

Impact of Extractant Type and pH on Yttrium Recycling from End of Life Fluorescent Lamp

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† Presented at 2nd International Conference on Raw Materials and Circular Economy “RawMat 2023”, Atina/Greece, and 28.08.2023/02.09.2023.

Abstract: Rare earth elements (REEs), which are indispensable for high technology and renewable energy, are becoming more significant due to their distinct properties (e.g. catalytic, metallurgical, magnetic, etc.) and their diverse applications in a wide range of contemporary technologies, environmental initiatives, and economic domains. In the pursuit of an environmentally friendly, sustainable, circular approach, recycling and utilizing secondary rare earth resources as potential reservoirs of REEs may present an alternative to primary mining, addressing future raw material demands. Secondary REE sources include various products such as fluorescent lamps, light emitting diodes (LEDs), magnets, wind turbines, electric motors, and batteries. Powders used in fluorescent lamps contain approximately 3% phosphorus, and these powders comprise a high ratio of precious REEs such as Y, Eu, La, Ce, and Tb. This study involves the recovery of Yttrium from end-of-life fluorescent lamps. The composition of the end-of-life fluorescent lamp was analyzed using X-ray fluorescence (XRF) and X-ray diffraction (XRD) techniques subsequent to grinding. The leaching process was conducted to investigate the effects of leach parameters on the efficiency of the reaction. In the subsequent phase of the study, a solution obtained with the optimum leaching efficiency was subjected to the purification of Y using the Solvent Extraction (SX) method. The effect of each different extractant and pH values on Y-recovery were investigated for SX process. Yttrium oxide powders were characterized by XRF and ICP(OES) techniques and high-purity Y₂O₃ powders were obtained with high yield.

Keywords: Rare Earth Elements (REE), end-of-life Fluorescent Lamp, Recycling, Yttrium, Solvent Extraction.

1. Introduction

Rare earth elements (REE), also known as rare earth metals, is a group of 17 naturally occurring elements in the periodic table that includes Yttrium and Scandium as well as lanthanides [1]. The importance of REEs are growing in advanced technologies and renewable energy applications. REEs appear as the key components employed in numerous applications in various modern technological, environmental, and economic domains due to their catalytic, metallurgical, nuclear, electrical, magnetic, and luminescent properties. As a result, demand for REEs has increased significantly in recent years [2]. Technology advancements boosted the demand for REEs, and their limited global distribution has increased REE prices [3]. Therefore, recycling and the utilization of secondary rare earth resources for a sustainable and circular economy appear to be an alternative to meet the demand on these raw materials in the future[4][5]. Fluorescent lamps, tube lamps, cathode

ray tubes, LEDs, hard disks, wind turbines, electric motors and end-of-life batteries are examples of secondary REE sources [6].

A significant amount of REEs are used in the preparation of luminescent materials, commonly known as phosphors. Fluorescent lamps contain a significant amount of one or more rare earth phosphors: A typical 40W fluorescent lamp contains 4 to 6 g or 2% by mass of phosphor powder, depending on the type and location of manufacturing [7]. These compositions might appear insignificant at the outset, however, to produce the same quantity of REEs, 19 tons of ore minerals must be processed for 1 ton of phosphorous powder. Phosphorus powder can also be a cleaner alternative source due to its lower elemental composition—apart from REEs—when considering the mineral content [8].

High performance fluorescent lamps contain a combination of red, green and blue rare earth phosphors. The powder coating of a typical tri-phosphor fluorescent lamp contains roughly 55% red (YOX), 35% green (LAP, CAT) and 10% blue (BAM) phosphors. While red phosphorus mainly consists of yttrium (Y) and europium (Eu), approximately 10% of green phosphorus and less than 5% of blue phosphorus constitute terbium (Tb)[9]. The contents of YOX, CAT, LAP and BAM constructs are represented in Table 1.

Table 1. Phosphor waste composition in waste fluorescent lamp powder [10]

Phosphor Type	Phosphor Structure	Content(wt%)	Economic Value
White	$\text{Ca}_{4.86}\text{Mn}_{0.10}\text{Sb}_{0.04}\text{Sr}_{0.004}(\text{PO}_4)_3\text{Cl}_{0.10}\text{F}_{0.90}$ (HALO)	40–50	Low
Red	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (YOX)	20	High
Green	$\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ (LAP)	6–7	High
	$\text{CeMgAl}_{11}\text{O}_{19}:\text{Tb}^{3+}$ (CAT)	6–7	High
Blue	$\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (BAM)	5	Low

Although various methods are used for the recovery of these elements, selective separation of REEs is extremely challenging due to small variation in ionic radius, propensity to interact with hard sphere-based donor atoms and predominance of +3 oxidation state within the lanthanide series. For the selective leaching of REEs and their specific separation by eliminating impurities, different approaches such as solvent extraction (SX) [11][12], precipitation[13], supercritical fluid extraction[14], ion exchange [15]and ionic liquid methods[11][16] have been developed. Due to its highly efficient extraction capability and selectivity, SX is one of the most prevalent hydrometallurgical processes. Solvent extraction has also developed industrially to separate REEs independently since this method can treat larger volumes of diluted charged solutions at an industrial scale [17].

