

## RECOVERY OF LANTHANUM FROM THE DEPLETED CATALYST OF THE FLUIDIZED CATALYTIC CRACKING UNIT (FCC).

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### ABSTRACT

This work presents an acid leaching process to establish the best leaching agent, for the recovery of lanthanum from the depleted catalyst of the FCC unit at the Esmeraldas Refinery using the following leaching reactants; hydrochloric acid, nitric acid and sulfuric acid. The laboratory work included the physical, chemical and mineralogical characterization of the depleted catalyst sample. From the physical characterization, the granulometry, the real density, and its bulk density were established. The mineralogical analysis was performed by X-ray diffraction, while the chemical analysis was performed by acid digestion and atomic absorption. Subsequently, the best leaching agent was evaluated, for which some conditions were modified, such as: concentration of the leaching agent (0.5; 1.0; 2.0; 3.0; 4.0; and 6.0; M), the incidence of the percentage of solids (10, 20, 30, 40 and 50%) and the leaching time of the process (2, 6, 9, 15, 18 and 24 hours). The maximum recovery of lanthanum achieved was 93.7 % when leaching with hydrochloric acid at a concentration of 2 M for a time of 24 hours and with a solids content of 10 %. Lanthanum recovery analyses in the depleted catalyst were investigated by inductively coupled plasma: ELMER OPTIMA 8000 PLASMA OPTICAL SPECTROMETRY (IPP). Therefore, the intensive research

in this field is not only expanding the possibilities of recovery and recycling but also is leading to new and interesting cost-effective and sustainable approaches, as well as providing a reliable industrial perspective to recover and purify rare earths within the framework of a sustainable recycling strategy.

**Key words:** lanthanum, leaching, acid, depleted catalyst, plasma optical spectrometry.

## 1. INTRODUCTION

Fluidized cracking unit catalysts aim to increase the rate at which the equilibrium of a reaction is achieved, lowering the activation energy without being consumed in the reaction (Shah et al, 2010). In addition, they help in the molecular breakdown of hydrocarbons to achieve superior-quality fuels (Torres and Torres, 2010). These catalysts, in first world countries, due to strict environmental regulations and depending on the high degree of toxicity, must be managed to comply with environmental laws, hence preliminary treatments are required before their final disposal of storage (Ramírez, et al 2008).

In recent decades, rare earths have become one of the main raw materials due to their great electrical, optical and magnetic properties (Henderson, 2000, p. 39). Lanthanum is one of the elements that has presented a growing demand in recent years, due to its low availability and the multiple applications found for its use. The main application of lanthanum as oxide is in the production of FCC catalysts, but also It is used in the manufacture of special optical glasses, such as infrared, camera lenses and telescopes, due to your index of refraction is high and has low dispersion. In addition, lanthanum can confer malleability, impact resistance and ductility when added to steel (El - Naby, 2006, p. 122). Regeneration processes are currently used to extend the life of the catalyst, however, the limitation of this method is that catalysts are rarely regenerated and there are a defined number of catalytic systems (Amiri, Mousavi, Sheibaniand Yaghmaei, 2011, p. 66).

At present the leaching process is used in extraction, in the field of Hydrometallurgy, where the important metal is dissolved from the ore to an aqueous solution. That is, it involves the selective dissolution of valuable minerals, in which the concentrated mineral enters into relation to an active chemical solution called leaching solution (Smit, 2013, p. 7).

In this way, the present research seeks to study fundamental aspects of the acid leaching of lanthanum from a spent cracking catalyst, which is a material consisting of an amorphous aluminosilicate matrix and a zeolite promoted by lanthanum. For which hydrochloric acid, nitric acid and sulfuric acid will be used, modifying some conditions such as the concentration of the leaching agent, incidence of solid percentages, temperature and duration of the process.

## 2. METHODOLOGY

## **2.1. PHYSICAL, CHEMICAL AND MINERALOGICAL CHARACTERIZATION OF THE DEPLETED CATALYST OF THE FCC of the Esmeraldas Refinery.**

The raw material used is the depleted catalyst, which was collected in the waste area of the Esmeraldas State Refinery, where, according to reported data, it was determined that 480 tons per year of depleted catalyst are discarded.

The procedure prior to the characterization of the depleted catalyst was to sift the material, using a mesh No. 16 in order to classify the size of the particles, discarding the larger ones and having a uniform particle distribution.

### **2.1.1. PHYSICAL CHARACTERISATION OF THE SPENT CATALYTIC CONVERTER**

The methodology used to establish the physical properties of the depleted catalyst is based on granulometry, density and BET analysis tests, which are described in the following sections:

#### *2.1.1.1 Granulometric analysis*

The particle size analysis was performed under the criteria of ASTM C136-05. For this purpose, mechanical separation was performed using Tyler sieves with different aperture (850  $\mu$  m – 38  $\mu$ m) of mesh that were incorporated into the laboratory ATM ARROW vibrosieve (ASTM C136-05, 2014, pp. 1-15).

The sieves were placed in descending order from largest to smallest opening, one after the other and at the bottom a container in which the finest material was deposited. A 300 g sample of catalyst powder was placed on the top sieve, capped and the vibrosieve was started for 15 minutes.

