



Treatment of fluid catalytic cracking spent catalysts to recover lanthanum and cerium: Comparison between selective precipitation and solvent extraction



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ABSTRACT

The paper is focused on the study of hydrometallurgical processes for recovery of rare earths (RE) from fluid catalytic cracking catalysts (FCCC). According to the experimental results two processes were proposed: in the first one RE were recovered as double sulfates by selective precipitation with sodium hydroxide after leaching with sulfuric acid. The second approach consisted of dissolution of powder by acids, solvent extraction by (2-ethylhexyl)phosphoric acid (D2EHPA), stripping and precipitation of RE oxalates using oxalic acid.

Experiments showed that solvent extraction was found to be beneficial in terms of achieving improved final products quality with greater purity (~98%).

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Introduction

FCC waste catalysts have several uses once spent: for example, are reutilized in cement and ceramic industry, as a wastewater filtering agent and as a component in asphalt mixtures [1].

The demand of these catalysts will increase in the incoming years and consequently their production and wastes; in order to reduce the quantity and the catalyst cost it is necessary to limit the fraction discarded and improve the development of processes for recovery and reuse of them as raw material. Furthermore, FCC catalysts contain rare earths, in particular lanthanum and cerium, and as it is well known these elements are necessary for many technological sectors in the most industrialized countries. For these reasons it is important to develop processes for treating this type of catalysts at the end of their technical life in order to reduce the amount of waste and recover strategic materials, especially RE.

The recovery of rare elements (Y, Eu, La, Ce, Tb.) awoke a great interest in the last years and many scientific works were focused on this field. The main researches were summarized in recent relevant reviews [2,3].

As regards lanthanum and cerium, they can be recovered from several industrial wastes. Some papers that describe the recovery

of such rare earths from Ni-MH spent batteries [4–10] and glass scraps [11,12] are reported in the following. Pietrelli et al. [4] proposed a process that includes leaching with 2 M of H₂SO₄ at 20 °C, 2 h, solid to liquid (S/L) ratio of 1:10, filtration and selective precipitation by addition of NaOH at pH lower than 1.5. At this pH range rare earths precipitated as NaRE(SO₄)₂. The overall recovery of rare earths was 80%.

Li et al. [5] described a method that includes leaching with 3 M of H₂SO₄ at 95 °C, 4 h and S/L ratio of 1:7.5. About 95% of rare earths precipitated as Re₂(SO₄)₃, whereas the other 5% remained in the solution. The precipitated rare earths were dissolved by water with a S/L ratio of 1:5 and treated by 1 M NaOH solution to form RE(OH)₃; instead, rare earths in the solution were stripped with 2 M HCl. The final recovery of rare earths was 97.8%.

Zhang et al. [6] developed a process consisting of a leaching stage by 3 M HCl at 95 °C, 3 h and S/L ratio of 1:9. Recovery of rare earths from the solution was obtained by solvent extraction using 25% v/v D2EHPA in kerosene, stripping with 2 M of HCl and precipitation by oxalic acid at pH 3. The recovery of La, Ce, Pr and Nd was around 98%.

The same authors [7] proposed another process that includes leaching with 2 M H₂SO₄ at 95 °C for 4 h. Rare earths were recovered by using solvent extraction with 25% v/v of D2EHPA in kerosene, followed by stripping with 1 M sulfuric acid solution, precipitation by oxalic acid and final calcination to oxides. In this treatment RE recovery was 93.6%.

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Several articles described the recovery of La and Ce with leaching of Ni-MH spent batteries using sulfuric acid in different conditions followed by selective precipitation adding NaOH until pH 2.5 with recovery of around 90–99% [8–10].

Hydrometallurgical processes were developed for recovery of La from exhaust optical glass and glass polishing sludge. Jiang et al. [11] developed a process to recover rare earths from optical glass containing 43.12% w/w of lanthanum oxide, 9.37% w/w of yttrium oxide and 4.60% w/w of gadolinium oxide. The process includes the initial conversion of RE into hydroxides by borosilicate followed by leaching of the solid residue with hydrochloric acid. Examination of the process parameters showed that an increase in NaOH concentration, S/L ratio and conversion time accelerated the transformation into hydroxide.

The optimal conditions for leaching of such rare earth hydroxides were: HCl 6 M, 368 K, liquid to solid ratio of 4 and 30 min as leaching time. One of the results obtained was a chloride solution of rare earths containing 36.54 g/L of La, 7.38 g/L of Y and 3.93 g/L of Gd corresponding to a recovery yield of 99.4%, 100% and 100%, respectively.

Jong et al. [12] proposed a work in which cerium was recovered from glass polishing slurry. Initially, glass frit and flocculants were removed by froth flotation and dissolution. The recovered rare earth slurry exhibited very similar particle size distribution as the original one, which could be reused as slurry for glass polishing operation. From the rare earth slurry, a cerium-containing solution was obtained by an oxidative thermal treatment and subsequent chemical leaching. That solution was further purified up to 94% by selective precipitation of rare earth salts.

