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Recycling of Cerium and Lanthanum from Glass Polishing Sludge

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To examine the efficiency of La and Ce recycling processes from the sludge, two major methods were used, namely leaching and precipitation. The findings suggest that 12% of La and 24.2% of Ce were contained in the sludge. The sludge was leached in an optimum condition of 6N HCl at a temperature of 70°C with a 3g/50 mL solid/liquid ratio for 3 h to obtain a 100% leaching recovery of La and Ce. After pH adjustment of the obtained La and Ce optimum leaching solution to 6 with NH_4OH and a simultaneous addition of H_2O_2 in a ratio of 1:1, Ce precipitated out with 65.9% recovery. On the other hand, La was not precipitated. The results obtained in this study reveal that leaching and pH adjustment method could be used to recover the valuable REE of La and Ce from glass polishing sludge in order to reach the goals of resource recycling.

Keywords: Cerium, Lanthanum, Waste, Sludge, Leaching, Recycling.

INTRODUCTION

Rare earth elements (REE), such as cerium (Ce) and lanthanum (La) are the main components of glass polishing powder materials. These elements are used for a broad range of polishing work, especially for glass parts of hard disk drives (HDD), high refractive index glass, camera lenses and photomasks. During the production process, the glass polishing powder does not produce any waste; but after an unsuccessful use, every ton polishing powder used will produce about 3 tons of solid waste[1]. Most of the wastes are discarded with wastewater sludge without further exploitation[2]. To preserve REEs, it is therefore necessary to investigate REE recovery from glass polishing sludge, even though most wastes are presently buried in landfills because it is not easy to treat them chemically or physically[2]. Although Taiwan does not have any REE resources, the country can boast an effective sludge glass polishing management system that helps increase the recycling of REE resources to some extent. Thus, the purpose of this research is to assess the recovery of La and Ce from glass polishing sludge.

Prior research was focused on recovery of REEs from various kinds of waste, such as waste phosphor and NdFeB magnet[3–6]. Recovery of these REEs is done by leaching followed by several purification processes. The amount of recovery using these methods is generally between 80% and 90%[7–8]. Leaching is a widely used hydrometallurgical technique which converts metals into soluble salt in aqueous media. Compared to pyro-metallurgical operations, leaching is less expensive and offers more flexibility in terms of establishment and operation. Acid leaching is a common industrial practice for the recovery of metals from mineral ores. The most common acids used for leaching recovery of REEs are hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and nitric acid (HNO_3)[9–13]. Precipitation is also a commonly used method to remove metal ions from solutions. The precipitation process usually starts by pH adjustment, precipitation stimulation with chemicals and heat, conversion of metal ions into metal hydroxides or insoluble metal salts. La and Ce can be recovered from leaching solution by precipitation as oxalate[10]. Some researchers used the precipitation method to separate La and Ce from the concentrates with the aid of ammonium carbonate[14–16]. Khawassek[17] utilized HCl as a precursor to precipitate RE carbonates. Several researchers have successfully used urea to precipitate REE into its carbonates[18–20]. Kim[21] for instance recovered 94% of Ce from glass polishing slurry using an oxidative, thermal treatment and subsequent chemical leaching. However, this process appeared to be expensive[21]. The dominating oxidation state of La and Ce is due to a small difference in ionic radii; hence the relative difficulty in separating these REEs[22]. According to Qi's research[22], the common methods used for separating La and Ce are crystallization, precipitation, pH adjustment, replacement, oxidation, and reduction[23]. Crystallization and precipitation are slow and tedious methods whilst the leaching reagent extraction and replacement are much more effective methods for REEs separation[22].

In this research, the REEs of La and Ce are recovered from glass polishing sludge not only by using various leaching reagents such as H_2SO_4, HNO_3, NaOH, and HCl, but also through utilization of the best leaching agent. Furthermore, batch experiments were conducted to optimize leaching conditions: solid/liquid ratio, leaching time, the concentration of the leaching reagent and leaching temperature. The optimum leaching solution containing La and Ce was subjected to precipitation (pH adjustment) in order to recover the La and Ce. The goal was to use a simple precipitation method with varying pH trends to separate and recover pure Ce by leaving La as an un-precipitated state in the optimal leaching solution obtained from glass polishing sludge.

