



# Recovery of rare earth elements from spent fluid catalytic cracking catalysts using leaching and solvent extraction techniques



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## ABSTRACT

This paper investigates the recovery of rare earth elements (REEs, mainly lanthanum and cerium) from spent fluid catalytic cracking (FCC) catalysts via the hydrometallurgical processes of leaching and liquid-to-liquid extraction. The maximum leaching efficiency (99.3% for REEs) was achieved under the following conditions: 2 mol/L HCl, a solid-to-liquid (S/L) ratio of 1:10, leaching at 60 °C for 2 h, and 2 h of roasting at 750 °C prior to leaching. Because the main impurity element in the leachate was aluminum, the extractions of REEs and aluminum using di-2-ethylhexyl phosphoric acid (D2EHPA) and 2-ethylhexylphosphonic mono-2-ethylhexyl ester (HEHEHP) under different conditions were compared. The results indicated that D2EHPA and HEHEHP exhibited large extraction differences for REEs but small extraction capacity differences for aluminum. Based on the analysis of the experiments, the optimum extraction conditions for REEs were determined to be 0.5 mol/L D2EHPA, equilibrium pH = 2.5, ambient temperature and then stripping with 2 mol/L HCl. The overall REEs recovery efficiency was 62.88%.

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## 1. Introduction and background

Rare earth elements (REEs) play an increasingly important role in the global economy and 'green technology'. The European Union and some developed countries, such as the United States and Japan, have even placed REEs among the list of 'critical' and 'strategic' elements (McLellan et al. 2014). Due to their unique physical and chemical properties, REEs are widely used in fluorescent lamps, permanent magnets, batteries, catalysts, and by the metallurgical and nuclear energy industries (Alonso et al. 2012; Ochsenkühn-Petropulu et al. 1995). There is a global supply shortage of REEs because China accounts for more than 90% of the global production of REEs and the export of REEs is restricted. Recovering REEs from industrial applications has been gaining great interest in recent years to relieve the burden on manufacturers and support the recycling economy.

Numerous laboratory-scale studies have been published regarding the recovery of REEs from various pre-consumer scrap, industrial residues and REE-containing end-of-life products (Binnemans et al. 2013). Binnemans et al. (2013) reviewed the recycling of REEs from end-of-life streams such as permanent magnets, nickel metal hydride batteries and lamp phosphors. Liu et al. (2014) developed a novel method of two-step leaching using hydrochloric acid, followed by solvent extraction and precipitation to recycle REEs from waste phosphor. Jiang et al. (2005) proposed a hydrometallurgical process to recover REEs from

spent optical glass involving the conversion of REEs from a borosilicate phase to the hydroxide form using sodium hydroxide solution and leaching the residual with hydrochloric acid. The recovery rates were 99.4%, 100%, 100% for lanthanum, yttrium and gadolinium, respectively. Yang et al. (2014) investigated the recycling of REEs from waste nickel-metal hydride batteries and used hydrochloric acid leaching, oxalic solution addition, and roasting to obtain a final product of 99% pure rare earth oxides. Itakura et al. (2006) described a method of REEs recovery from a Nd-Fe-B sintered magnet using a mixed solution of hydrochloric acid and oxalic acid. Both leaching and oxalic acid precipitation were realized simultaneously, and more than 99% of the Nd was collected as a solid precipitate of  $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O}$ , with a purity as high as 99.8%.

Currently, rare earth catalytic materials play an important role in the petroleum chemical industry (Zhan et al. 2014). The fluid cracking catalyst is indispensable for petroleum refining. With the development of petroleum refining, a large amount of spent fluid catalytic cracking (FCC) catalysts have been discarded in landfills in the past; however, the environmental pollution of air, soil and ocean contaminated by these waste catalysts has become a serious global problem (Yoo 1998). Typically, FCC catalyst consists of a rare earth-exchanged USY-zeolite held in an amorphous silica-alumina matrix, as well as several additives (Silva et al. 2016). Recycling REEs from spent FCC catalysts and converting them into an environmentally acceptable safe material represents a new opportunity for businesses.

Innocenzi et al. (2015) proposed a process consisting of the leaching of spent FCC powder with 2 mol/L sulfuric acid for 3 h at 80 °C. Selective precipitation of REE double sulfates using sodium hydroxide was

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compared with solvent extraction with di-2-ethylhexyl phosphoric acid (D2EHPA), followed by stripping and precipitation of REE oxalates with oxalic acid. The results showed that solvent extraction was better able to achieve a high quality final products with higher purity (~98%). Sun et al. (2013) reported a method to recover REEs from spent vanadium-nickel catalysts, such as FCC, involving the following steps: 1) leaching with sulfuric acid, 2) adding salt to obtain a sediment of rare earth double salt, 3) transforming the sediment into rare earth hydroxides and sodium hydroxide using sodium hydrate, 4) using hydrochloride to leach the rare earth hydroxides, and 5) obtaining rare earth oxalate or rare earth carbonate through the addition of oxalic acid or ammonium bicarbonate.