The material retained in each sieve was weighed. Based on the results achieved, calculations were made to obtain the particle size curve and establish  $d_{80}$ .

#### *2.1.1.2 Bulk density of depleted catalyst*

In the determination of the bulk density, a 50 mL specimen was used, previously weighed in an analytical balance, 20 mL of sample were placed, the weight was noted and divided for the volume obtained in the specimen, establishing the bulk density.

#### *2.1.1.3 Actual density of depleted catalyst*

The actual density was obtained based on the INEN NTE 0856:2010 Standard, which requires the use of a pycnometer. The procedure was as follows: the empty pycnometer + lid was weighed on

an analytical balance (Po), a sample of one gram of depleted catalyst was placed and the weight (P1) was recorded, the pycnometer was weighed with the catalyst adding distilled water to the edge (P2) (INEN NTE 0856, 2010).

Finally, distilled water was added to the empty pycnometer and weighed (P3). Once the weights have been obtained, the corresponding calculations are made.

### 2.1.2. CHEMICAL CHARACTERISATION OF THE SPENT CATALYTIC CONVERTER

#### 2.1.2.1. *Determination of the semi-quantitative chemical composition of the depleted catalyst by scanning electron microscopy (EBM)*

Through scanning electron microscopy analysis (Tescan-Vega), with a Quantax (Bruker) energy scattering X-ray (EDX) micro-analyzer, it was possible to establish the semi-quantitative composition of the depleted catalyst. Additionally, the structure of the raw material used was observed.

#### 2.1.2.2. *Determination of the elemental chemical composition of the spent catalyst*

For the determination of the elemental chemical composition of the depleted catalyst, the acid disintegration of the material in microwaves was first performed, with the following procedure:

A 0.2 g sample was taken in a Teflon reactor, 3 mL of nitric acid (HNO<sub>3</sub>) and 3 mL of hydrofluoric acid (HF) were incorporated, microwaved for 2.5 minutes, removed the Teflon reactor from the microwave and allowed to cool, 5 mL of hydrochloric acid (HCl) was added to the sample, the teflon reactor was hermetically closed, taking care that there are no leaks, and again the sample was put in the microwave for 2.5 minutes, removed and cooled in the same way as in the previous procedure. The sample obtained was measured with distilled water in a 100 mL balloon. Subsequently, the content of nickel, vanadium and molybdenum by atomic absorption in the equipment was analyzed (A. Analyst 300). For the concentration of lanthanum, the analysis was performed in the optical spectrophotometry equipment with plasma ICP ELMER ÓPTIMA 8000.

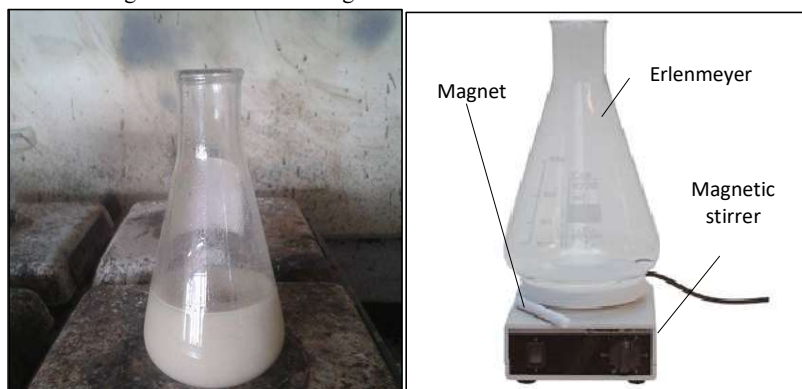
### 2.1.3. MINERALOGICAL CHARACTERISATION OF THE SPENT CATALYTIC CONVERTER

The mineralogical characterization of the catalyst was carried out using an X-ray diffractometer model D8 Advance (Bruker). 2 g of sample was sprayed and placed in a sample holder trying to obtain a strictly flat surface layer. Later it was placed in the X-ray diffraction equipment, where the qualification of the crystalline components was carried out using the Diffrac Plus program.

## 2.2. EVALUATION OF THE ACID LEACHING PROCESS FOR THE RECOVERY OF LANTHANUM from FCC spent catalyst.

### 2.2.1. Influence of the Leaching Agent

To perform the leaching test, the best conditions were established to recover lanthanum by solution in as much quantity as possible, for this purpose the powder sample of the FCC depleted catalyst was used. Figure 1 shows a leaching scheme.



**Figure 1** Leaching test performed on depleted catalyst powder under normal conditions.

**Source:** Authors.

The procedure used to establish the best leachate was as follows:

As leaching agents for the solution, the following acids were used: hydrochloric, nitric and sulfuric, for the purpose 100 mL of solutions of concentration 2 M and 3 M were prepared, with a percentage of solids of 10% (Ron, 2016, p.64). 250 mL erlenmeyers sealed with paraffin were used to prevent acid losses by evaporation under constant stirring for 24 hours (Veglio and Innocenzi, 2012, p. 184), after the stirring time the pulp was filtered, obtaining the strong solution and the cake (tailings) according to the methodology suggested by Barrera, (2015, p. 43).