MATERIALS AND METHODS

Sample collection and chemicals

The glass polishing sludge used in this research was collected from local manufacturers in Taiwan. The chemicals used were the following: H_2SO_4 (95%, guaranteed reagent (GR) grade), HNO_3 (65%, GR grade), HCl (37%, GR grade), and sodium hydroxide (NaOH) as leaching reagents from Merck (a global and research-intensive biopharmaceutical company). All experiments were conducted with de-ionized water (DI-water).

Composition analysis

The parameters such as water content, ash content, density and metal concentration were analyzed with <100 mesh (0.149 mm)-screened glass polishing sludge samples. Water content, ash content and density of ground samples were analyzed using two industrial wastewater measurement methods of the Taiwan Environmental Protection Administration (EPAT); these two measurement methods are NIEA R203.02C[24] and NIEA R205.01C[25]. The method used for determining the metal concentrations was the TEPA's established heavy metal digestion method known as NIEA S321.64B[26]. The experiment involved a series of steps: 3g of glass polishing sludge mixed with a 250 mL reactor containing 1 mL DI-water for wetting the sample. To this solution mixture, were gradually added 21 mL HCl and 7 mL HNO_3 solutions allowed to react for 16h at 27°C. The reaction temperature was also increased gradually, and the solution was boiled for 2 h. After the reaction temperature was cooled, 10 mL of a 0.3 N HNO_3 solution was used to wash the condenser and then added to the reactor. The REE concentration of La and Ce were analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Leaching

Leaching experiments were conducted with HNO_3, HCl, H_2SO_4, and NaOH to determine the level of La and Ce present in the glass powder samples and to optimize the leaching conditions of reaction time, concentration of leaching reagent, solid/liquid ratio, and temperature. For each experiment, 50 mL of leaching reagent was used with an agitation speed of 150 rpm on a heating magnetic stirrer. The percentage of leaching recovery was calculated using Equation (1).

$$\text{Leaching recovery (\%)} = \frac{W_1}{W_2} \times 100\%; \qquad (1)$$

where w_1 is the weight of metal leached, and w_2 is the weight of metal contained in the sample.

Precipitation

To separate La and Ce from the optimal HCl leaching solution, a hydrometallurgical precipitation method with varying pH levels was adopted. The results obtained at various time intervals of precipitation were analyzed by using ICP-AES[27]. Precipitation recovery of La and Ce at various pH values were calculated based on Equation (5), and the solubility response equation is as shown in Equation (2, 3 and 4)[28].

$$Ce^{+4} + OH^{-} \rightarrow Ce(OH)_4 \quad Ksp = 4\times10^{-49} \qquad (2)$$

$$Ce^{+3} + OH^{-} \rightarrow Ce(OH)_3 \quad Ksp = 1.5\times10^{-20} \qquad (3)$$

$$La^{+3} + OH^{-} \rightarrow La(OH)_3 \quad Ksp = 1.0\times10^{-19} \qquad (4)$$

$$\text{Precipitation recovery (\%)} = \frac{W_b - W_c}{W_b} \times 100\%; \qquad (5)$$

where w_b is the weight of metal in solution before precipitation and w_a is the weight of metal in solution after precipitation.

RESULTS AND DISCUSSION

Sample composition analysis

The collected glass polishing sludge had a size of <0.149 mm and the amount of La and Ce present were 12% and 24.2%, respectively. Water content, ash content, combustible material and specific gravity of these ground samples were also analyzed, and the results were respectively 7.23%, 27.61%, 65.16%, and 2.65 g/cm^3.

