

# Efficient recycling of La (and Al) from fluid cracking catalysts using environmental-friendly strategies: a contribution to the circular economy

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Fluid cracking catalysts (FCCs) are widely used in the petroleum industry to crack large molecules into smaller hydrocarbons of interest, such as gasoline and other products. They are mainly made of crystalline microporous aluminosilicates, also known as zeolites, stabilized with rare earths metals (REEs), such as lanthanum (La) and cerium (Ce).

In 2008, 1980 tons of cerium(IV) oxide ( $\text{CeO}_2$ ) and 17800 tons of lanthanum oxide ( $\text{La}_2\text{O}_3$ ) were used for FCC production and it is expected that these values have increased since then (Akah 2017). Considering the large volume of FCCs waste generated on a yearly basis as well as its content in REEs of strategic importance, recycling of this material may be a relevant secondary source of La and Ce. Moreover, in the context of the circular economy, the production of new FCCs, based on recycled materials from spent ones, is the most energy efficient strategy, maximizes the reuse of the recycled materials and contributes to "closing the loop" of the FCCs lifecycle.

Thus, the main aim of this work was to develop a simple zero-waste hydrometallurgical process for recycling aluminium (Al) and La from a spent FCC catalyst supplied by a Portuguese refinery. For this purpose, a sequential process, which combined an acid leaching step for the metals present in the residue followed by a bi-stage purification step to recover sequentially Al and La from the leachate, was developed.

Firstly, the spent FCC catalyst was characterized by total acid digestion with aqua regia using a liquid-solid (L/S) ratio of 10 and boiled during 4 hours. Subsequently, three different leaching strategies (conventional, ultra and microwave-assisted leaching) were performed with  $\text{H}_2\text{SO}_4$  and HCl using a L/S of 5 to compare the leaching efficiencies. The conventional leaching experiments were carried out using falcon tubes with conical bottoms, immersed in a shaking water bath with temperature control ( $60^\circ\text{C}$ ) (OLS200, Grant) and stirring of 150 rotations per minute (rpm). For ultrasound-assisted leaching, tests were accomplished using a Bandelin Sonoplus HD 2200 (power of 200 W and output frequency of  $20\text{ kHz} \pm 500\text{ Hz}$ ) with a titanium microtip of 3 mm. (Berlin, Germany) using constant ultrasonic parameters (pulse: 0.1s and wave amplitude: 20%). Microwave-assisted leaching assays were performed inside a polytetrafluoroethylene (PTFE) bomb including 23 mL container and using a domestic microwave oven (800 W, 2.45 GHz). The effects of the acid concentration (0.5, 1 and 1.5 M for  $\text{H}_2\text{SO}_4$  and 1, 2 and 3 M for HCl, respectively) and time (conventional leaching: 1 and 3 h; ultrasound-assisted leaching: 5, 10, 20, 30 and 60 min; microwave-assisted leaching: 30, 60 and 90 seconds) on the La and Al dissolution were studied. Note that these concentrations of acids were chosen to have similar concentrations of  $\text{H}^+$ . Finally, the recovery of Al and La was performed sequentially from the leached solution resultant using microwave-assisted leaching with 1M HCl for 90 s. For this purpose, firstly, Al was precipitated by raising the pH of the leached solution up to 6 using sodium hydroxide. Subsequently, La was recovered, as a precipitate of lanthanum oxalate, from the filtrated solution using oxalic acid 0.1 M. All REEs (La and Ce) determinations were performed by inductive coupled plasma-atomic mass spectroscopy (ICP-MS) using The iCAPTM Q (Thermo Fisher Scientific, Bremen, Germany) instrument equipped with a MicroMistTM nebulizer, a Peltier-cooled baffled cyclonic spray chamber, a standard quartz torch and a two-cone interface design (sample and skimmer cones). Atomic absorption spectroscopy with flame atomization (AAS-FA) using an Analytik Jena AG – novAA 350 (Jena, Germany) spectrophotometer was used for the determination of all other metals, with air-acetylene flame for Fe, Ni, Cu, Zn, Pb and Mn and nitrogen protoxide-acetylene flame for Al, V and Ti.

