

Selective Separation of Rare Earth Chlorides Utilizing Vapor Phase Extraction

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Abstract The Metallurgical and Materials Engineering Department at Montana Tech is investigating a new method of extracting and refining rare earth elements (REEs) from mineral ores and concentrates. The relative stabilities of various REE compounds at elevated temperatures were evaluated using thermogravimetric and differential thermal analyses (TGA/DTA). The results, in combination with thermodynamic analyses, revealed that vapor phase extraction and selective condensation is a potentially viable separation method for rare earth halides. Selective vaporization and condensation experiments were performed on selected rare earth chlorides. A series of close-coupled tube furnaces provided a temperature gradient ranging from 1150 to 400 °C. Within the condensation regions, a series of one-inch-diameter ceramic tube sections were packed with stainless steel (316L) wool to create high surface area for condensate collection. The ceramic tube sections and stainless steel wool were leached in 18 MΩ water. Analysis of the leachate samples revealed that selective separation had occurred but oxychlorides were detected in the non-volatile matter.

Keywords Rare earth elements · Vapor phase extraction · Thermodynamics

Introduction

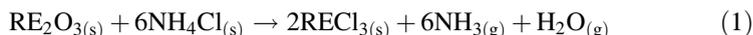
In the past four decades, technological and environmental applications of rare earth elements have grown significantly in diversity and importance. REEs are critical for a number of key defense systems and advanced materials as well as for emerging technology in cellphones, alternative energy, and medical devices such as MRI's and PET scanners, and batteries for hybrid vehicles. Currently, the worldwide production of rare earth oxides is dominated by China, which may cause the

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United States to face supply uncertainty in the future and lose its longstanding leadership in many areas of rare earth technology. Due to continued advances in material development, the demand for REE has increased and is expected to continue to increase [1].

The term “rare” is a historic misnomer for rare earth elements because some rare earth oxides or carbonates are similar in crustal abundance to that of copper, zinc, and other common industrial metals. The difference is that REEs have little tendency to become concentrated in ore deposits that are economically viable to mine. Also, due to their similar physical and chemical properties, REEs are difficult to separate from one another. Current separation methods are hydrometallurgically intensive and produce large amounts of waste, including contaminated wastewater. Rare earth resources could greatly benefit from a process that could effectively separate the REEs while lowering waste generation [1].

The objective of this research is to evaluate an alternative method for separating and recovering rare earth chlorides (RECl). Recent research demonstrated that rare earth oxides can be successfully converted to rare earth chlorides using ammonium chloride (NH_4Cl) as the chloritizing agent [2, 3]. The conversion proceeds according to the general net chemical reaction shown in Eq. (1).



Rare earth chlorides are extremely soluble in water, which makes them easy to recover by hydrometallurgical processes. A disadvantage of hydrometallurgical processing is the difficulty in separating individual rare earth elements, often requiring multiple solvent extraction stages. By exploiting differences in rare earth chloride vapor pressure, it should be possible to selectively vaporize and condense certain rare earth chlorides at their characteristic temperatures.

Experimental

The individual vaporization temperatures for each RECl were determined by thermodynamic modeling and thermogravimetric analysis/differential thermal analysis (TGA/DTA). The TGA/DTA plots for dysprosium chloride and europium chloride are illustrated in Figs. 1 and 2.

HSC Chemistry 7.0 (Outotec) [4] software was used to model multiple reactions with the same set of species within the system. HSC uses a free energy minimization algorithm that compares multiple chemical reactions and their free energies to predict stable species at equilibrium. Figures 3 and 4 show the predicted stable phases generated by HSC.

Utilizing the information in Figs. 3 and 4, the vaporization temperature for dysprosium chloride (DyCl_3) and europium chloride (EuCl_3) are determined to be 880 and 1870 °C, respectively. The objective of this research is to selectively