Leaching

In order to recover the La and Ce from glass polishing sludge, and to examine the optimum leaching conditions for the target metal dissolution, the leaching experiments were conducted with four reagents, namely HNO_3, HCl, H_2SO_4, and NaOH at various experimental conditions. The results are presented in Figures. 1, 2, and 3. Figure. 1 shows the effect of leaching reaction time on recovery of La and Ce at 70°C, the concentration of leaching reagent 1N and the solid/liquid ratio of 1g/50 mL. The result in Figure. 1 indicates that with an increase in the reaction time from 0.5 to 3 h, the leaching recovery of La and Ce for HNO_3, HCl, and H_2SO_4 also increased. However, the recovery of La and Ce with NaOH was nearly 0% and therefore, considered as ineffective. Figure. 1 also reveals that the leaching recovery of La was higher than the recovery of Ce with HNO_3, HCl, and H_2SO_4 reagents. For example, we obtained 67.59% recovery of La and 1.85% recovery of Ce with 1N HCl under the same experimental conditions. Leaching recovery of La

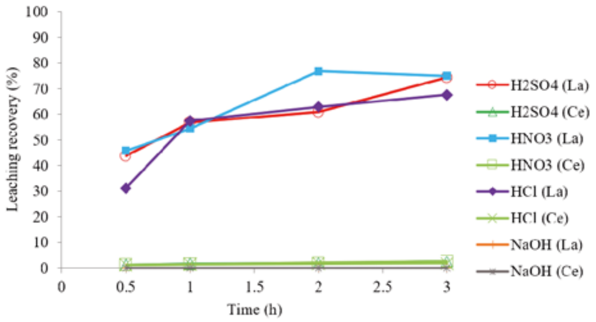

Figure 1. Effect of time on leaching recovery of La and Ce with HCl, H_2SO_4, HNO_3 and NaOH from glass polishing sludge (concentration of leaching reagent = 1N, temperature = 70°C, solid/liquid ratio = 1g/50 mL)

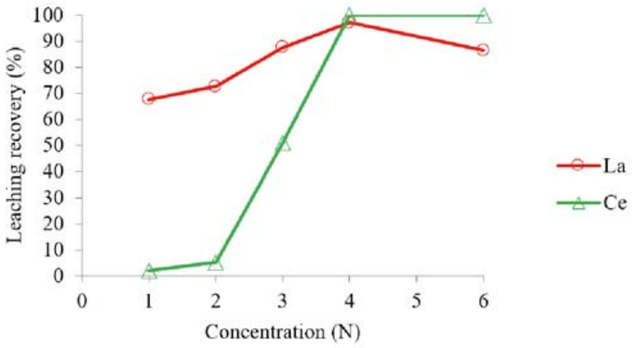

Figure 2. Effect of HCl leaching reagent concentration on leaching recovery of La and Ce (leaching time = 3 h, temperature = 70°C, solid/liquid ratio = 1g/50 mL)

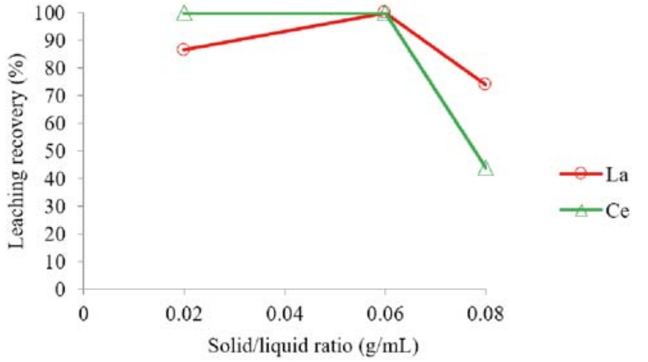

Figure 3. Effect of solid/liquid ratio on the leaching recovery of La and Ce with 6N HCl (Leaching time = 3 h, temperature = 70°C)

and Ce also amounted to 74.96% and 2.67% (with 1N HNO_3), and 74.38% and 2.54% (with 1N H_2SO_4).

Figure. 2 shows the leaching recovery percentage of La and Ce with varying HCl concentration levels from 1N to 6N at a reaction time of 3 h, a temperature of 70°C and a solid/liquid ratio of 1 g/50 mL. Therefore, further leaching experiments were conducted with HCl for the recovery of La and Ce in order to find the optimum conditions, such as leaching time, leaching temperature, and solid/liquid ratio.