In this work, the effects of certain parameters on the leaching process, that is the initial step of hydrometallurgical methods, such as the type and concentration of extractant, the reaction temperature and time, and the solid/liquid ratio were investigated. SX parameters were optimized by determining the solvent type, solvent concentration, organic/aqueous phase ratio, mixing and resting time, pH effect, number of stages, type and concentration of stripping solution in the next part of the study.

2. Result and Discussion

End-of-life fluorescent lamps were pulverized after crushing, grinding and mercury removal process. The supplied end-of-life fluorescent powder was analyzed by XRF method for determination of composition prior to any processing. Table 2 represents the REEs composition of the powder with approximately 8% of the total weight.

Table 2. Chemical composition analysis of fluorescent powder

Content	Concentration (%)	Content	Concentration (%)
O	50,21	Si	10,26
Na	3,53	P	6,34
Al	6,49	La	0,598
Si	10,26	Ca	11,00
P	6,34	Ce	0,60
Y	5,73	Tb	0,35

The phase structure of the powder was determined by XRD analysis (Figure1) and XRF analysis confirmed the composition of the given powder. The primary phase was identified as $Y_2O_3:Eu^{2+}$ in the phase the matches) and the structure also contains $(Ce,Tb)MgAl_{11}O_{19}$, $BaMgAl_{10}O_{17}:Eu^{2+}$, and $LaPO_4:Ce^{3+},Tb^{3+}$. Then, the chemical recovery process for fluorescent powders containing high REEs was initiated.

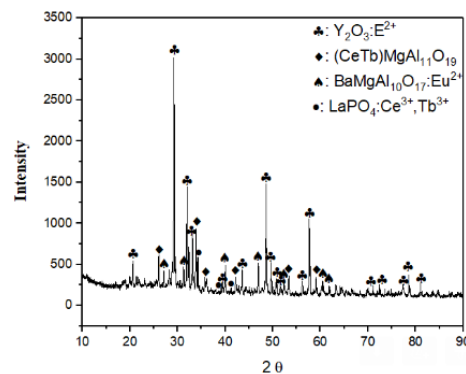


Figure 1. XRD diffraction pattern of fluorescent lamp powder

After the composition analyses of the end-of-life fluorescent lamp powders, the hydrometallurgical method was preferred for the recovery of REEs. At the initial step, leaching experiments were carried out at different K/S ratios (1/5, 1/10, and 1/20). Gelation was observed using 1/5 solid/liquid ratio, thus leaching cannot succeed. Although the highest efficiency was obtained at a 1/20 K/S ratio, the industrial feasibility of the process is low. 1/10 solid/liquid ratio was accepted as an optimum parameter for the K/S ratio.

In order to maximize the leaching process' efficiency, the effect of acid molarity for various acid types was investigated. For the hydrometallurgical process, hydrochloric (HCl) and sulfuric acid (H_2SO_4) acids were used preferably and the leaching efficiency at different molarities of the acids was studied. The efficiency of REE leaching was found to be directly proportional to the acid concentration for both types of acids and contaminants in the structure such Al, Fe, and P dissolve into the leaching solution, rapidly (Figure 2).

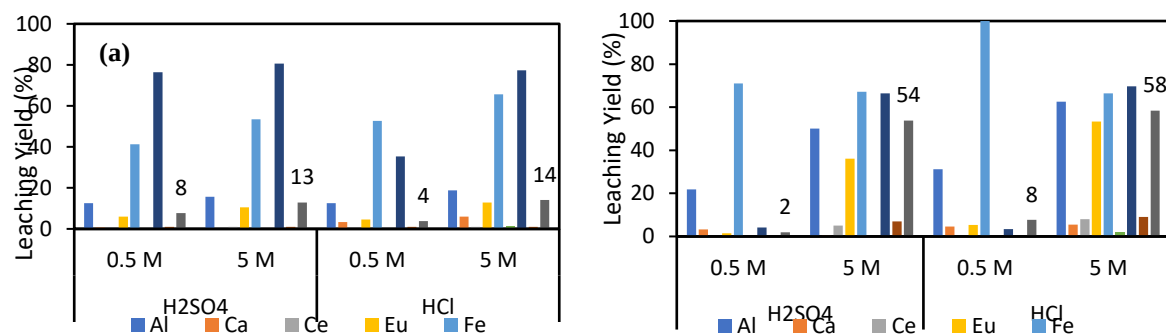


Figure 2. Effect of acid molarity on leaching efficiency ((a)=K/S: 1/10, leaching time: 1 h, reaction temp: 20 °C; (b) =K/S: 1/10, leaching time: 1 h, reaction temp: 80 °C)

