Recycling spent fluid cracking catalysts for rare earth metal recovery - a review

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A B S T R A C T

Fluid cracking catalysts (FCC) are widely used in the petroleum industry and generate significant amounts of waste with rare earth (RE), such as Lanthanum (La) and Cerium (Ce). Therefore, proper recycling of these materials is of paramount importance. This review paper highlights the most recent developments in this field regarding the different leaching and separation processes, such as solvent extraction and precipitation. Leaching of these wastes was found to be more effective using hydrochloric acid (HCl) and higher temperatures. On the other hand, the effectiveness of both solvent extraction and precipitation, as separation methods, are dependent on the end result required and strategy used. Regardless, saponified solvent extraction provides extraction with higher efficiency but also less selective. In terms of precipitation, if a mischmetal of La and Ce is the goal, either the double sulphate or the oxalic acid addition method are equally effective on a HCl pregnant solution. Based on these conclusions, a process flowsheet is herein proposed, adaptable to variations in economic feasibility. In addition, several research gaps are identified throughout this review in order to further advance and explore recycling possibilities for FCC recycling.

1. Introduction

Fluid cracking catalysts (FCCs) are components used for hydrocarbon processing in the petroleum industry. FCCs aid in the cracking of large molecules from feedstocks, such as heavy or vacuum gas oil. Although their constitution can vary, they are mainly made of crystalline microporous aluminosilicates also known as zeolites, which are synthetized in such a way as to increase its potential as a catalyst.

The zeolite is responsible for cracking due to its acid sites that can convert molecules to the shorter and desired gasoline range. However, other components are required to pre-crack larger molecules as well as to act as binding agent (Vogt and Weckhuysen, 2015).

Zeolite Y is one of the main types of zeolites used in the industry and is stabilized with rare earths metals (REEs), such as lanthanum (La) and cerium (Ce). These metals not only enhance the catalyst activity but also prevent loss of acid sites due to metal poisoning, mostly vanadium (V) and nickel (Ni).

After reaction at high temperatures, the FCCs are separated from the products and regenerated by burning off the carbon, also known as coke, that has been deposited; therefore, FCCs are continuously regenerated. However, this process cannot be repeated endlessly; due to the harsh temperature and pressure conditions in the reactor, a complete catalyst deactivation eventually occurs. Thus, fresh catalyst needs to be added to sustain the conversion reactions (Ferella et al., 2016).

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The spent FCCs can be rejuvenated mostly by removing impurities, such as V and iron (Fe), which concentrate in the outer surface and reduce the active surface available for reaction. However, despite several developed methods, rejuvenation is not always an option and has limited commercial application, namely due to associated costs (Marafi and Stanislaus, 2008). Once rejuvenation is no longer a possibility, spent FCCs can be reused in other applications without the need of any further processing.

One such reuse option is its application in cement production. It is estimated that FCCs can replace up to 15–20 % of cement content or 10 % of sand without adverse effect (Al-Jabri et al., 2013) although some disadvantages of this reuse are also reported (Soriano et al., 2016).

As a last resort, spent FCCs are still being sent for disposal in landfills. However, the price of such option has been increasing steadily. As a hazardous waste, spent FCCs require several pre-treatments to ensure its safe disposal and to reduce heavy metal leaching (Marafi and Stanislaus, 2008).

Before opting for landfill disposal, metal recovery of spent FCCs should be considered due to the sheer volume of REEs used in the catalyst; in 2008, 1,980 tons of cerium(IV) oxide (CeO_2) and 17,800 tons of lanthanum oxide (La_2O_3) were used for FCC production and it is expected that these values have increased since then (Akah, 2017).

Recycling these spent FCCs with the intention of recovering REEs (La and Ce) have been the subject of recent research efforts. As a result, this review aims to assess the existing literature with a focus on hydrometallurgical processes, to isolate the most efficient yet simple and cost efficient process flowsheet for an environmentally friendly recovery of REEs from spent FCC.

