factor.
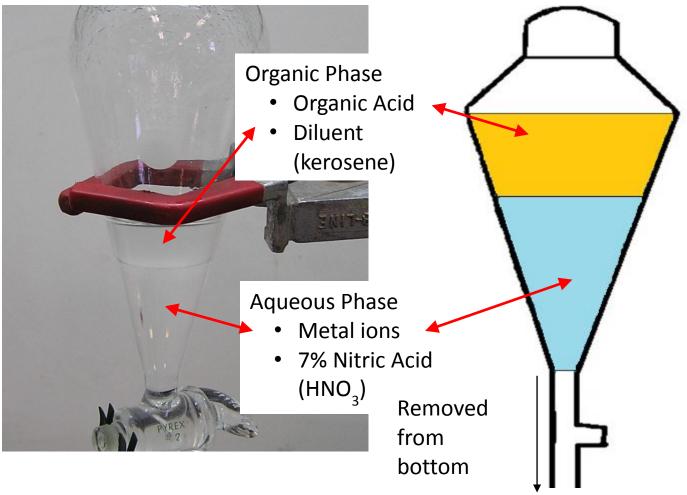
Figure 4

Experiment after extraction has taken place and has time to separate back out into the aqueous and organic phase. (Author's Work)

Analysis of Samples. After the aqueous phase is removed from the separatory funnel, it needs to be diluted for analysis. The name given to this value is called the dilution factor. The dilution factor is used to scale down the concentration so that this concentration can fit within the calibration curve of the AAS or ICP. A calibration curve that was used in this study is shown below in Figure 5. The calibration curves are used to get the relationship between the absorption that the AAS machine gets to the concentration of the specific ion. A picture of the

AAS that was used in this study is shown below in Figure 6. The concentration can be scaled

back up to show the relationship between the initial concentration and the final concentration
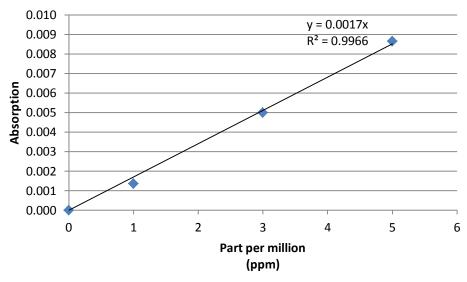
of the metal ions in the solution.

Figure 5
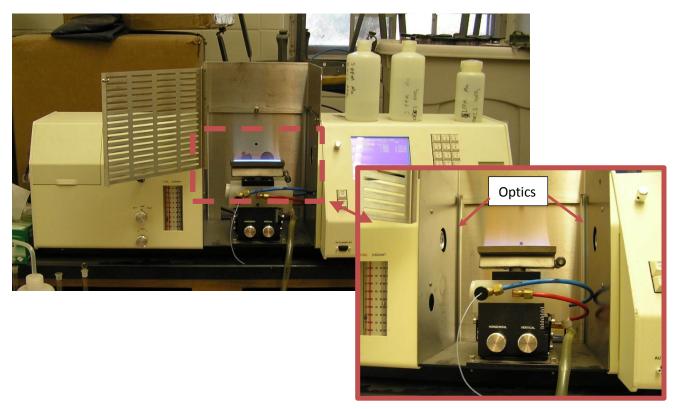Calibration curve used for analysis using the AAS. (Author's Work)

Figure 6
Atomic Absorption Spectroscopic (AAS). (Author's Work)