The effect of quantity on glass polishing sludge in 50 mL of leaching solution on the recovery efficiency of La and Ce was found by using the solid/liquid ratio 1 g/50 mL (0.02), 3 g/50 mL (0.06), and 4 g/50 mL (0.08) with 6N concentration of HCl solution, and 3 h of contact time at 70ºC. The leaching of different solid/liquid ratios and recovery rates are presented in Figure. 3. Results showed that the leaching recovery of La and Ce present in glass polishing sludge was high for solid/liquid ratio from 1 g/50 mL to 3 g/50 mL and decreased afterwards. The results also indicated that the leaching recovery of La and Ce present in glass polishing sludge was 100% at a solid/liquid ratio of 3 g/50 mL by using a 6N HCl leaching acid. Thus, the optimum leaching conditions finalized in this study were HCl as a leaching reagent with 6N concentration, 3 h of leaching time, a 3 g/50 mL solid/liquid ratio, and a temperature of 70ºC. The implication is that an optimum leaching solution with a 100% leaching recovery of La and Ce can be obtained by using optimum leaching conditions.

Precipitation

The La and Ce leached in the optimum solution can be converted into metal precipitate by changing the solution's pH value. Since the leaching was conducted with HCl, the pH of the solution was adjusted by ammonium hydroxide (NH_4OH) and NaOH. At the end of each pH adjustment experiment, the metal concentrations of La and Ce in the solution were analyzed using ICP-AES. Then the precipitation recovery of La and Ce was calculated based on Equation (5). The obtained precipitation recovery of La and Ce of the optimum leaching solution by adding NaOH and NH_4OH under different pH values are shown in Figures. 4 and 5. Result indicated that when the pH values were increased, the precipitation recovery also increased. Also, the NH_4OH precipitation recovery of La and Ce were better than NaOH, as the recovery of La and Ce at pH 9 were 99.99% and 100%, respectively. However, both pH adjustments by using NaOH and NH_4OH couldn't help achieve the separation of La and Ce.

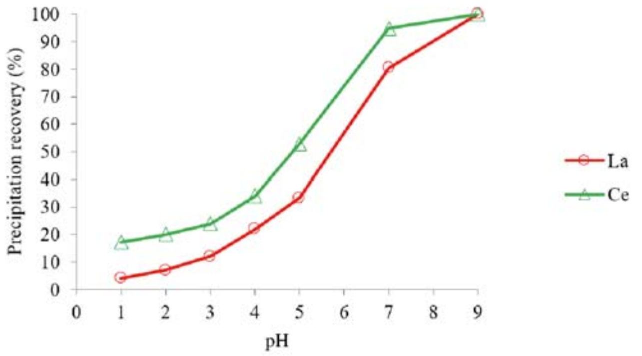

Figure 4. Precipitation recovery of La and Ce under different pH values by using NH_4OH

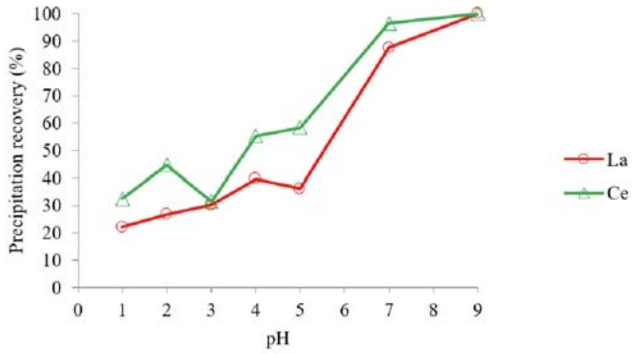

Figure 5. Precipitation recovery of La and Ce under different pH values by using NaOH

In order to achieve the separation of Ce and La, the optimum leaching solution was adjusted over the range of 0.5–9 with ammonia water and simultaneous addition of hydrogen peroxide (H_2O_2) with a concentration of 30% in a ratio of 1:1. The precipitation recovery of La and Ce of the pH adjustment experiments mentioned above is illustrated in Figure. 6. The precipitation recovery of Ce increased from 32.99% to 99.99% with increasing pH values from 0.5 to 9.