Then the washing of the cake (tailings) was carried out with 75 mL of distilled water forming the washing solution, then these solutions were sent to plasma optical spectrometry (ICP) ELMER ÓPTIMA 8000, to determine the amounts of lanthanum present in each of them.

The cake (tailings) was dried in a MEMERT stove at 95 °C for 2 hours, to remove moisture, then proceeded to weigh on a SARTORIUS BALANCE TE 1245. From the dry cake 0.2 g were extracted, this material was disaggregated applying the method indicated in Section 2.1.2.2, the disaggregated sample was graded to 100 mL, with distilled water and the solution obtained was analyzed in the ICP spectrophotometer. This procedure was performed with each of the proposed

acids, with the results obtained the metallurgical balance of the strong solution of the washing solution and the cake product of the acid disintegration was carried out.

Table 2.1 shows the working conditions using different types of acid for these studies.

**Table 2.1.** Working conditions in the leaching tests of the depleted catalyst.

Leaching agent	Hydrochloric acid	Nitric acid	Sulphuric acid
Concentration	2.0 m, 3.0 m	2.0 m, 3.0 m	2.0 m, 3.0 m
Solids	10 %		
Volume	100 mL		
Mineral	Exhausted catalyst		
Ore weight	10 g		
Temperature	Environment (18 °C)		

Source: Authors.

### 2.2.2. Acid leaching at different concentrations.

According to the results obtained, the best leaching agent is hydrochloric acid. Hydrochloric acid at different concentrations: 0.5 M (18.25 g/L), 1.0 M (36.50 g/L), 2.0 M (73.00 g/L), 3.0 M (109.50 g/L), 4.0 M (146.00 g/L), 6.0 M (219.00 g/L), with 10 % solids, was used to carry out the process explained in Section 2.2.1.

Table 2.2 shows the working conditions under which these tests were performed.

**Table 2.2.** Conditions used in the leaching tests of the depleted catalyst using hydrochloric acid.

Leaching agent	Hydrochloric acid
Concentration	0.5 m, 1.0 m, 2.0 m, 3.0 m, 4.0 m, 6.0 m
Solids	10 %
Volume	100 mL
Mineral	Exhausted catalyst
Ore weight	10 g
Temperature	Environment (18 °C)

Source: Authors.

### 2.2.3. Analysis of the influence of the percentage of solids in the leaching of depleted catalyst.

The influence of the percentage of solids was performed using hydrochloric acid as a leaching agent. The depleted catalyst powder ore was then weighed to obtain a quantity of 10, 20, 30, 40, 50%. The leaching process is performed as in the procedure proposed in Section 2.2.1. According to the tests carried out in Section 2.2.2 the best concentration is 3.0 M. Table 2.3 establishes the operating conditions of the tests carried out.

**Table 2.3.** Conditions used in the leaching tests of the depleted catalyst using hydrochloric acid and modifying the percentage of solids.

<b>Leaching agent</b>	<b>Hydrochloric acid</b>
<b>Concentration</b>	<b>3.0 M</b>
<b>Solids</b>	<b>10, 20, 30, 40 and 50 (%)</b>
<b>Volume</b>	<b>100 mL</b>
<b>Mineral</b>	<b>Exhausted catalyst</b>
<b>Ore weight</b>	<b>10, 20, 30, 40 and 50 (g)</b>
<b>Temperature</b>	<b>Environment (18 °C)</b>

### 2.2.4. Establishment of the best leaching time using hydrochloric acid.

For the tests, different leaching times 2, 6, 9, 15, 18 and 24 hours were used, under the best conditions of the percentage of solids and the best concentration of hydrochloric acid with the same methodology proposed in Section 2.2.1, in order to establish which of these times will allow the best extraction of lanthanum. Through this procedure it was possible to know the kinetics of leaching.

## 3. RESULTS AND DISCUSSION

### 3.1. RESULTS OF THE PHYSICAL CHARACTERIZATION OF THE DEPLETED CATALYST OF FCC.

The use of catalysts in the Fluidized Catalytic Cracking Unit (FCC) is necessary to reduce operating temperatures and pressures, give stability to cracking gases and mitigate the production of unwanted elements in order to obtain quality hydrocarbons. The usefulness of catalysts is limited, at the end of their useful life and working capacity is removed, and it becomes a waste product with toxic elements.

#### 3.1.1. Analysis of particle size, actual and bulk density of FCC spent catalyst.

Table 3.1 presents the results of the physical properties of the samples of the depleted catalyst obtained at the Esmeraldas State Refinery, obtained according to the experimental procedure described in Section 2.2.1. The work of the catalyst in the reactor depends to a large extent on the bulk density (the porosity of the solid), which when kept at an adequate limit favors the fluidization process. The actual and bulk density values found in this study were 1.02 and 0.99 g/cm<sup>3</sup>, as proposed in Table 3.1.

**Table 3.1.** Results of the actual density, granulometry and bulk density of the depleted catalyst.

Physical property	Value
Actual density	1.02 g/cm <sup>3</sup>
Granulometry d <sub>80</sub>	105 μm
Bulk density	0.99 g/cm <sup>3</sup>

Source: Authors.