Although REE recovery from spent catalysts is of commercial value, only a few articles have been reported on this topic. The aim of this research was to investigate a hydrometallurgical process to recover REEs, mainly La and Ce, from spent FCC catalysts via acid leaching and liquid-liquid extraction. The factors evaluated in the optimization of the leaching parameters included the acid types, leaching time, temperature and solid-to-liquid (S/L) ratio. Moreover, the effect of the organic impurities adsorbed under the FCC operating conditions and the roasting temperature before leaching were analyzed. Regarding solvent extraction, 2-ethylhexylphosphonic mono-2-ethylhexyl ester (HEHEHP) and di-2-ethylhexyl phosphoric acid (D2EHPA) were chosen as extractants to compare the extraction behavior from the complex composition of the leaching liquor with low concentrations of REEs and a high aluminum (Al) content. The effective factors of extractants concentration and pH were investigated for both REEs and Al extraction. The study mainly focused on the leaching and extraction of REEs from spent FCC catalysts; the complete study, including the subsequent process, is not discussed in detail here.

## 2. Experiment

### 2.1. Materials and chemicals

The spent FCC catalyst in this study was collected from an oil-refining factory in southern China. The catalyst sample was dried at 105 °C, passed through a 160-mesh sieve, and then stored in the drying oven. Sulfuric acid (98%), nitric acid (65%) and hydrochloric acid (37%) were used as stock solutions to prepare the leaching agents. Ammonium hydroxide (26%) was used to adjust the pH of the leaching liquids. D2EHPA and HEHEHP were used to extract the REEs from the leaching liquids and were diluted in kerosene to the required concentrations during use. The kerosene was sulfonated kerosene, also known as #260 solvent oil. All reagents used in the study were of analytical grade and used without purification.

### 2.2. Experimental process and analytical methods

The initial catalyst was characterized by X-ray fluorescence (XRF) analysis to determine the chemical composition. The organic matter adsorbed in the spent FCC catalyst was observed via thermogravimetric analysis (TGA).

The optimal roasting temperature for removal of the organic matter was acquired from the TGA result. The REE leaching experiments were performed with hydrochloric acid, sulfuric acid and nitric acid to compare the leaching efficiencies. Then, the factors affecting the leaching of REEs were studied including leaching time, temperature, S/L value, and roasting temperature. Leaching was conducted in glass bottles using thermostatic water bath oscillators. The samples were then filtered, and the solution was diluted to 1:100 with distilled water for inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis.

For the extraction, two common REE extractants, D2EHPA and HEHEHP, were used to compare the extraction behavior and the extraction efficiencies of La, Ce and impurity metal Al under different

**Table 1**  
Element content of the spent FCC catalyst by XRF analysis.

Element	Content (wt.%)
Al	27.28
Si	20.48
La	1.92
P	0.30
Ce	0.29
Na	0.18
Fe	0.15
K	0.10
S	0.10

extracting conditions. With ammonium hydroxide and 2 mol/L hydrochloric acid solution controlling the pH, equal volumes of the organic and aqueous phases (O/A = 1:1) were placed in contact for 10 min in a separating funnel. After equilibration, the pH of the aqueous phase (equilibrium pH) was measured. All of the extraction experiments were conducted at room temperature (25 ± 1 °C). The concentration of metal ions in the aqueous solution was determined by ICP-OES analysis, and the concentration of metal ions in the organic phase was calculated using mass balance.

Eq. (1) is the expression for the extraction efficiency (E%) based on the fact that equal volumes of the organic and aqueous phases were used. Eqs. (2) and (3) show the expressions for distribution ratio (D) and separation factors ( $SF_{A/B}$ ) of metal A from metal B.

$$E\% = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$D = \frac{C_o - C_e}{C_e} \quad (2)$$

$$SF_{A/B} = \frac{D_A}{D_B} \quad (3)$$

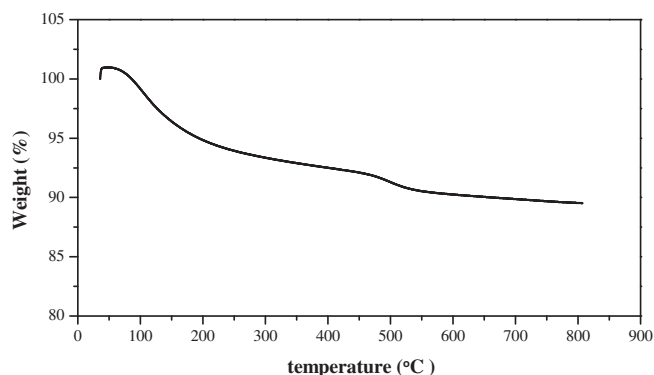
where  $C_o$  and  $C_e$  are the initial and equilibrium aqueous phase concentrations, respectively, of La, Ce and Al ions.  $D_A$  and  $D_B$  respectively denote the distribution ratio of metal A and metal B.

Each leaching and extraction experiment was conducted three times. The final result was the average of the three obtained values, and the error bar represents ± standard deviation.

## 3. Results and discussion

### 3.1. Characterization of the initial material

Table 1 lists the elementary composition of the spent FCC catalyst based on XRF analysis. The elements with the highest concentrations are Al and Si, and the observed REEs are La and Ce, with total REE



**Fig. 1.** TGA curve of the spent FCC catalyst.

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