The metal composition of the spent FCC, based on the total acid digestion, has shown that Al was the metal present at the highest concentration, ( $135 \pm 2$ ) mg/g, with minor contents of Ce [ $0.057 \pm 0.005$  (mg/g)], V [ $3.7 \pm 0.2$  (mg/g)], Fe [ $2.5 \pm 0.1$  (mg/g)] and Ti [ $0.30 \pm 0.04$  (mg/g)]. REE content consisted mainly of La [ $28 \pm 2$  (mg/g)]. The levels of other metals (Cu, Mn, Ni, Pb and Zn) were lower than 0.1%.

Table 1 summarizes the results obtained for all three leaching strategies considering a compromise between the best La leaching efficiency and minimizing the acid consumption and time. Conventional strategy was capable of obtaining a maximum La leaching efficiency of ( $55.7 \pm 0.1$ ) and ( $83 \pm 2$ ) % for  $\text{H}_2\text{SO}_4$  and HCl, respectively, with a simultaneous Al co-extraction of ( $14.0 \pm 0.8$ ) and ( $42 \pm 2$ ) %, respectively. Using ultrasound-assisted leaching for 1 hour, results for these two acids were increased to ( $69.8 \pm 0.8$ ) and ( $97 \pm 3$ ) % for  $\text{H}_2\text{SO}_4$  and HCl, respectively, with a simultaneous Al co-extraction of ( $23 \pm 1$ ) and ( $25.8 \pm 0.8$ ) %, respectively. Ultrasound proved to be an effective strategy to maximize La extraction, when HCl was used as extractant, minimizing the Al co-extraction.

However, the reaction time was too long (1 h), which may limit its real application due to the potential associated costs for maintaining ultrasound equipment. Among the three leaching methods tested, microwave-assisted leaching resulted in an increase of the extraction of La with (73±2) with 60 seconds and H<sub>2</sub>SO<sub>4</sub> and (99±1) % with 90 seconds and HCl. However, Al co-extraction was greater than in the other strategies. Thus, microwave-assisted leaching proved to be significantly less time consuming and also able to obtain high extraction efficiency with lower concentration of acid. The solid remained from the leaching can be reused for zeolite production (Wang, Xu et al. 2017).

**Table 1** – La and Al extraction efficiencies for the best performing conditions of each acid type and leaching strategy.

Strategy	Acid	Concentration (M)	Time (h)	Metal leaching (%)	
				La	Al
Conventional	H <sub>2</sub> SO <sub>4</sub>	1	1	55.7±0.1	14.0±0.8
	HCl	3	3	83±2	42±2
Ultrasound	H <sub>2</sub> SO <sub>4</sub>	1	1	69.8±0.8	23±1
	HCl	3	1	97±3	25.8±0.8
Microwave	H <sub>2</sub> SO <sub>4</sub>	1	0.017	73±2	48±2
	HCl	1	0.025	99±1	34.1±0.3

From the microwave-assisted (1M HCl for 90 s) leached solution, Al and La were sequentially recovered using a stepwise precipitation process. Firstly, the pH was increased up to 6 with sodium hydroxide to precipitate Al. Under these conditions, 98% of Al and 98% of Fe were precipitated with negligible loss of La by co-precipitation (2.8%). This process originated a high purity (88.7%) Al salt, which can be used for Al-Fe alloys production. Subsequently, after filtration, the remaining liquid containing a high amount of La and low quantities of Al and Fe, was further processed by addition of oxalic acid to selectively precipitate La, as lanthanum oxalate, with high yield (99.9%) and purity (99.8%). This salt can be calcinated into lanthanum oxide and be directly reused in the production of new FCC catalysts.

A comparative analysis of the flowsheet developed in this work with others described in the literature (Innocenzi *et.al.* 2015) evidences that it is capable of recovering efficiently La (as well as Al) with high purity grade in a faster and costlier effective way, making it ideal to industrial applications.

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