The literature reports that the distribution of the appropriate particle size for catalytic cracking catalysts is between 40 to 105 μm, however, it is assumed that the reality is different, being found in sizes between 40 to 150 μm in fresh catalysts (Barrera, 2015, p. 49) (Carrera, 2013). Catalysts have an average particle size of 75 μm and consist of an active component, a matrix and additives (Flores, 2007, p. 14).

The results of the particle size study performed are shown in Table 3.2. It is observed that the particle size is less than 106 μm, the acquired value is within the established range.

**Table 3.2.** Results of the particle size performed on the depleted catalyst

Mesh	μm	Retained Weight (g)	(%) retained	(%) retained accumulated	(%) accumulated passed
20	850	0,55	0,19	0,19	99,80
30	600	0,32	0,11	0,31	99,69
40	425	0,30	0,11	0,41	99,58
50	300	0,58	0,21	0,62	99,38
60	250	0,35	0,12	0,74	99,25
70	212	0,10	0,03	0,78	99,22
80	180	0,40	0,14	0,92	99,07
100	150	4,80	1,70	2,62	97,37
150	106	47,60	16,90	19,52	80,47



200	75	139,00	49,37	68,89	31,10
270	53	66,30	23,55	92,44	7,55
325	45	14,80	5,25	97,69	2,30
400	38	4,20	1,49	99,18	0,81
Bottom	-----	2,20	0,78	100,00	-
	<b>TOTAL</b>	281,50	100,00	<b>d<sub>80</sub>=</b>	105 um

Source: Authors.

Figure 3.1 is from the particle size curve of the depleted catalyst. In this study, 80% of the depleted catalyst shows a particle size of 105  $\mu\text{m}$ , being at the appropriate level

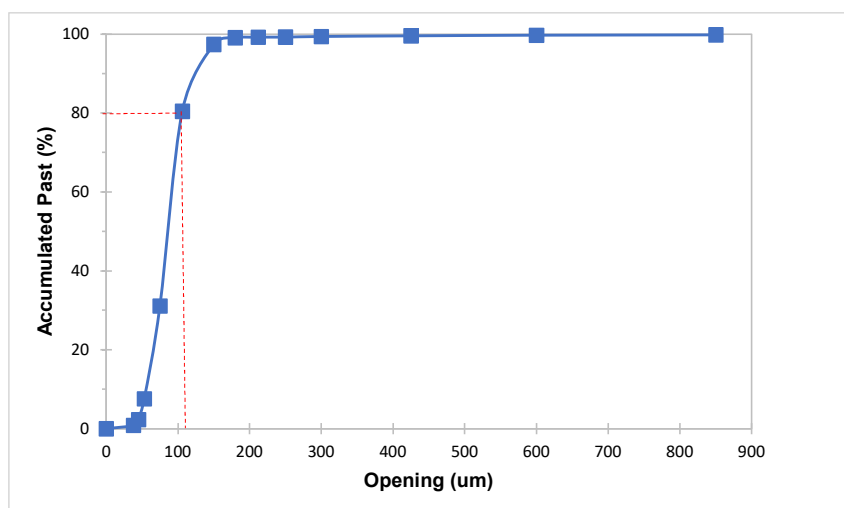


Figure 3.1. Cumulative past percentage of depleted catalyst vs sieve mesh size ( $\mu\text{m}$ )

Source: Authors.

### 3.1.2. RESULTS OF THE CHEMICAL CHARACTERIZATION OF THE DEPLETED CATALYST OF FCC.

#### 3.1.2.1. Analysis of the chemical composition of the depleted catalyst using scanning electron microscopy with x-ray analyzer.

The results of the chemical composition of the depleted catalyst were analyzed in a Bruker scanning electron microscope (MEB-EDX Tescan) with X-ray analyzer (Quantax), finding the presence of 30.4% aluminum, 29.7% silicon, 2.3% lanthanum and 22.0% vanadium, and values lower than 1.6% in the other elements of the depleted catalyst, while in the virgin catalyst the presence of iron, lead and mercury is not observed, and vanadium and nickel are also found in a percentage less than 0.1%, as shown in Table 3.3.

**Table 3.3.** Results of the elemental composition of the depleted catalyst

Element	Exhausted catalyst	Virgin Catalyst
Aluminium (%)	30,4	32,0
Silicon (%)	29,7	30,0
Lanthanum (%)	2,3	2,5
Vanadium (%)	2,2	<0.1
Molybdenum (%)	1,6	1,5
Titanium (%)	1,4	1,4
Nickel (%)	1,2	<0.1
Iron (%)	1,1	-----
Lead (mg/kg)	20,0	-----
Mercury (mg/kg)	15,0	-----

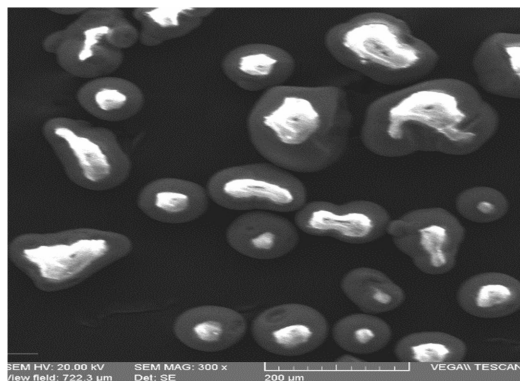
(Barrera, 2015, p. 50)

The majority presence of metals such as aluminum and silicon, 30.4% and 29.7% has, as a purpose, to give greater thermal stability and better responsiveness to acid agents (Márquez, Herrera and Gutiérrez, 1999, p. 5).