2. FCC recycling process

The process of FCC recycling can be roughly divided in two major steps. The initial step is the leaching process, in which strong acid solutions are used to transfer the metals into a liquid phase. A second step (or series of steps) involves the separation of the REEs from contaminants and, eventually, between them, if desirable, in order to enable their complete recovery. Aspects such as leaching efficiency and the influence of temperature, type of acid, etc. will be explored in an initial section below. Subsequently, two other sections will focus on the most widely used separation methods, namely solvent extraction and selective precipitation.

2.1. FCC leaching

The first stage of REEs recovery from spent FCC or other derivatives is the acid leaching. There is a variety of numerous inorganic acids studied, which may exhibit different leaching efficiencies.

To better assess the performance of different acids as well as other varying conditions, this study compares the performance of several different works dedicated to this matter. Although not a complete meta-analysis, some screening parameters were used to ensure the quality and relevance of potential comparisons. The studies included in Table 1 all have the following characteristics:

- Studies of leaching of spent FCC or FC slag,
- Studies that have individual leaching efficiency values for La and Ce,
- Studies with original data and present in the Scopus database.

Furthermore, to enable a more comprehensive comparison of the data, the molar quantity of the leachant per gram of waste is also reported. Table 1 summarizes the results compiled from studies on FCC acid leaching, reported by increasing order of molar acid used per g of waste.

By analysing Table 1, it can be seen that the lowest values of Ce leaching efficiencies (25 and 53.5 %, respectively) were obtained when nitric acid (HNO_3) and sulphuric acid (H_2SO_4) were used as leachants. However, the same pattern cannot be found for La leaching efficiency. Furthermore, Zhao et al., (2017) also details that preliminary tests indicate that H_2SO_4 and HNO_3 up to 4 M in similar conditions as described in Table 1 are only able to recover around 70 % of existing rare earth elements while HCl is able to obtain 84.3 %. One possible explanation for this difference presented by Zhao et al., (2017) was that chloride (Cl^-) ions have a higher coordination effect than nitrate (NO_3^-) or sulphate (SO_4^{2-}). Another aspect is that HNO_3 and H_2SO_4 are also reported to lead to Ce precipitation, which would require a secondary leaching in order to increase the recovery of this rare metal (Zhao et al., 2017).

Regardless of the mechanism in question, the data in Table 1 suggests that HCl is the most effective mineral acid that can be used for REEs extraction from FCC. This is further confirmed in Innocenzi et al., (2015) where a second leaching with H_2SO_4 did not significantly increase the leaching of REEs.

Little to no conclusions can be made regarding the time and temperature required for leaching. Based on the results of Zhao et al., (2017), 0.5 hours is clearly insufficient for leaching and higher temperatures (60 ℃) are preferable.

The experimental setup and conditions can be difficult to compare. For instance, Wang et al., (2017b) used a preliminary caustic selective leaching of aluminium before the acid leaching, which seemingly increases the efficiency of the latter.

Other aspects can also be seen in Table 1, like the influence of varying the solid-to-liquid (S/L) ratio.

Table 1
Acid leaching of FCC or FC related wastes for La and Ce recovery

Source	Type	S/L ratio (g/mL)	Leachant	mmol H⁺/ g waste	Time (h)	T (°C)	Initial Concentration (%)	La (%)	Initial Concentration (%)	Ce (%)
(Nguyen et al., 2018)	FCC	0.33	HNO$_3$ 2 M	6	1	80	1.82	88.00	0.06	25.00
(Zhao et al., 2017)	FCC	0.20	HCl 2 M	10	2	60	1.92	84.00	0.29	83.00
(Zhao et al., 2017)	FCC	0.09	HCl 1 M	11	9	25	1.69	76.60	1.57	95.50
(Zhao et al., 2017)	FCC	0.10	HCl 2 M	20	2	45	1.92	83.50	0.29	86.40
(Zhao et al., 2017)	FCC	0.10	HCl 2 M	20	2	30	1.92	76.00	0.29	81.00
(Zhao et al., 2017)	FCC	0.10	HCl 2 M	20	0.5	45	1.92	68.10	0.29	72.80
(Zhao et al., 2017)	FCC	0.10	HCl 2 M	20	2	60	1.92	92.00	0.29	96.00
(Zhao et al., 2017)	FCC	0.09	HCl 2 M	22	9	25	1.69	75.80	1.57	94.50
(Zhao et al., 2017)	FCC	0.05	HCl 1 M	22	9	25	1.69	71.38	1.57	90.30
(Innocenzi et al., 2015)	FCC	0.15	H$_2$SO$_4$ 2 M	26.70	3	25	3.02	61.20	0.23	53.50
(Innocenzi et al., 2015)	FCC	0.15	H$_2$SO$_4$ 2 M	26.70	3	80	3.02	89.00	0.23	81.70
(Wang et al., 2017a)	FC slag	0.25	HCl 9 M	36	2	20	1.20	91.00	2.40	92.20
(Wang et al., 2017a)	FCC	0.25	HCl 9 M	36	2	20	0.38	86.18	1.60	82.30
(Wang et al., 2017a)	Rey Zeolite	0.25	HCl 9 M	36	2	20	1.10	97.94	4.00	99.90
(Wang et al., 2017b)	FC slag	-	HCl 3 M	-	3	20	3.80	98.60	0.25	98.80