Although there are many researches in the recovery of RE from waste, as described before, a few articles deal with recovery from FCC spent catalyst. Chen et al. [13], García de Lomas et al. [14] and Al-Jabri et al. [15] in their scientific works described a viable way to reuse them in the production of cement.

In their patent Gao and Owens [16] described a method for recovery of rare earths from FCCC by acid leaching with HNO₃, HCl or H₂SO₄ at 70–85 °C from 5 min to 3 h. After dissolution, NH₃, NH₄OH or NaOH were added to increase the pH until 4–6 to precipitate aluminum that was the major contaminant. Rare earths were indeed recovered using precipitation agents such as alkali salts or alkaline carbonates, ammonia, ammonium hydroxide, ammonium carbonate, mixtures of ammonia/carbon dioxide, or alkali metal hydroxides to form carbonates or hydroxides of rare earths.

Moreover, rare earths could be recovered as oxalates at low pHs without removal of impurities after leaching. The final product showed high purity (nearly 97% w/w RE content) and the main contaminant was Na₂O that mostly came from the unwashed mother liquor in the rare earth precipitates. Al₂O₃ and SiO₂ impurities were less than 1% w/w.

Han-Wei and Jia [17] described a process for treating rare earths from FCCC by leaching with HCl and following solvent extraction with P₅O₇ in kerosene. The optimal conditions were: P₅O₇ 60% v/v, pH 2.5, organic to aqueous phase volume ratio (O/A) equal to 2/1, 30 min as contact time to reach the equilibrium between the two phases. After that, the rare earths were stripped with HCl (2 M) for 60 min, recovered and calcined.

Given the few works in this context and the strategic importance of rare earths, in the present manuscript our research focused on recovery of La and Ce was presented with the aim to contribute and promote the future activity in this field.

The main topics of the present research work are: (1) characterization of FCCC spent powders; (2) leaching of the catalysts with several acids to extract lanthanum and cerium; and (3) recovery of lanthanum and cerium by selective precipitation as a concentrate of RE double sulfates and, alternatively, by solvent

extraction using D2EHPA diluted in *n*-heptane, hence stripping with acid and RE precipitation using oxalic acid.

Experimental

Materials

The spent fluid catalytic catalyst was collected by ORIM Spa (Macerata, Italy).

Sulfuric acid (Carlo Erba, 96%), nitric acid (Riedel-de-Haën, 65%) and hydrochloric acid (Carlo Erba, 37%) were used to leach FCCC powder. Sodium hydroxide (Fluka Chemika, ≥97%) was used to adjust the pH of those solutions during selective precipitation and solvent extraction tests.

D2EHPA (Aldrich) was used as extractants diluted in *n*-heptane (Carlo Erba) during the liquid–liquid extraction tests. Oxalic acid (Fluka, ≥97%) was used as precipitating agent for lanthanum and cerium after extraction and stripping.

Experimental procedures

The initial material was characterized by X-ray fluorescence (XRF) analysis to determine the concentration of the elements.

The leaching tests were carried out with different strong acids as described below using a solid to liquid ratio (S/L) equal to 15%, at 25 °C and 80 °C depending on the specific experiment. After 3 h leach solution samples were withdrawn, filtered, diluted 1:10 with acidified distilled water and analyzed by an inductively coupled plasma (ICP-OS) spectrometer. Furthermore, the residual solids were recovered, washed with water, dried at 105 °C for 24 h and analyzed by XRF. After leaching, La and Ce recovery tests were carried out by means of two different hydrometallurgical techniques: selective precipitation and solvent extraction. In the first method NaOH solution (35% w/v) was added to increase the pH of leach liquors until 2. At this pH a RE concentrate precipitated and the remaining solid was recovered by vacuum filtration, dried and analyzed by XRF.

In the second series of tests three different kinds of leach liquors were prepared by dissolution in sulfuric, nitric and hydrochloric acids. The leach solutions were used for extraction tests using D2EHPA in *n*-heptane. The pH was adjusted to the required levels by addition of concentrated acid or NaOH solution. During the experiments all the solutions were recovered and analyzed by ICP-OS. Finally, stripping tests were carried out by means of nitric and hydrochloric acid solutions and then REs were precipitated by addition of oxalic acid.

After 1 h of reaction RE oxalates were recovered, washed and dried. La and Ce content in the oxalates was analyzed by XRF.

Analyses

X-ray fluorescence spectroscopy method (SPECTRO XEPOS) was used to determine metal concentration in solid material samples, while concentrations of metals in the aqueous phase were determined by ICP method (ICP-OES, SPECTRO FM S16). Concentrations of lanthanum and cerium in the organic phases were calculated by subtracting the refined concentrations from the initial ones in the aqueous solutions.

Results and discussion

Characterization of the initial material and leaching tests

Table 1 shows the XRF analysis of initial powders. The most concentrated metals were aluminum and silicon. Lanthanum was

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