However, precipitation recovery of La decreased from 23.53% to 0% with increasing pH values from 0.5 to 5 and followed the same trend up to pH 6. Then La in-

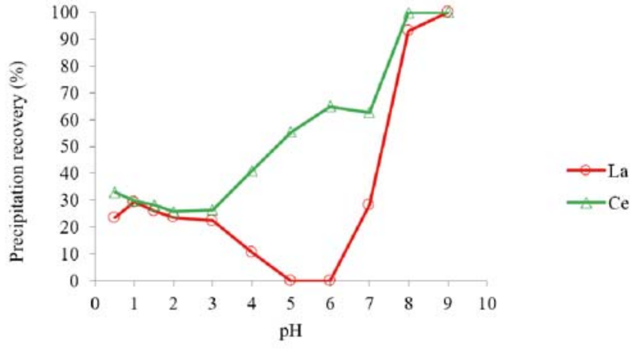

Figure 6. Precipitation recovery of La and Ce under different pH values by using NH_4OH with an H_2O_2/solution volume ratio of 1

creased from 28.18% to 100% with increasing pH values from 7 to 9. Ce was successfully separated with 65.9% through precipitation by adjusting pH from optimum HCl leaching solution, whilst La was not separated.

Therefore, precipitation with a pH adjustment method by adding NH_4OH and H_2O_2 was the best option for the separation of La and Ce. The precipitation recovery of La and Ce under different H_2O_2 solution volume ratios at pH6 is shown in Figure. 7. It clearly shows that the best separation of Ce and La is under the H_2O_2/solution volume ratio of 1:1 by using NH_4OH at pH6. This means that 65.9% of the Ce contained in the glass polish sludge can be separated and purified under this best precipitation condition.

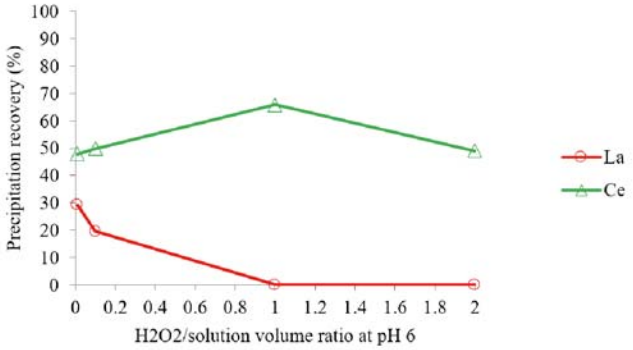

Figure 7. Precipitation recovery of La and Ce under different H_2O_2/solution volume ratios at pH6 by NH_4OH

CONCLUSIONS

This paper assesses the recovery and purification process of lanthanum (La) and cerium (Ce) from glass polishing sludge by using the hydrometallurgical method for limited rare earth elements (REE) resources conservation with the goal to help reduce waste disposal problems. The major metals contained in the glass polishing sludge were La (12%) and Ce (24.2%). Acid leaching recovery furnished the results in the range of La and Ce and the trend of leaching recovery was $HCl>HNO_3>H_2SO_4>NaOH$. The ore sample was leached in an optimum condition of 6N HCl at a temperature of 70ºC and 0.06 g/mL solid/liquid ratio for 3 h to obtain 100% leaching recovery of La and Ce. Furthermore, pH adjustments recovery of La and Ce were $HN_4OH>NaOH$. However, both pH adjustments by using NaOH and NH_4OH couldn't help achieve the separation of La and Ce. 65.9% Ce contained in the optimum leaching solution was precipitated and purified with precipitation method by using ammonia water to adjust the solution pH to 6 while simultaneously adding H_2O_2 to a leaching solution volume ratio of 1:1. La, however, did not precipitate. Therefore, we conclude that leaching and precipitation with pH adjustment by adding NH_4OH and H_2O_2 could be used to recover and purify the valuable REE of Ce from glass polishing sludge. Results obtained in this work reveal that leaching and pH adjustment methods could be used to recover valuable metals from glass polishing sludge in order to reach the goals of resource recycling.

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