In Zhao et al., (2017), for the same H^+ content (the same number of H^+ moles), it was found that the efficiency of the leaching of REEs increased with the S/L ratio; i.e., the lower volume of acid, which corresponded to a more concentrated acid but for the same quantity of H^+ originated a higher efficiency. Further studies are therefore needed to confirm that acid concentration, not just its molar quantity, affects the leaching process and how.

Yet another aspect is the prospect of leaching both spent FCC as well as the slag from its production and other wastes of similar characteristics. This aspect was explored in depth by Wang et al., (2017a). These authors found similar recovery values of La and Ce from spent FCC, FCC slag and Rey Zeolite despite their different initial compositions. However, the extremely high HCl concentration used can be unpractical. This might be mitigated by increasing the S/L ratio and/or the temperature.

Most studies do not report the extraction efficiency of other metals (e.g. Al) also present in the spent FCCs. This means that there is almost no information on the selectivity of different leaching tests, which limits the analysis of options for subsequent purification of the REEs from the leachate.

2.2. Separation techniques

Following the leaching step, the recycling process for FCC moves into a separation and recovery step: a series of different processes to separate the REEs from contaminants, such as Al, as well as between the REEs, if needed. The following sections will explore the two most widely used processes up to now; aspects related with their performance will also be discussed.

Firstly, the use of solvent extraction will be explored taking into consideration the specific characteristics of the REEs and how these affect the performance. Subsequently, another section will explore the potential of consecutive selective precipitation as a low cost alternative, detailing the most recent research in this field.

2.2.1. Solvent extraction

The separation of REEs from each other and other elements by liquid-liquid extraction techniques have been applied for decades. However, the processes are more complex than for other metals (as it will be explained below) and even more so considering the impurities that are associated in the pregnant solutions of FCC leaching.

This section aims to succinctly explore existing possibilities to overcome difficulties in liquid-liquid extraction techniques and how these might be incorporated into a flowsheet of La and Ce recovery from spent FCC recycling process.

Simple solvent extraction with commercially available extractants has very limited extraction capabilities when applied to REEs. This is because of the characteristics of the metals and its reactions with most extractants as demonstrated below: using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) as an example, REEs react with simple extractant (represented as H_2L_2) according to the following equation (Hou et al., 2016):

$$REE^{3+}(aq) + 3H_2L_2\ (o) \leftrightarrow RE(HL)_3L_3(o) + 3H^+(aq) \tag{1}$$
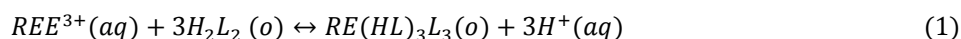
Considering that most extractants are acidic, the release of H^+ promotes the reverse reaction; therefore, the formation of the REE complex with the extractant is limited. One way to overcome this problem is to partly saponify the extractant.

For the same example of EHEHPA, Hou et al., (2016) was able to determine the molar ratio and the complex formed when the extractant was saponified with ammonia hydroxide (NH_4OH), enabling the description of the following equation 2:

$$2REE^{3+}(aq) + 3H_2L_2\ (o) + 6NH_4L\ (o) \leftrightarrow 2RE(HL)_3L_3(o) + 6NH_4^+(aq) \tag{2}$$

In which NH_4L represents the saponified portion of the extractant.