The important percentage of lanthanum present in the catalyst is due to the fact that it constitutes a stabilizing bridge of the aluminium atoms in the structure of the zeolite when the catalyst is subjected to high temperatures. On the other hand, it promotes the action of the catalyst, facilitating the selectivity of gasoline but reducing octane (Flores, 2007, pp. 14-15).

According to Barrera (2015) the depleted catalyst differs from the virgin catalyst by the size and volume of pores being 7.9 Å and 0.08 cm<sup>3</sup> and 8.0 Å and 0.10 cm<sup>3</sup> respectively, which helps in cracking reactions because the atoms belonging to the hydrocarbons through the pores reach the acid spaces.

Figure 3.2 presents an image of the FCC catalyst mineral, where the lanthanum structures present in the mineral associated with faujassite can be identified in the different particles. There are particles of different sizes between 25 to 200 µm. This analysis was performed in the scanning electron microscopy equipment (Tescan-Vega).



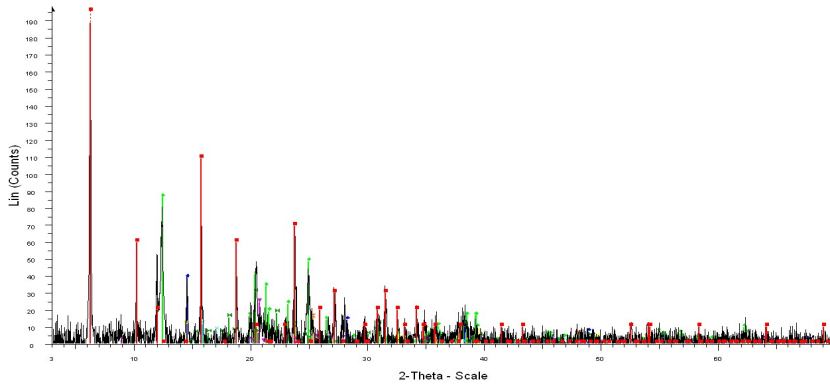
**Figure 3.2.** FCC Spent Catalyst Ore Particle Photography (200 and 500  $\mu\text{m}$ )

### **3.1.3. RESULTS OF THE MINERALOGICAL CHARACTERIZATION OF THE DEPLETED CATALYST OF FCC.**

Faussite is the main mineralogical component found in the samples of depleted catalyst of the State Refinery of Esmeraldas presenting in an approximate percentage of 80% (Barrera, 2015, p. 161). The presence of faujassite, kaolinite, bohemite and muscovite was found, these four compounds form the zeolitic crystal lattice of the catalyst, this is understood because the zeolite of structural type FAU has high thermal stability, pores of large diameter with rigid structure and presence of a high sodium content, characteristics that give it preference for use in the cracking of hydrocarbons, it is also used in more than 95% of the catalyst market (Díaz et al, 2012, p. 454).

Guisnet and Ramoa (2006) state that lanthanum enters the zeolite in hydrated form and after the dissociation of water molecules, the formation of acid sites occurs. Therefore, the greatest presence of lanthanum will be in the faujassite since it is hydrated pentadeca, and when the faujassite is 80%, it will favor the activation of the catalyst.

Figure 3.3 shows the acquired diffractogram, which shows that the peaks with the largest size in altitude correspond to the mineral faujassite.



**Figure 3.3.** Diffractogram of the exhausted catalyst of the Esmeraldas Refinery, with greater presence of faujassite.

Table 3.4 shows the minerals found in the depleted catalyst.

**Table 3.4.** Mineralogical composition present in the depleted catalyst

Component	Formula
Faujasita	$(\text{Na,Ca,Mg})_5(\text{Si,Al})_{12}\text{O}_{24} \cdot 15\text{H}_2\text{O}$
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Bohemita	$\text{AlO}(\text{OH})$
Muscovite	$\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH,F})_2$
Millerita	$\text{NiS}$
Molybdenite	$\text{MoS}_2$
Anatase	$\text{TiO}_2$

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### 3.2. EVALUATION OF THE ACID LEACHING PROCESS FOR THE RECOVERY OF LANTHANUM deL deL dethe depleted catalyst of fcc.