Results

Determining Optimal pH

The initial set of experiments were done to develop the experimental procedure and to compare the results to the literature to verify the procedure is being performed correctly. After the initial experiments, other metal ions were added to the simulated leach solution (aqueous phase) in order to determine how the addition of the other ions effect the extraction of the desired rare earths. An isotherm made for europium extraction from 100 ppm solution at room temperature, is shown in Figure 8. The isotherm of the single ion solution containing europium that was created is compared to literature. The s-shaped extraction curve can be observed in the europium, which was also seen in literature. Figure 7, which is shown below, shows an isotherm that contains five different elements, and the s-shaped extraction curve can be seen.
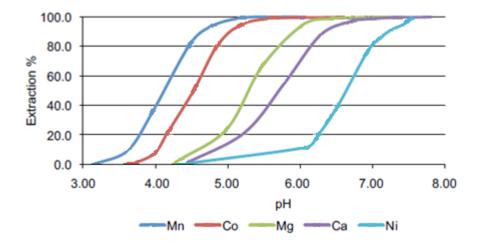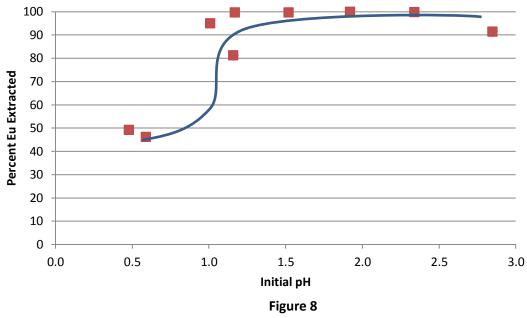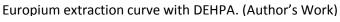

Figure 7
Metal ion extraction isotherms from Cyanex 272 literature [11]. There is a distinct s-shaped curve that can be seen for all the elements tested.

Figure 8
Europium extraction curve with DEHPA. (Author's Work)

The isotherms shown in Figures 7 and 8 show how the initial pH of the aqueous phase

determines how well the metal ion can be extracted into the organic phase. In the experiments

using europium and praseodymium, the organic phase stayed the same with 3.3 mL of DEHPA

(the extractant) and 6.7 mL of the kerosene (the diluent). The pH was changed by adding

sodium hydroxide to the aqueous phase to increase the overall pH of that solution. The

isotherm shown in Figure 8 is similar to what was seen in literature [1] [4].

The next step in the study was to determine if other rare earths extracted similarly to

europium. Therefore another isotherm was created to see if these hypothesis was correct.

Shown in Figure 9, is an isotherm of praseodymium. The same set of parameters was used for

this isotherm as those for europium. Building on what was learned from the construction of the

isotherm with europium. a much lower range of pHs was used in Firgure 9. The s-shaped curve

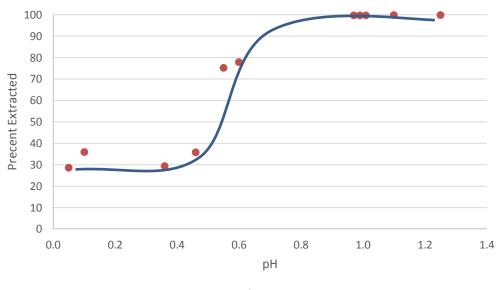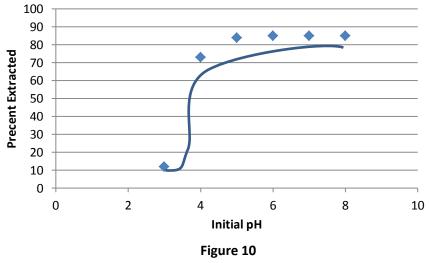was also observed in this isotherm that can be compared to literature [3] and also the isotherm of europium.

Figure 9
Praseodymium extraction curve with DEHPA. (Author's Work)

Multiple Ion Solutions

The next phase of the study was to try to simulate a more realistic leach solution. To do this, other ions were added to the aqueous phase and tested to see how the desired ion extraction was affected by the presence of the other metal ions. Figure 10, is a single ion isotherm for manganese that was obtained by Kelsey Fitzgerald, another team member in the research group. This was added to the paper to help compare and contrast the solutions with just one ion with different metal ions in them. It can be observed that the extraction of manganese occurs at a much higher pH than europium and praseodymium.

Figure 10
Manganese extraction isotherm

Figure 11 shows the extraction of europium with differing amounts of manganese. On the x-axis in this figure, will be the different ratios of manganese and europium, and on the y-axis, there will be the percent extraction from the aqueous phase to the organic phase. There was two experiments ran at each ratio. The pH of the aqueous solution was adjusted to be within a range of 1.3 to 1.6, which is within the optimal pH for europium extraction. There was some extraction observed with the manganese and this was also to be expected because of what has shown above in Figure 10.
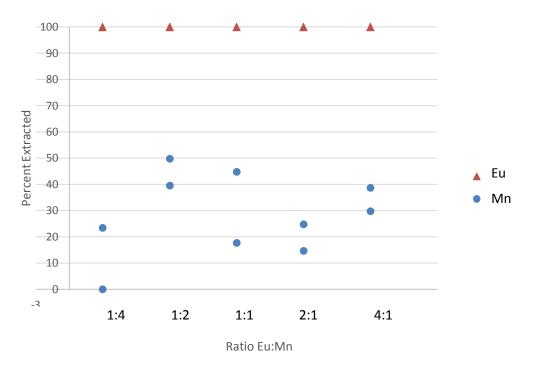
Figure 11
Europium and manganese extracted with DEHPA. (Author's Work)

