

A Simple and Flexible Flowsheet Process for Efficient and Selective Metal Recycling from Spent Fluid Cracking Catalysts

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Abstract

This paper investigates the recovery of the main metals (La and Al) present in a spent fluid cracking catalyst (FCC) through the hydrometallurgical processes of leaching and selective precipitation. Complete La leaching (99±1)% was achieved under microwave-assisted leaching with the use of 1 M HCl and a liquid-solid (L/S) ratio of 5 for 90 s. Since the main impurity presented in the leachate was Al, an initial process was developed to selectively recover Al by alkaline precipitation. At pH 6, almost total Al (98%) was precipitated with purity of 88.7% while La co-precipitation was insignificant (2.8%). The second approach consisted of La recovery as lanthanum oxalate [La₂(C₂O₄)₃], using low oxalic acid concentration (0.1 M). The results indicate high La recovery (99.7%) with very high purity (99.9%) when applied on the solution pre-purified and free of Al. Results strongly demonstrated that the simple and universal approach created is beneficial in terms of high metals recovery and final product quality from spent FCC without the need of highly concentrated chemicals and time-consuming processes.

Keywords: Fluid cracking catalysts, simple and nearly-closed process, recovery of La, recovery of Al

1. Introduction

Fluid cracking catalyst (FCC) is a fine powder used in petroleum refinery industry. This catalyst is notably characterized by its content in rare metals elements (REE), such as lanthanum (La) and cerium (Ce). The presence of REE in FCC is to preserve catalyst effectiveness, improve the cracking activity and to breakdown heavy hydrocarbon fractions into lighter hydrocarbons. REEs are critical raw materials for the EU (European Commission, 2017) and its increasing demands. For instance, it is estimated that about 18000 tons of La were used for FCC production in 2008 alone, which represents 46% of all La use worldwide (Aka, 2017). Therefore, metal recovery would prove to be strategically and environmentally important. Despite many developed processes studied in the literature for REE recycling from FCC, the hydrometallurgical process has been the most commonly studied using concentrated acids and with significant leaching time (Wang et al., 2017; Zhao et al., 2017). Subsequent purification steps are

mainly performed by solvent extraction. However, solvent extraction present significant limitations, such as producing contaminated wastewaters and the need of a high concentrated acid for stripping REE from organic phase, which limits its implementation at an industrial scale (Hongtao et al., 2010).

In this context, the objective of this study mainly focuses on recycling La and Al from spent FCC using auxiliary energy sources such as microwave to enhance extraction yield followed by simple and selective precipitation processes in which Al is separated as an aluminum hydroxide by alkaline precipitation. The goal is to obtain REEs with high yield and purity recovered subsequently by oxalate precipitation strategy with minimum chemical use.

2. Experimental

2.1. Characterization of FCC and leaching tests

A representative spent FCC was directly used without any further treatments. Chemical composition of the spent FCC was characterized by total acid digestion with aqua regia.

Two acid leaching processes with HCl were performed: conventional and microwave-assisted leaching. The conventional leaching experiments were conducted in falcon tubes with conical bottoms immersed in a shaking bath with stirring at 150 rotations per minute (RPM) at 60 °C. Under these conditions, variations of acid concentration (1, 2 and 3 M) and time (1 and 3 h) were investigated. Microwave-assisted leaching was carried out in a domestic oven (800W, 2.45GHz) using a polytetrafluoroethylene (PTFE) bomb for heating. Different parameters were tested, such as the acid concentration (1 and 2 M) and time (30, 60 and 90 s). In both methods, after leaching process, the reaction mixture was filtrated ($\varnothing = 0.45 \mu\text{m}$) and metal concentrations were determined by inductive coupled plasma-atomic mass spectroscopy (ICP-MS) for REEs metals and atomic absorption spectroscopy with flame atomization (AAS-FA) spectrophotometer for the other metals. The liquid/solid (L/S) ratio of 5 was used for all leaching conditions. Each data set was performed at least three times.

2.2. Selective separation process

Computational model using MINEQL+ has been developed to predict the chemical equilibrium behavior of chemical constituents in solution. Based on these predictions, set of tests at final pH (between 4.5-6) were used to precipitate Al, as Al(OH)₃, selectively from the solution. Later, to recover La from the solution as lanthanum oxalate, La₂(C₂O₄)₃, based on chemical speciations, oxalic acid (0.1 M) at pH 6 was used.

3. Results and Discussion

3.1. Characterization of FCC and Leaching tests

The elemental contents of the spent FCC after total digestion shows that the catalyst consists mainly of Al (135±2) mg/g and minor amount of other metals, such as V (3.7±0.2) mg/g, Fe (2.5±0.1) mg/g and Ti (0.30±0.04) mg/g while REEs content was La (28.1±2) mg/g.

The leaching of La and Al was performed using conventional and microwave-assisted leaching strategies. The summary of the main results achieved under these two methods are presented in Table.1.

Table 1. Influence of the time and acid concentration on La extraction (%) using different leaching methods.

Method	Time	[HCl]		
		1 M	2 M	3 M
Conventional	1h	46	59	70
	3h	57	71	83
Microwave	30s	83	93	-
	60s	88	-	-
	90s	99	-	-

Microwave-assisted leaching represented a considerably greater percentage of La extraction (99±1) % in a very rapid process (90 s) using a lower concentration (1 M) of HCl compared to conventional process (HCl 3M and 3h; 83% of La). The high La extraction yield may be due to the excellent heat isolation of the PTFE bomb in microwave-assisted leaching method, which internally raised the temperature and pressure of the vessel very quickly (Sadeghi et al., 2017). These results clearly evidence that microwave-assisted leaching appears to be a more promising option than conventional leaching.

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3.2. Selective precipitation and metal recovery

Two sequential steps were studied in this work for selective metal recovery:

- (1) Alkaline precipitation to remove Al selectively.
- (2) Oxalate precipitation using oxalic acid for La recovery.

Considering chemical simulations of La and Al using MINEQL+, theoretically all Al precipitates up to pH 6 while all La remains in the solution without co-precipitation. The experimental results proved that at pH 6 almost 98% of Al precipitated. However, co-precipitation of La was negligible (< 3%). For pH values higher than 6, a significant La loss (> 40%) occurred. Based on this fact, the influence of the pH on the selective precipitation of Al versus La was evaluated (data not shown). Therefore, leachate at pH 6, which is free of Al was used for oxalate precipitation to recover La with high yield and purity. This procedure using 0.1M oxalic acid at pH 6 allowed the total recovery of La (99.9%), as a solid, and simultaneously improved the purity of the solid of La (99.7%).

4. Conclusions

In conclusion, the present work allowed the development of a nearly closed process to recycle the main valuable metal (La) and Al from spent FCC. The application of a microwave-assisted leaching method for metal extraction resulted in complete dissolution of La (99%) and proved to be more environmental-friendly since it was more efficient from a reagent use and time consumption. Subsequently, two sequential selective precipitation, (alkaline leaching by increasing the pH of initial leachate up to 6 followed by oxalate precipitation using a low oxalate concentration, 0.1 M, respectively) steps resulted in complete recovery of Al (98% with purity of 88%) and La (99.7% with purity of 99.9%) from the leachate.

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