This reaction leads to the release of NH_4^+ instead of H^+, therefore not limiting the reaction as previously mentioned. Other saponification reagents include magnesium oxide (MgO) and calcium hydroxide [$Ca(OH)_2$] (Liu et al., 2017).

Saponified solvent extraction is one of the most widely used purification method for REEs, including La and Ce from both primary and secondary sources (Wu et al., 2010). However, this approach raises some problems. On the one hand, it leads to the production of wastewaters with high quantities of NH_4^+, which requires treatment prior to discharge into the environment (Chang et al., 2010). On the other hand, this approach is limited by the saponification rates, i.e., the extent of saponification: a low saponification rate might mean that the reaction will remain limited while a high saponification may lead to emulsification of the extractant and, therefore, the formation of a third phase, which is also negative and affects the extraction efficiency (Zhao et al., 2017).

Furthermore, several impurities also affect emulsion formation, leading to lower extraction capacities. Several of these impurities are present in spent FCC wastes, such as SiO_2 as well as Fe and most notably Al, which directly and indirectly (for instance, due to the precipitation as

$(Fe(OH)_3SiO_2 \cdot NH_2O)$ increase and stabilize emulsification (Wu et al., 2010). Due to the limitations of the saponified solvent extraction method, several other avenues have also been explored in liquid-liquid extraction of REEs. One such possibility is the complex induced extraction. This method aims to replace saponification as a solution to the abovementioned issue of H^+ production by adding a complexing agent.

One such complexing agent is lactic acid, which forms several complexes with the REEs and enables the following extraction reaction - equation 3 (Yin et al., 2013):

$$RE(Lac)_x^{(3-x)+}(o) + 3\,H_2L_2\,(o) \leftrightarrow REA_3 3HA\,(o) + (3-x)H^+(aq) + xLAC\,(aq) \qquad (3)$$
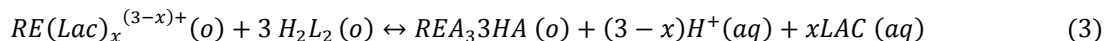
In which 'x' represents the number of the moles of the ligand in the REE complex and 'Lac' represents the lactate ion. The higher the 'x' the lower the H^+ produced.

Several other compounds have been tested, such as citric acid, acetic acid, ethylenediamine tetraacetic acid (EDTA), etc. to name a few (Kashi et al., 2018).

It is reported that the addition of these complexing agents enhance the selectivity among different REEs as well as improves the overall extraction efficiency. For instance, Zhang et al., (2016) found that the presence of 0.6 mol/L of lactic acid combined with the extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester P507 increased the distribution ratio up to 8 times for Ce (at pH 2) and up to 25 times for La (at pH 3.5).

Another strategy that might even allow the use of unsaponified extractant is the synergetic extraction. As the name suggests, it involves the synergetic combination of two or more different extractants in such a way that the extraction efficiency is improved, being higher than the sum of the individual extractants (Song et al., 2009).

For instance, a combination of the extractant 8-hydroxyquinoline (HQ) with bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) has a La distribution ratio up to 3.3 times higher than the ones observed for HQ and Cyanex 301 when tested independently (Tian et al., 2013).

Zhang et al., (2014) combined both principles using a complex induced synergetic solvent extraction – a mixture of 2-ethylhexylphosphonic mono-2-ethylhexyl ester (HEHEHP) and di-2-ethylhexyl phosphoric acid (D2EHPA), as extractants, and lactic and citric acids, as complexing agents.

In this study, it was found that lactic acid was able to increase the extraction capacity of Ce and La by two-fold for both extractants separately.

However, this value decreased when the two extractants tested were mixed. However, mixing the two extractants with the lactic acid increases the separation factor.

Only a few recent studies have analysed the potential and limitations of liquid-liquid extractions when applied to FCC recycling and metal recovery (Table 2).