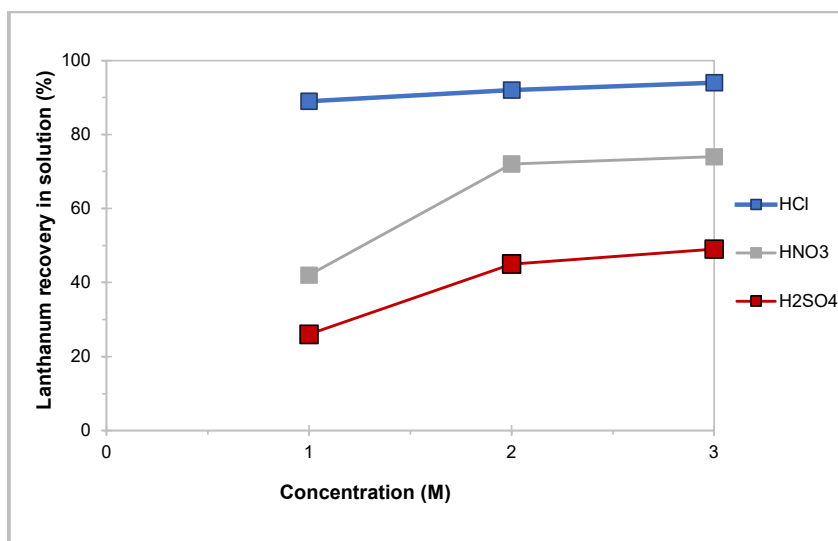
#### 3.2.1. LEACHING TESTS

The recovery of lanthanum was carried out through a leaching process using hydrochloric acid, nitric acid and sulfuric acid for which the incidence of the leaching agent, the concentration, the percentage of solids and the leaching time were analyzed.

##### 3.2.1.1. Influence of the leaching agent

For this analysis, hydrochloric acid (HCl), nitric acid (HNO<sub>3</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) were used as leaching agents, leaching tests were carried out at concentrations of 1 M, 2 M, and 3 M, at a time of 24 h, we worked with a solids content of 10 %, The objective was to evaluate the recovery of lanthanum and determine which acid gives better recoveries, to choose the most suitable leaching agent, the methodology outlined in Section 2.2.1 was used.

Figure 3.3 shows the recoveries of lanthanum to the above conditions and shows that the dissolution values show high percentages of lanthanum recovery in all three cases, reaching 89%, 42% and 26% in tests with HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> at a concentration of 1 M respectively.



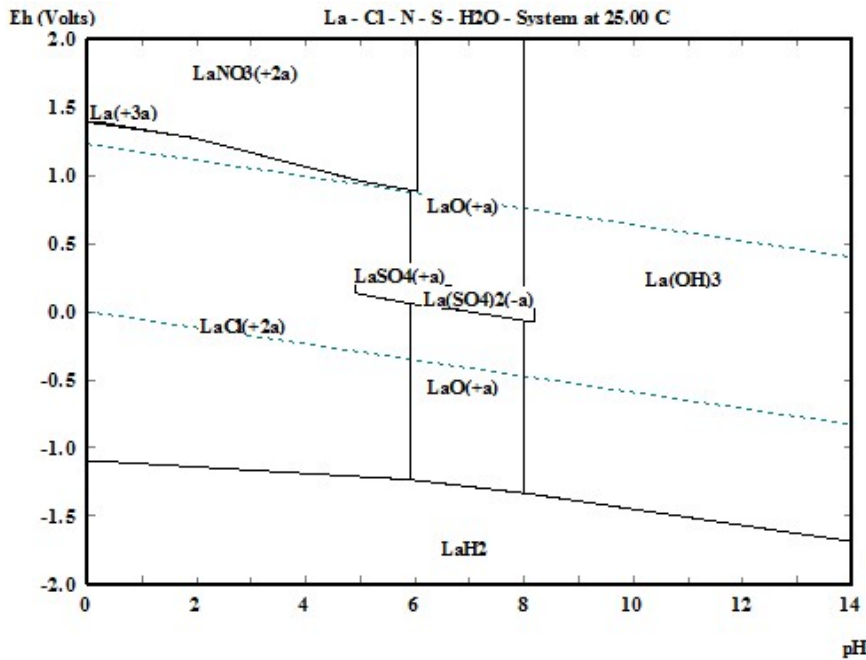
**Figure 3.3.** Recovery of lanthanum in leaching tests using hydrochloric, nitric and sulfuric acid at 1 M, 2 M, 3 M, 10% solids and 24 h.

**Source:** Authors.

For a concentration of 2 M of leaching agent it can be observed that the trend of greater recovery with hydrochloric acid and lower recovery with sulfuric acid continues to be maintained, in all leaching tests there is an increase in recovery, having 92% in tests with HCl, 72% with HNO<sub>3</sub>, and 45% with H<sub>2</sub>SO<sub>4</sub>.

By increasing the concentration of the leaching agent to 3 M an increase in the recovery values of lanthanum with HCl approximate to 94 % is acquired, it is observed that the recovery increased in each of the leaching agents, but hydrochloric acid continues to be the one that provides better

results in relation to those obtained with nitric acid with which a recovery of 74% is reached and with sulfuric acid is obtained with a recovery of 49%.



**Figure 3.4.** Pourbaix diagram for the interaction of lanthanum with hydrochloric and sulfuric nitric acid at 25 °C (HSC Chemistry 6.0 Simulation)

According to the results obtained it is observed that the best leaching agent is hydrochloric acid, if the Pourbaix diagram mentioned in Figure 3.4 is analyzed, it is shown that HCl is in a stable zone and at low pH so it facilitates the formation of lanthanum chloride, while HNO<sub>3</sub> is outside the stability zone, so nitric acid is unstable and much more difficult to form. On the other hand, for the formation of lanthanum sulfate it is observed that it is in a neutral and non-acidic range, this is the reason why it is very difficult to obtain, and if it were desired to produce better percentages of recovery of lanthanum with sulfuric acid it is necessary to raise the pH value until reaching those indicated in the zone of stability of sulfuric acid.