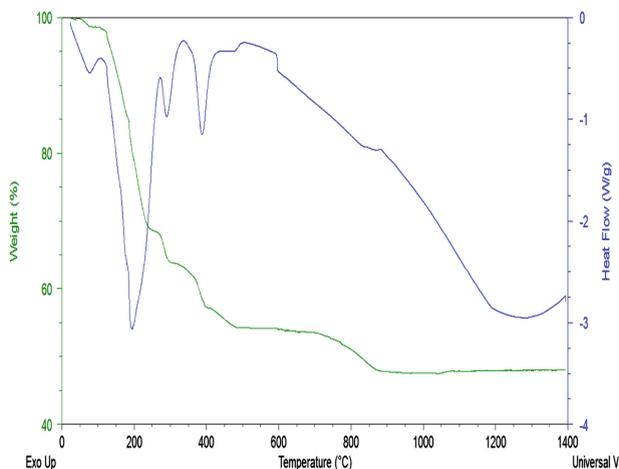


Fig. 1 TGA/DTA for dysprosium chloride

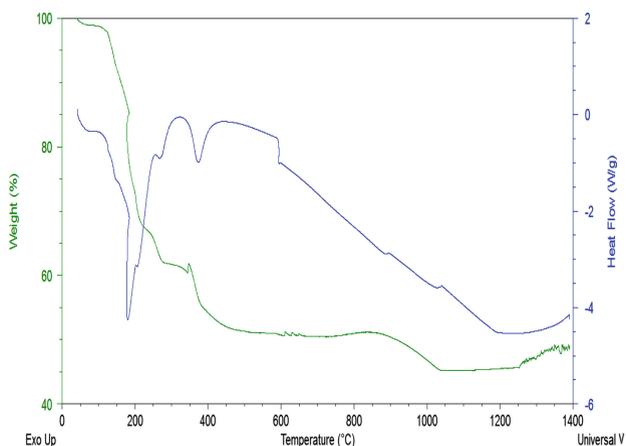


Fig. 2 TGA/DTA for europium chloride

isolate rare earth chlorides through differences in their vapor pressures. If the rare earth chlorides can be elevated to a high enough temperature to convert them to a vapor phase, they could be selectively collected as condensate upon cooling. When the equilibrium vapor pressure exceeds the partial pressure, a gas is formed. StabCal [5] was used to evaluate thermodynamic data generated in HSC and compare vaporization temperature to the partial pressure of the RECl (Fig. 5).

Based on thermodynamic analysis, it was determined that europium chloride and dysprosium chloride would be the initial focus of separation because they have the greatest difference in partial pressure and vaporization temperature.

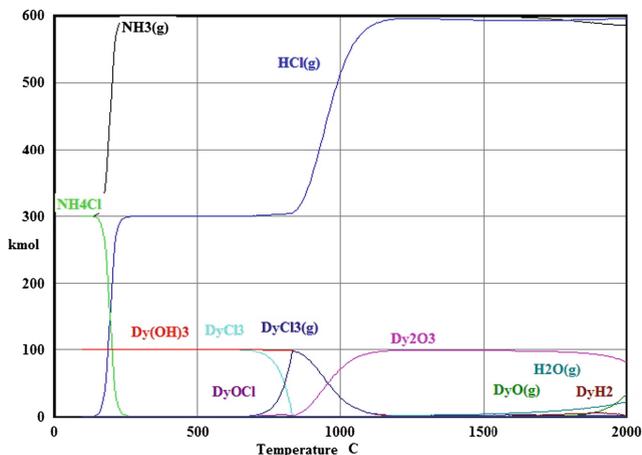


Fig. 3 Thermodynamic model for dysprosium species generated using HSC Chemistry 7.0

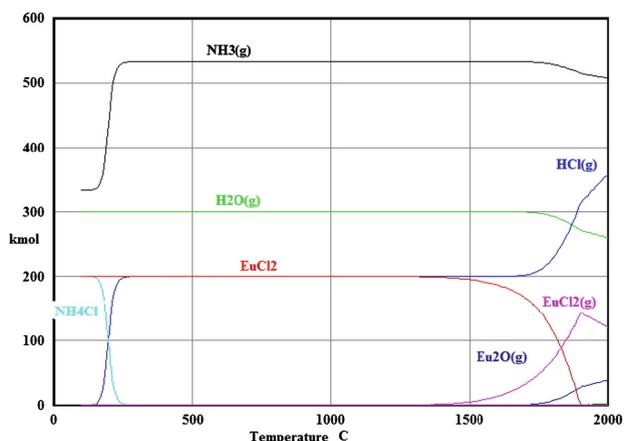


Fig. 4 Thermodynamic model for europium species generated using HSC Chemistry 7.0

A 3-zone MTI OTF-1500X tube furnace was used for proof of concept experimentation. Experiments were run with dysprosium chloride and europium chloride under an inert argon atmosphere varying time. The heating profile of the furnace was set to peak at 1150 °C and gradually decline along the length of the tube. From the thermodynamic data analyzed, this temperature profile would allow for the dysprosium chloride to vaporize, transport with the argon carrier gas, and condense in the cooler regions of the furnace. Europium chloride, which has a very high vaporization temperature, would remain in the boat. Within the condensation regions, a series of one-inch-diameter stainless steel washers were spaced one inch