Table 2
Solvent extraction applied to FCC pregnant solutions containing La and Ce (pHe – equilibrium pH; SE – stripping efficiency)

Source	(Innocenzi et al., 2015)	(Zhao et al., 2017)	(Nguyen et al., 2018)	(Ye et al., 2017)
Extractant	D2EHPA* 20 % (v/v)	D2EHPA* 16 % (v/v)	D2EHPA* + TBP** (4:1 ratio)	EHEHPA*** (20 % saponified w/ammonia)
Solvent	*n*-hexane	kerosene	*n*-octane	kerosene
pHe	2.25	2.5	< 1	3.17
Time (min)	-	10	10	-
A/O ratio	-	1	-	2
La extraction (%)	95	85	72	100
Ce extraction (%)	98		89	100
Al extraction (%)	-	50	0	100
Stripping agent	HNO₃ 4 M	HCl 2 M	-	HCl 1 M
SE (%) - La	82	62.88	-	96
SE (%) - Ce	79		-	

* D2HPA - di-2-ethylhexyl phosphoric acid

** TBP - tributyl phosphate

*** EHEPA - 2-ethylhexyl phosphoric acid-2-ethylhexyl ester

To the best of the authors' knowledge, these 4 studies are the only ones that incorporate liquid-liquid extraction into a spent FCC recycling flowsheet. This obviously represents a data gap in this field that needs to be addressed. Based on Table 2, D2EHPA is the most tested extractant with *n*-hexane being the solvent that seems to enable a better extraction performance when compared to kerosene and *n*-octane. However, with *n*-octane and added TBP, a high extraction is possible even at low pH; this extraction was extremely selective to the REEs with no Al being co-extracted. Saponification, as demonstrated in Ye et al., (2017), leaded to very high extraction, but not selective to REEs; under these conditions, all Al was also co-extracted. Stripping performance varies with the different studies, likely a reflection of the different quantities being extracted in the first stage of the process. The challenge is to explore the incorporation of these techniques into a flowsheet of spent FCC recovery taking into consideration the specific characteristics of the leachates that are formed during the process, particularly its impurities.

2.2.2. Consecutive selective precipitations

Another strategy to recover the REEs present in the FCCs leachates is to selectively precipitate them. However, as is the case for solvent extraction, research on this issue remains scarce.

There are two main issues to be addressed: (i) to separate the REEs, La and Ce, from the rest of the impurities and (ii) separate La and Ce from each other.

The choice of one over the other depends on the end use and the necessary purity; a precipitated containing both La and Ce can still be used as a mischmetal for several applications, whilst specific needs require pure La or pure Ce. To accomplish the second option, Ce^{3+} can be selectively precipitated from La and Al by oxidation whilst Al and La remain in the solution. For a simplified simulation of the potential selectivity of this approach, Medusa software (Puigdomenech, 2004) was applied to draw Pourbaix diagrams for Ce, La and Al using data from Zhao et al., (2017). The concentrations considered in this simplified model were: 0.013, 0.002 and 0.48 mol/L for La, Ce and Al, respectively.

Results are represented in figure 1, which shows that Ce can be easily separated and purified from La and Al by raising the redox potential (Eh) to approximately 1.6 V in the pH range between 1.0 and 2.5; under these conditions, Pourbaix diagrams predict that Ce^{3+} is oxidized to Ce^{4+}, which precipitates as cerium (IV) oxide (CeO_2) while La and Al remain soluble as M^{3+}.

However, this strategy, should only be applied if an appreciable amount of Ce is present in the leachate and the ultimate goal is to recover Ce and La with high purity.

For the separation of La and Ce from the rest of the impurities in the pregnant solution, two main options are