Discussion

The isotherm shown in Figure 6 for europium indicates that DEHPA, extracts europium at a much lower pH than what was observed in the literature with the Cyanex 272 with the other metal ions. The extraction of manganese does go down to zero in the literature, while the europium does not. One possible explanation for this occurrence is that the water itself in the aqueous solution is starting to compete with the reaction at such low pHs. The proposed reaction that takes place during the experiment is shown below in Equation 1. Also shown below Figure 12 is further explanation of how the reaction takes place.

$$3(\text{HA})_{2\,(org)} + RE^{+3}_{(aq)} \leftrightarrow 3H^+_{(aq)} + \text{REA}_3 * 3\text{HA}_{(org)} \qquad \textbf{(1)}$$

Where $(\text{HA})_{2\,(org)}$ is the dimer extractant that is in the kerosene, $RE^{+3}_{(aq)}$ is the rare earth element is the aqueous phase, $H^+_{(aq)}$ is the ion that comes off from the extractant during the reaction, and $\text{REA}_2 * 3\text{HA}_{(org)}$ is the rare earth – extractant complex that forms during the reaction. Equation taken from source [4].
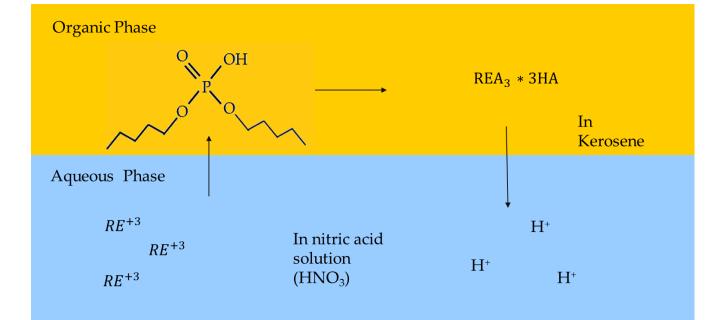

Figure 12
Visual representation of Equation 1.

Because this is the proposed reaction that takes place, it must correspond with the behavior

observed in Figure 6 because, with the lowered pHs, the percent extracted is reduced because

of the low pH. Also because the pH is low, the reaction is not going to want to proceed as

strongly from left to right, resulting in a lower percent extracted. At pH 3.0and therefore, the

single europium aqueous solution started to precipitate out of the aqueous phase. Therefore,

the percent extraction from the aqueous phase into the organic phase was lowered. One possible explanation for this is that there are less rare earth ions for the reaction shown in equation 1 to take place. It was also observed that at relatively high pHs (pH > 3.0), praseodymium also precipitates out at similar pHs to europium. The results that are displayed in Figure 11 are what was expected from the isotherms of the same elements in the multiple ion solutions. The pH of aqueous solution was kept within the optimal pH, 1.3 to 1.6 pH, of europium. That this range of pH, it has been seen that some manganese will extract which can be seen in the single isotherm of manganese shown in Figure 10.

Conclusion

Summary

The study explored the extraction of different rare earths from single ion solution along with solutions that contained multiple ions in solution. The extraction of the rare earths is affected by the initial pH of the aqueous solution. The proposed reaction explains why this was observed. The optimal pH for the extraction of both europium and praseodymium was seen to be approximately 1.3 to 2.5 pH. The addition of manganese to the solution had no effect on the extraction of europium.

Future Work

In order to better understand how the extraction of rare earths will be extracted in a real leach solution. More ions are going to be added to the aqueous solution to help simulate a leach solution, with a range of different pHs. Also further knowledge is need to understand how the extraction of rare earths are extracted over time. To do this, kinetic experiments should to be completed.

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