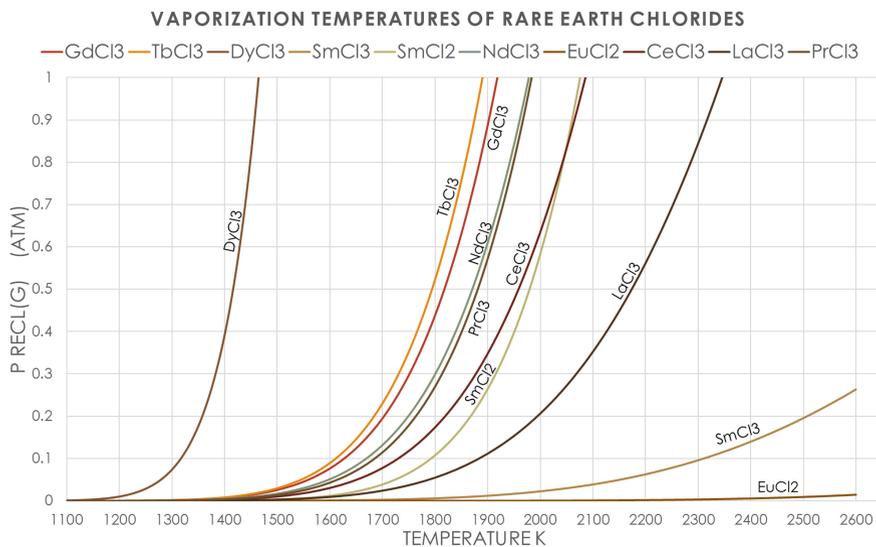


Fig. 5 Vaporization curve for select RECl_s



Fig. 6 MTI furnace train consisting of MTI OTF-1500X, OSL-1500X and GSL-1000X tube furnaces

apart from each other to create high surface area for condensate collection. The stainless steel washers were leached in 18 MΩ water for two hours.

Similar experiments were conducted in a furnace train comprised of three MTI furnaces: OTF-1500X, OSL-1500X and GSL-1000X, shown in Fig. 6. The furnace train allowed for larger vaporization and condensation regions. Within the

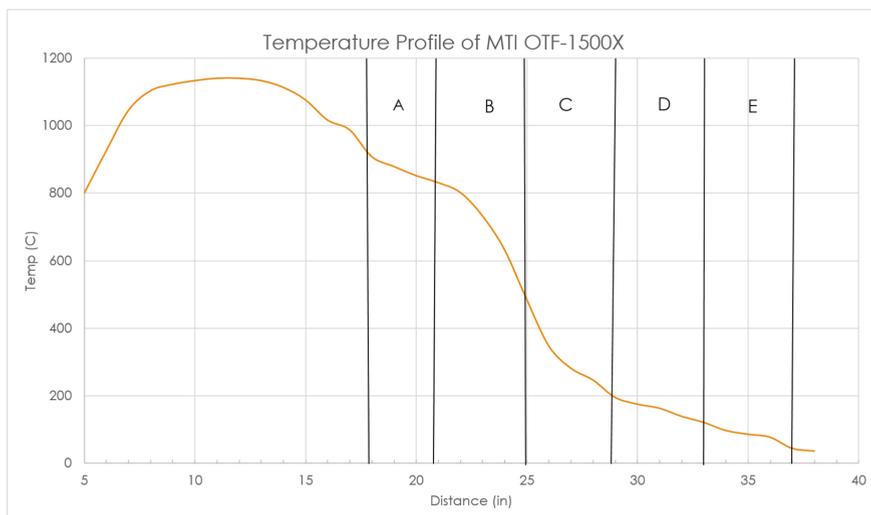


Fig. 7 Temperature profile of MTI OTF-1500X tube furnace used for experimentation

condensation regions, a series of one-inch-diameter ceramic tube sections were packed with stainless steel (316L) wool to create high surface area for condensate collection. Following each experiment, the ceramic tube sections and stainless steel wool were leached in 18 MΩ water for two hours. Analysis of the leachate samples revealed that selective separation had occurred but oxychlorides were detected in the non-volatile matter.

Results and Discussion

Figure 7 illustrates the temperature gradient of the MTI OTF-1500X three zone tube furnace. Letters A–E represent approximately three to five inch sections in the furnace where the condensate was recovered. Figures 8 and 9 show the results of the rare earth chloride recovered from the proof of concept experiments. *Dy/Eu* represent the leachate of the non-volatile material remaining in the boat. The data are summarized in Table 1.

By analyzing the data in Table 1, it can be determined that, for experiments less than 8 h, dysprosium is at least ten times the concentration of europium at a temperature less than 800 °C. According to thermodynamic analysis previously discussed, dysprosium chloride should condense anywhere below a temperature of 880 °C. In the two-hour experiment, dysprosium concentration was 1600 times that of europium in the coldest region in the furnace, verifying potential for separation. The low selectivity ratios for the eight-hour experiment are likely due to the limited