described in the literature: (i) the precipitation of double sulphate salts – $NaRE(SO_4)_2 \cdot H_2O$ and oxalate precipitation in the form of $RE_2(C_2O_4)_3$. In this case, the main precipitates are either $NaLa(SO_4)_2$ or $La_2(C_2O_4)_3$ for the double salt precipitation or the oxalate precipitation strategies, respectively.
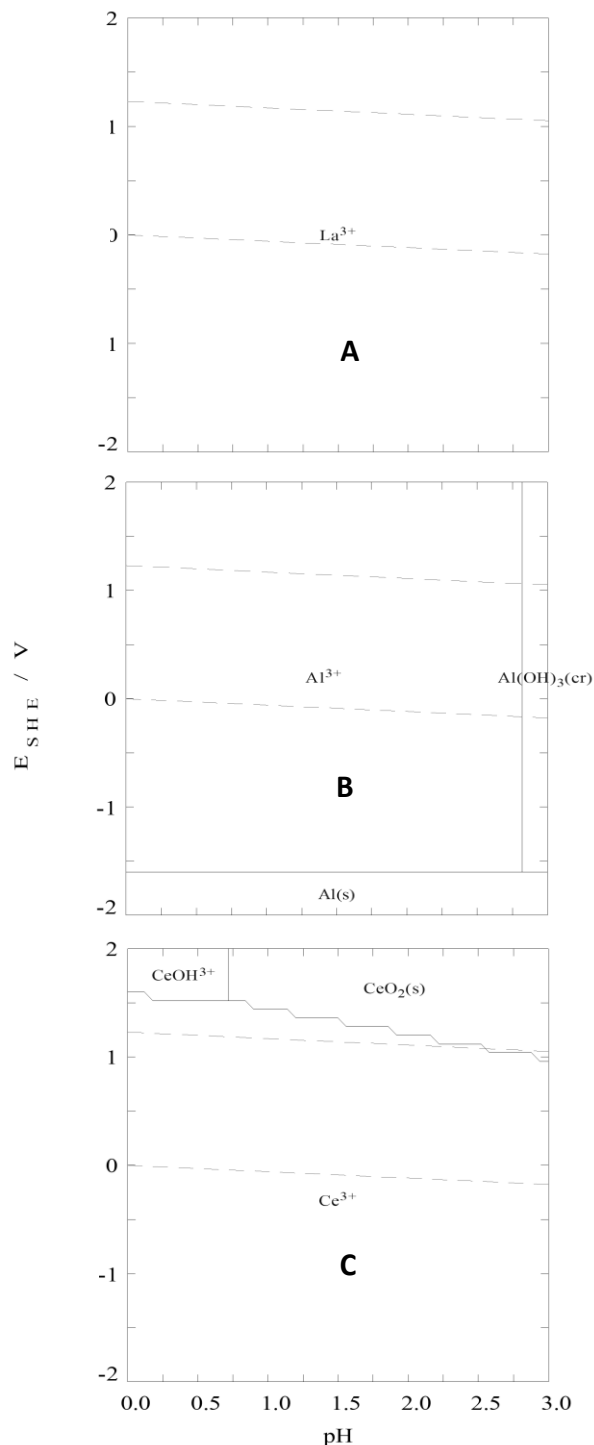

Figure 1. Pourbaix diagrams for Ce (A), La (B) and Al (C) in the pH range 0.0 and 3.0. Initial conditions Al 0.48 M, La 0.002 M, Ce 0.0013 M

Although scarcely, literature describes application of these two precipitation methods for recovering REEs from FCCs leachates. For example, Innocenzi et al., (2015) initially precipitated La and Ce as double sulphate salts by increasing the pH up to 2 after extraction with sulphuric acid. This lead to a precipitation yield of 100 %, with a RE purity between 75 and 80 %.

These authors have also tested oxalic acid precipitation, achieving a precipitate with 37-47 % La and 3.06-3.11 % Ce (w/w) content.

However, this precipitation was only performed after solvent extraction; even though an absolute comparison between the different precipitation approaches is extremely difficult, results suggest that oxalic acid precipitation is capable of yielding a precipitate with higher purity in REEs.

Wang et al., (2017b) performed oxalic acid precipitation prior to any other separation method and was able to achieve a final product with 98.7 % RE purity after calcination. This again seems to confirm that oxalic acid precipitation is capable of producing a final product with very high purity.

Finally, Wang et al., (2017a) tested a sequence of precipitation steps for recovering REEs from a hydrochloric acid leachate. Initially, REEs were precipitated, as $NaRE(SO_4)_2 \cdot H_2O$, using Na_2SO_4 at 300 % of its stoichiometric proportion with 99 % efficiency; under these conditions, only 2 % of Al co-precipitated together with REEs.