The solubility of lanthanum chloride is 3.895 g/L in water (Saeger, 1990, p. 36), while that of lanthanum sulfate is 2.130 g/L in water at conditions of 25 °C respectively, confirming what is observed in the Pourbaix diagram.

The best leaching conditions for the recovery of rare earths obtained from spent nickel-metal hydride batteries occur with sulfuric acid, obtaining a recovery of 98% (Innocenzi and Veglio, 2012, p. 185).

On the other hand, Jorjani et al (2012) report an average of 88% recovery of rare earths, including lanthanum, in the leaching process with nitric acid, concentrated apatite.

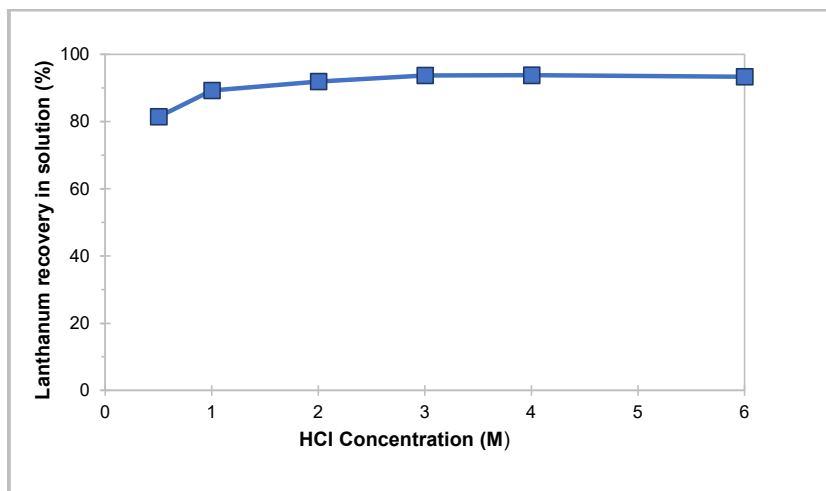
Kim et al. (2016) report a 90% recovery of rare apatite earths. Ensuring that the best leaching agent is hydrochloric acid. Based on the aforementioned reports and according to the results achieved in this research, the percentages of rare earth recovery obtained in the leaching process depend on the type of material to be used, so it is ensured that the best leaching agent for the recovery of lanthanum from FCC depleted catalyst is hydrochloric acid. This is corroborated according to the Pourbaix diagram mentioned in Figure 3.4 where it is observed that of the three acids mentioned (HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>), lanthanum chloride is the easiest to form, due to its low pH and is also in the zone of solubility and stability of lanthanum as mentioned above.

#### 3.2.1.2. Acid leaching at different concentrations

Once hydrochloric acid was shown to be the best leaching agent for the recovery of lanthanum from FCC depleted catalyst, it was necessary to determine the appropriate concentration level to maximize the results, for this purpose, tests were performed for concentrations of 0.5 M; 1.0 M; 2.0 M; 3.0 M, 4.0 M and 6.0 M establishing that concentrations of 3.0 M and 4.0 M allow maximum recoveries to be achieved with 93.7% and 93.8%, respectively.

Figure 3.5 shows the values of lanthanum recoveries at different concentrations of hydrochloric acid where an increase can be observed from 89 % when working with a concentration of hydrochloric acid of 0.5 M and up to a maximum of 93.8 % when working with a concentration of 4.0 M, On the other hand, the increase in the recovery of lanthanum with increasing concentration is due to the large amount of chloride ions consumed in the leaching process by metals and elements found in the depleted catalyst powder that tend to form new soluble compounds. Clarifying that for subsequent tests we worked with concentrations of 3.0 M because the percentage of recovery was similar to that of 4.0 M and because of the high cost of hydrochloric acid.

According to the results achieved, in the trials with several concentrations the percentage differences are not significant, in this sense Kim et al. (2016), report a recovery of 92% of rare earths at a concentration of 2.0 M of hydrochloric acid, while the recovery result obtained for this test with the same concentration is 91.9 % as shown in Figure 3.4. With these results, the good acceptance of lanthanum when treated with hydrochloric acid solutions is verified.



**Figure 3.5** Recovery of lanthanum in leaching tests using hydrochloric acid at different concentrations, 10% solids and 24 h.

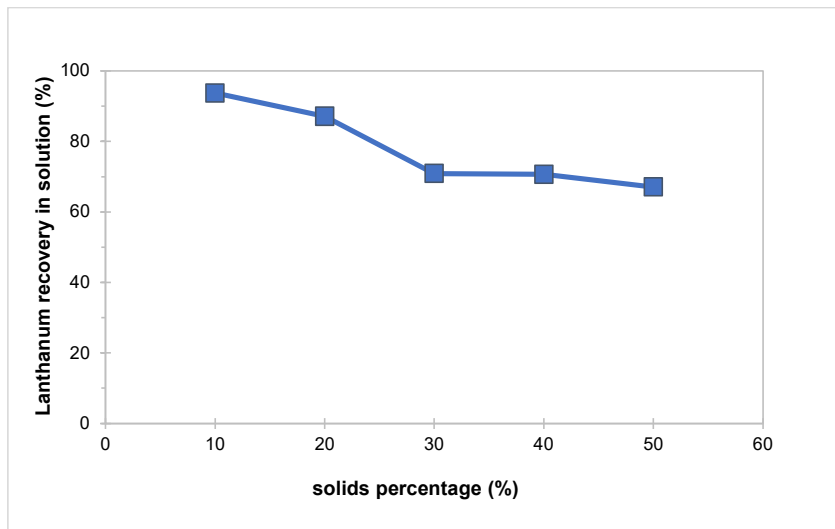
**Source:** Authors.