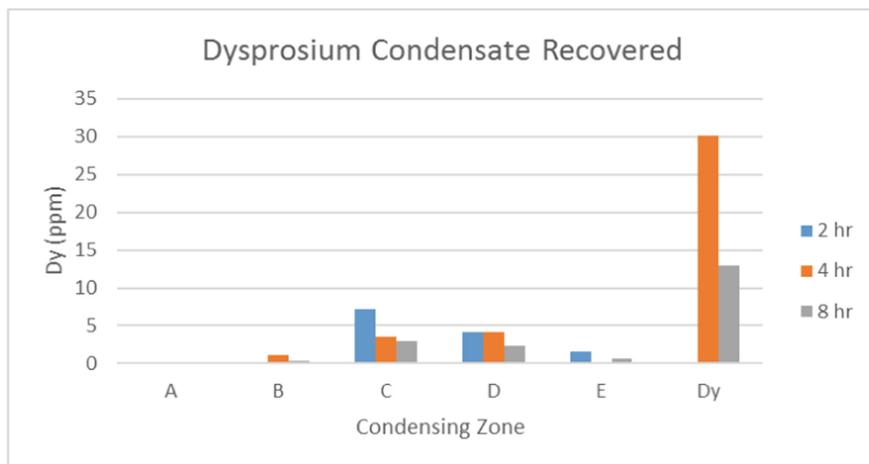


Fig. 8 Plot of dysprosium chloride condensate recovered from leach sections. A–E represent distance in furnace and Dy represent non-volatile matter remaining in boat

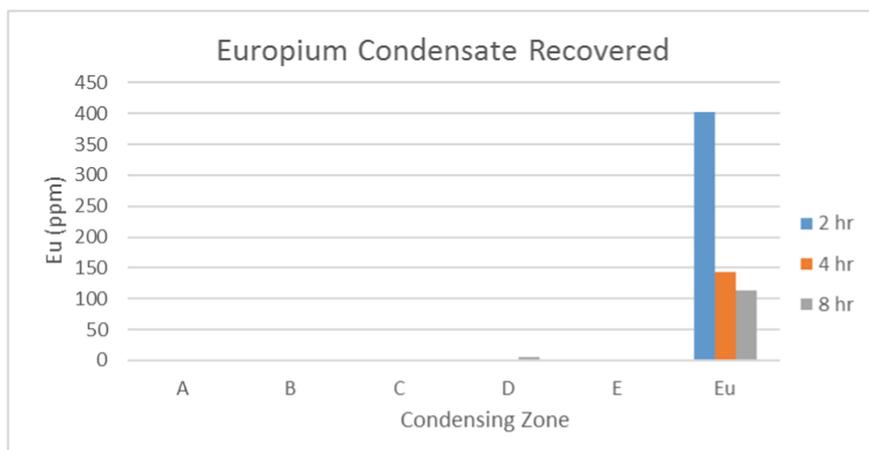


Fig. 9 Plot of europium chloride condensate recovered from leach sections. A–E represent distance in furnace and Eu represent non-volatile matter remaining in boat

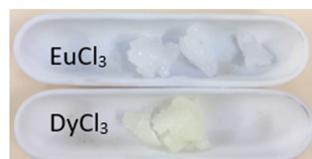
number of experiments and potential for europium chloride to become entrained in the carrier gas or attached to the waters of hydration.

The images in Figs. 10 and 11 show the dysprosium chloride and europium chloride boats preceding and following vaporization, respectively.

X-ray diffraction (XRD) analysis of the non-volatile matter remaining in the boat indicated the presence of rare earth oxychloride (REOCl). The remaining mass loss is likely waters of hydration in the rare earth chloride. Reagent grade rare earth chlorides are extremely hydrated so it is difficult to account for water loss.

Table 1 Selectivity ratios of recovered condensate according to temperature

Sample	Temperature range (°C)	2 h	4 h	8 h
		Selectivity ratio (Dy:Eu)	Selectivity ratio (Dy:Eu)	Selectivity ratio (Dy:Eu)
A	910–830	0.0	0.0	0.0
B	800–480	0.0	35.5	2.8
C	350–200	47.6	43.7	2.1
D	140–100	11.5	36.2	0.5
E	<100	1590.0	–	0.6
Dy:Eu	–	0.0	0.2	0.1

Fig. 10 Raw material placed in boat prior to vaporization**Fig. 11** Non-volatile matter remaining in boat post vaporization

Conclusions

Vapor phase extraction is a thermodynamically viable means of selectively separating rare earth chlorides. Leach solution analysis revealed that dysprosium is up to 1590 times more likely than europium to be recovered as condensate. The europium detected downstream is expected to be a result of a small amount of europium chloride powder becoming entrained in the argon purge gas or becoming attached to the waters of hydration. Despite the controlled atmosphere, hydration has been a chronic problem due to the hygroscopic nature of the RECl₃s. Thermodynamic modeling has been further assessed and experimentation is currently underway to evaluate ways to prevent oxychloride formation. Future experiments will also examine the degree of selectivity that can be obtained with other combinations of RECl₃s as well as with a rare earth bearing ore.

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