Subsequently, this precipitate was converted into $RE(OH)_3$ by reacting with NaOH and then to $RECl_3$ by dissolution in HCl; a final product with a total recovery of 90.2 % of the REEs ready for immediate and direct reuse in zeolite production was achieved. Even though high total REEs recovery with high purity was achieved, the recycling procedure is not simple containing several steps, which consume a huge amount of reagents. In conclusion, further studies seem to be required in order to better assess the potential of consecutive and selective precipitations, particularly considering its potential to substantially simplify the process and reduce operational costs without compromising the final purity of the recycled REEs.

2.3. Process analysis

Potential flowsheet(s) for complete recovery of REEs from spent FCC is shown in figure 2. Initially, an acid leaching step should be implemented in order to extract the REEs from the solid matrix into the aqueous phase as it was mentioned in section for FCC leaching. Literature describes the use of several mineral acids for this purpose but the nature of the anion may affect the yield of the REEs leaching and, consequently, the entire recovery process.

Preferably with HCl, as demonstrated in this article, leaching begins the process creating a solid waste made of zeolite from the FCC (which can, in theory, be reused to produce new FCC if reprocessed) and a leachate containing the REEs, such as La and Ce, plus Al, Si and other minor amounts of other metals, as for example Fe.

This leachate requires further processing with the goal to obtain either pure Ce or La or reusable mischmetals.

As it was discussed throughout this work, solvent extraction can be used either with a single extractant or with a synergetic combination of extractants.

Furthermore, solvent extraction can be also applied through saponified extractants or complex induced to enhance its extraction capacities. However, saponified extractants leads to the production of high-strength wastewater, particularly ammonia, which requires added and more expensive treatment.
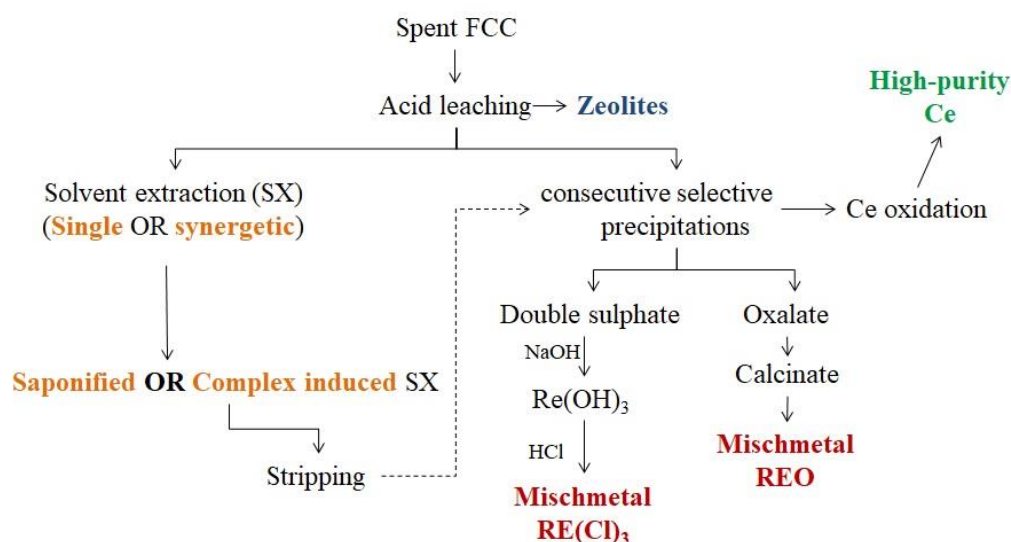

Figure 2. Schematic flowsheet for complete recovery of REE from spent FCC. Legend: Green – final, highly pure products for reuse; Red – final low purity products ready for reuse; Blue – potentially reusable wastes

Regardless of the solvent extraction type, a highly pure solution of La and Ce can be obtained from the stripping step of the solvent extraction, facilitating precipitation.

Alternatively, instead of using solvent extraction, precipitation can be performed directly either by adding Na_2SO_4 to obtain double sulphate salts of Ce and La or by adding oxalic acid or an oxalate salt to precipitate both La and Ce, as well.

Both these strategies required further purification steps. In the case of the double sulphate strategies, one possibility lays on converting the precipitate first to $RE(OH)_3$ (using NaOH) and then finally to an end product mischmetal of $RECl_3$, which is reusable to produce new FCC or other materials (Wang et al., 2017a). In the case of oxalate addition, a calcination step would yield a mischmetal of RE oxides, also directly reusable for FCC production (Geus and D'Appolonia, 2017).