The effect of the reaction time on the leaching efficiency was evaluated for the leaching parameter optimizations. The optimal yield was obtained when the material was

leached in 5 M HCl acid for 4 hours, as both reaction time and temperature increased. Figure 3 (a) represents the efficiency of Y for 2 and 4 hours of reaction time at room temperature. The efficiency increases to 90% as the reaction temperature is raised to 80 °C (Figure 3 (b)) For leaching efficiency capacities of 2 hours and 4 hours, approximations of the values were obtained 95% and 90%, respectively. According to obtained efficiency for 4h reaction time, 5% yield loss was disregarded since it is economically feasible in commercial applications, and it was determined that the next investigations would leach for 2 hours at 80 °C.

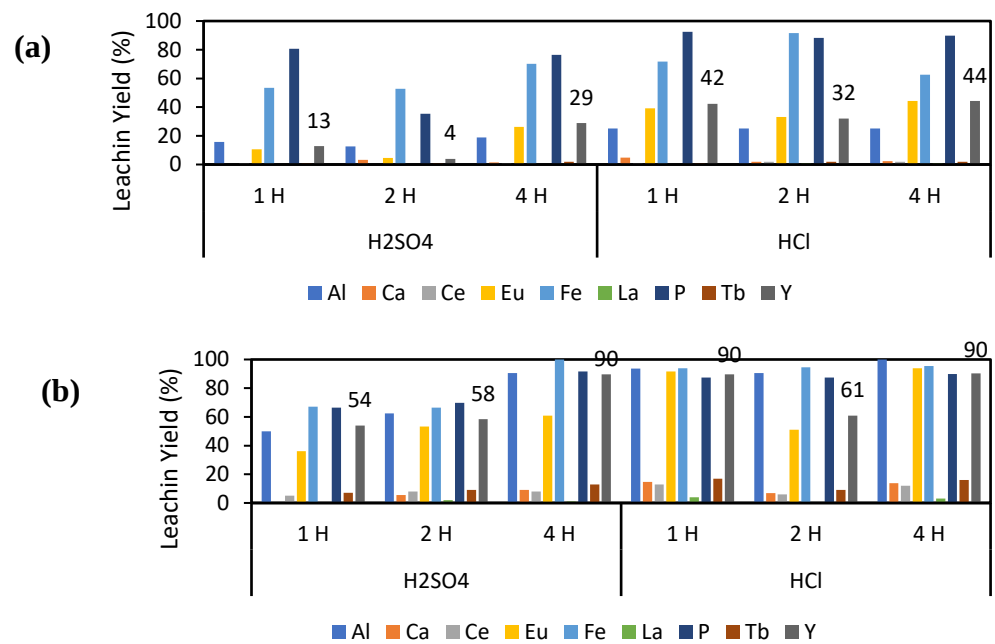


Figure 3. Effect of reaction time on leaching efficiency ((a)=K/S: 1/10, Acid concentration: 5M, reaction temp: 20 °C, (b)=K/S: 1/10, Acid concentration:5M, reaction temp: 80 °C)

For **further** evaluation of the temperature effect on leaching, experiments were carried out by reducing the temperature range, and the results are depicted in Figure 4. Leaching efficiency increased as the leaching temperature increased and red phosphorus was effectively transported to the leaching solution.

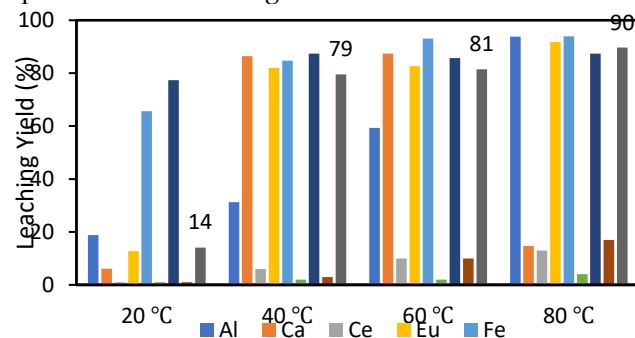


Figure 4. Effect of reaction temperature on leaching efficiency (K/S: 1/10, Acid concentration: 5M HCl, reaction time: 2h)

The leakage process in a 5 M HCl solution for 2 hours, **results** in 90% efficiency. In order to avoid highly concentrated acid consumption, optimization for acid concentration is performed: various HCl solution concentrations were investigated for 2 hours leaching process. Leaching efficiency in solutions of 3 M and 5 M HCl solutions were found to be relatively high and it was determined that 3 M HCl solution is appropriate for the amount of acid utilized.