### 3.2.1.3. Analysis of the influence of the percentage of solids on the leaching of depleted catalyst.

The study of the influence of the percentage of solids in leaching was worked with a concentration of 3.0 M hydrochloric acid and a leaching time of 24 hours, following the process presented in Section 2.2.1. Figure 3.5 shows the recoveries of lanthanum with different percentages of solids for the studies of the leaching process, observing that the recovery of lanthanum begins to decrease with increasing percentage of solids. For solids contents of 10, 20, 30, 40 and 50%, recoveries of 93.7% are obtained; 87.1; 70.8; 70.6% and 67.1% respectively.

In Figure 3.6 the recovery of lanthanum decreases because by increasing the amount of depleted catalyst there is less hydrochloric acid usable for leaching and the solution is saturated with the lanthanum chlorides formed, that is, there is very little acid for all possible lanthanum chlorides to form and therefore there is less soluble products and recovery decreases.



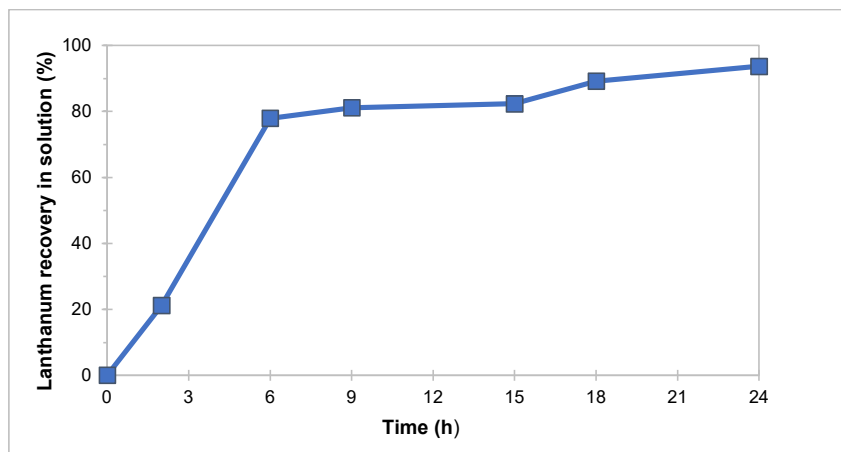


**Figure 3.6.** Influence of percentages of solids in the recovery of lanthanum with HCl, at a concentration of 3.0 M and time of 24h.

**Source:** Authors.

#### 3.2.1.4. Establishment of the best leaching time using hydrochloric acid.

To obtain the results of the leaching time, the samples were subjected to leaching with hydrochloric acid at different times of 2, 6, 9, 15, 18 and 24 hours. Considering the recovery data in each period of time, at two hours the recovery was barely 22.0%, however, from zero to six hours, the highest percentage of recovery occurs 77.9%, from that moment, the recovery is slower rising progressively until reaching 93.7% at 24 hours as maximum recovery, as shown in Figure 3.6. The rare earth extraction data reported by Kim et al. (2016), using hydrochloric acid at 20 ° C in 4 to 24 hours reach 70% and 90% respectively recovery, with this it is verified that tests at longer leaching times admit greater recoveries, because hydrochloric acid interacts for longer with the material to be dissolved, in this case the depleted catalyst powder.



**Figure 3.6.** Recovery of lanthanum in leaching tests with HCl at 3.0 M, 10% solids and different leaching times.

**Source:** Authors.

#### 4. CONCLUSIONS

- The dissolution of lanthanum in the leaching process when treated with sulfuric acid and nitric acid as leaching agents at concentrations of 1 M, 2 M and 3 M does not allow efficient recovery. On the other hand, when carrying out the leaching process with hydrochloric acid, acceptable recovery values exceeding 90% were achieved. The latter was due to the Eh/pH conditions, stability and solubility from the formation of lanthanum chloride.
- The leaching of lanthanum in the process is limited by the relationship between the percentage of solids and the concentration of the leaching agent, when the percentage of solids increases, the recovery of lanthanum decreases, because there is a minimum amount of hydrochloric acid available to leach a greater amount of depleted catalyst.
- The dissolution of lanthanum in the process is noticeably affected by the leaching time. Lanthanum recoveries reach a value of 93.7% in leaching tests carried out at a time of 24 hours.
- The elemental chemical composition of the depleted alizer cat is: lanthanum 2.3%. Lanthanum is what makes it possible for the catalyst to be activated, the value of lanthanum present in the spent catalyst is representative and is interesting for its recovery.

- The highest recovery value for lanthanum was 93.8%. This result was achieved by leaching with hydrochloric acid, at a concentration of 146 g / L, 10 % solids and a time of 24 hours.

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