Finally, a selective precipitation to separate Ce from La is also possible, but likely at a higher cost. Through oxidation of Ce^{3+} to Ce^{4+} and consequent precipitation as an oxide, a pure Ce precipitate could be obtained and reused as raw material. The La remaining in the solution could then be precipitated by the other methods referred in this study, preferably through oxalic acid addition plus calcination to obtain a pure La precipitate also ready to be reused as a raw material in the industry.

Considering the current prices of the REEs present in FCC, it seems to be of more practical use to precipitate them at low cost, as oxide mischmetal, to substitute existing mischmetal in the market. However, the proposed flowsheet can adapt to changing prices and market demands, and if prices will increase, the obtainment of pure Ce and/or La may became more advantageous.

3. Conclusion

This review aimed at presenting novel developments in the methodologies of recycling fluid cracking catalysts (FCC) as well as to formulate a tentative process flowsheet.

Regarding leaching and, based on the comparison of different leaching strategies, it can be concluded that hydrochloric acid is the most efficient acid tested across multiple studies. Using this acid, it is possible to extract high quantities of both La and Ce from FCC wastes as well as from FC slag and rey zeolites, two wastes from the FCC production itself.

Furthermore, temperature plays an important role on the extraction efficiency of the REEs during leaching. Some other aspects can be highlighted, although requiring further research, such as the fact that the concentration of acid, and not only its quantity, has a significant impact on the leaching efficiency.

The explored separation techniques for metal selection are characterized by a shortage of recent articles. Still,

through a combination of studies in similar fields and the existing studies dedicated to these techniques for FCC recycling, some conclusions can be drawn. Regarding solvent extraction, results suggest that saponified extraction can lead to higher extraction efficiencies but also to a higher wastewater production and lack of selectivity; in this aspect, a compromise between selectivity and extraction capacity will always depend on the subsequent treatments and recycling objectives.

Selective precipitation can also be applied in multiple forms, either through addition of oxalic acid or double sulphate precipitation with similar selectivity, final purity and precipitation yield (although more studies are needed to confirm these aspects further). Similar to solvent extraction, however, the methodology to be adopted depends heavily on the final objectives. Having these multiple possibilities in mind, a process flowsheet was developed and discussed in this study.

The proposed process is adaptable to variations in the price of the commodities to be extracted, in this case the REE La and Ce, with options to increase purity and selectivity, if economically viable, or to precipitate these two metals together into a mischmetal that can be used directly in the industry.

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Dobijanje retkih zemljinih metala recikliranjem istrošenih katalizatora - pregled

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I Z V O D

Katalitičko krekovanje u fluidizovanom sloju (eng. FCC) koje ima široku primenu u naftnoj industriji proizvodi značajnu količinu otpada koji sadrži retke zemljine elemente, kao što su lantan (La) i cerijum (Ce). Dakle, odgovarajuće recikliranje ovih materijala je od velike važnosti. U ovom pregledu se ističu najnoviji pomaci u ovoj oblasti hemijskih postupaka luženja i separacije, kao što su solventna ekstrakcija i taloženje. Luženje ovih otpada efikasnije je u prisustvu hlorovodonične kiseline (HCl) i na visokim temperaturama. S druge strane, efikasnost solventne ekstrakcije i taloženja kao metoda za separaciju zavisi od traženog krajnjeg rezultata i strategije koja se koristi. Uprkos tome, saponifikovanom solventnom ekstrakcijom se postiže veća efikasnost, ali i manja selektivnost. Što se tiče taloženja, ako je cilj da se dobije mišmetal koji sadrži La i Ce, podjednako je efikasan i metod sa dodavanjem sulfata i oksalne kiseline u rastvor HCl. Na osnovu ovih zaključaka, u radu je predložen dijagram postupka koji je podložan promenama u vezi sa ekonomskom ostvarivošću. Pored toga, u pregledu je uočeno i nekoliko propusta na osnovu kojih mogu da se unaprede i ispitaju mogućnosti recikliranja katalizatora.