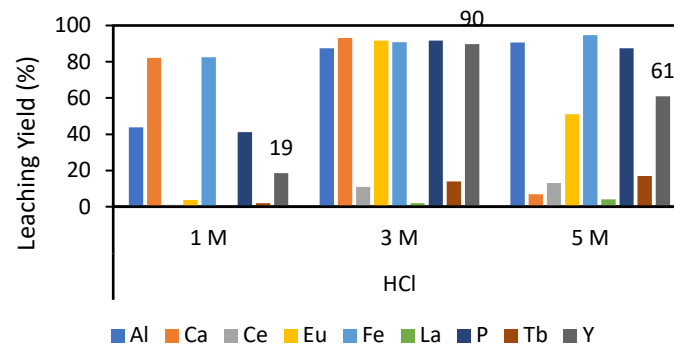


Figure 5. Effect of acid molarity on leaching efficiency ((a)=K/S: 1/10, leaching time: 2 h, reaction temp: 80 °C)

The leachability of various phosphor types obtained from end-of-life fluorescent lamp powder are different from one another, but red phosphors' YOX structure has a higher dissolution efficiency. Phosphorus dissolves as halo ($\text{Ca}_{10}(\text{PO}_4)_6\text{FCl}:\text{Sb}^{3+}, \text{Mn}^{2+}$) > YOX ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$) > LAP ($\text{LaPO}_4:\text{Tb}^{3+}, \text{Ce}^{3+}$) according to the literature [6]. The difference in the dissolving rate. Was attributed to YOX crystal lattice's less complexity as compared to the LAP and CAT structures.

Extraction of red phosphor from three phosphor mixtures was carried out at room temperature and Cyanex 923, Cyanex572, and D2EHPA were used in the initial studies to investigate the extractant effect utilized in the subsequent series of tests. The organic phase was composed of 35%, 33%, and 20% v/v extractant in kerosene, and also and O/A ratio was 2/1, 2/1, and 1/1, respectively. Sodium hydroxide solution was added to adjust the pH values of the leaching liquors and after achieving the required pH level, the organic and aqueous phases remained in contact until equilibrium.

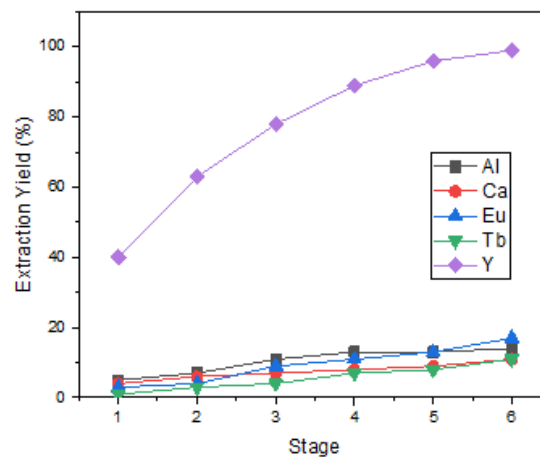


Figure 6. Extraction Yield of REE at different stage (pH=0.5, 20% D2EHPA in kerosene, O/A=1/1)

Figure 6 shows that Y was dissolved in the first-stage leach solution at a high concentration together with the presence of Eu and metal impurities like Ca, Al, Si, P, and Mn in small amounts. Rare earth metals in the feed solution were quantitatively transferred to the organic phase with 20% v/v D2EHPA in kerosene at pH 0.5. Few metallic impurities were transferred, although minor amounts of Fe and Ca were extracted. D2EHPA allows the selective and quantitative recovery of rare earth metals at pH 0.5 (Figure 6). Regarding grades and recovery of the separated products, red phosphor was 98.9% and 16.8%, blue phosphor was 11% and green phosphor was 14.6%.

3. Conclusions

The recovery of rare earth metals from an acidic leaching solution of phosphor powders in end-of-life fluorescent lamps was investigated using a liquid-liquid extraction technique. Initially, acid leaching was used to obtain rare earth elements from end-of-life phosphor powder and it was found that Y and Eu are dissolved in acidic solution relatively easily whereas a significant amount of energy is required for the leaching of other rare earth elements. It was difficult to separate rare earth metals such as Y, Eu, La, and Ce from metal impurities such as Fe, Al, and Zn, but rare earth metals were preferentially extracted against such metal impurities. Kerosene containing the extractants Cyanex 923, Cyanex 572, and D2EHPA, with a high affinity for rare earth metal ions, was used as the extraction solvent and D2EHPA was found to be the most efficient one. The highest extraction efficiency was obtained with 20% v/v D2EHPA in kerosene and an O/A=1/1 ratio at a pH of 0.5.

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