

Production of high purity rare earth mixture from iron-rich spent fluid catalytic cracking (FCC) catalyst using acid leaching and two-step solvent extraction process

Le-Phuc Nguyen^{*,†}, Yen Thi Hai Pham^{*}, Phuong Thuy Ngo^{*}, Tri Van Tran^{*}, Loc Vinh Tran^{*,****},
Nam Thi Hoai Le^{****}, Luong Huu Nguyen^{*}, Tung Thanh Dang^{*}, Duc Anh Nguyen^{*}, Marco Wenzel^{**},
David Hartmann^{**}, Karsten Gloe^{**}, Jan J. Weigand^{*,†}, and Klaus Kretschmer^{***}

^{*}Catalysis Research Department, Vietnam Petroleum Institute, Saigon Hi-Tech Park, District 9, Ho Chi Minh City, Vietnam

^{**}Department of Chemistry and Food Chemistry, TU Dresden, 01062 Dresden, Germany

^{***}Delta Engineering & Chemistry GmbH, 14476 Großgörschen, Germany

^{****}Vietnam Academy of Science and Technology, Vietnam

(Received 24 October 2017 • accepted 5 February 2018)

Abstract—Acid leaching and a two-step solvent extraction procedure were developed to produce high purity mixture of La and Ce from iron-rich spent FCC catalyst discharged from Dzung Quat refinery (Vietnam). Acid leaching of the spent catalyst with 2 M HNO₃ and a solid-to-liquid ratio of 1/3 at 80 °C in 1 h dissolved almost 90% of La while 12% of Al and 25% of Fe were transferred to the leachate. The extraction of RE metals and main impurities such as Al and Fe by a mixture of di-2-ethylhexyl phosphoric acid (D2EHPA) and tributyl phosphate (TBP) was investigated. Experiments showed that it was necessary to remove Fe before extracting RE and the optimum extraction conditions for a high recovery of RE while 0% of Al extraction were pH ≤ 1, contact time = 10 min, and D2EHPA/TBP volume ratio = 4 : 1. At these conditions, the extraction yields of La(III) and Ce(III) were 72% and 89%, respectively. A two-step solvent extraction was developed to achieve a high purity of RE mixture, which included (1) the removal of impurity Fe by 25% (v/v) diisooctyl phosphinic acid (DiOPA) in n-octane for 140 min, (2) the extraction of rare earths by a mixture of di-2-ethylhexyl phosphoric acid (D2EHPA) and tributyl phosphate (TBP) in n-octane for 10 min without the need for adjusting the pH of the leaching solution.

Keywords: Spent FCC Catalyst, Rare Earth, Leaching, Solvent Extraction, Dzung Quat Refinery, Iron

INTRODUCTION

Fluid catalytic cracking (FCC) is an important process that converts heavy and low-value gas oil into lighter and more valuable products such as gasoline, diesel, propylene and C₄ gases [1]. It is estimated that about 700,000 tons of FCC catalyst are used worldwide per year, which results in about 360,000 tons of waste catalyst each year [2,3]. In Vietnam, Dzung Quat refinery produces about 20 tons of spent catalyst per day, which sums up to 7,300 tons per year [4]. Due to the increased demand of high-grade refined oil products, the production of FCC catalysts will also go up as well as their waste. Therefore, an efficient way to reuse FCC catalysts is necessary to reduce the catalyst cost. Currently, spent FCC catalysts are usually disposed to land or used as cement additive [3]. However, many toxic metals such as Ni or V still reside within the catalysts, which possibly cause a negative impact on environment as those metal ions can be leached into the soil and ground water. Moreover, a typical spent FCC catalyst can contain at least 0.5 wt% of rare earth oxides [5]. With the current options of treating spent FCC catalysts, a considerably large amount of rare earth (RE) metals is wasted each year. Consequently, recovery of RE from the spent FCC catalysts not only limits the influence of the Chinese govern-

ment on RE market, but also provides a sustainable supply of RE metals for those countries that do not possess primary ores [3,6,7].

Hydrometallurgical process is a common method to recover metals from wastes. This technique usually consists of three steps: leaching, purification of the leach solution and metal recovery [8]. Many studies have used the above method to recover RE from several industrial wastes such as spent nickel-metal hydrides (Ni-MH) batteries [9-12], optical glasses [13,14] or spent permanent magnets [15,16]. However, only few studies have been carried out in the recovery from the spent FCC catalysts [17,18]. After acid leaching step, RE could be recovered from the leachate by precipitation [5] or by solvent extraction [17]. Solvent extraction was shown to obtain a higher recovery and purer product with 98% of purity [17]. Zhao et al. [18] recovered RE from the spent FCC catalyst through acid leaching and solvent extraction with 2-ethylhexylphosphonic mono-2-ethylhexyl ester (HEHEHP) and bis(2-ethylhexyl) phosphoric acid (D2EHPA) in kerosene. The maximum RE leaching yield was 99.3% when using 2 M HCl, the solid-to-liquid ratio of 1/10, at a temperature of 60 °C for 2 h, and 2 h of roasting at 750 °C prior to leaching. D2EHPA proved to be more effective than HEHEHP in extracting RE, while the difference in extracting Al (the main impurity) between these two extractants was small. About 85% of RE could be extracted by D2EHPA; however, at least 30% of Al was also co-extracted.

Our previous work [19] also studied the hydrometallurgical recovery of rare earths from the spent FCC catalyst. The study focused

[†]To whom correspondence should be addressed.

E-mail: nguyenlp.pvpro@vpi.pvn.vn, jan.weigand@tu-dresden.de
Copyright by The Korean Institute of Chemical Engineers.

on investigating factors that possibly affected the leaching step such as types of acid, acid concentration, temperature, time, and solid-to-liquid ratio. In addition, some first experiments towards solvent extraction using a 1 : 1 mixture of 25% (v/v) TBP (0.92 M) and 25% (v/v) D2EHPA (0.76 M) in *n*-decane were performed. The results show that La(III) and Ce(III) can be extracted with 60% and 74% yield, respectively, in one stage and no extraction of Al(III) could be observed. However, up to 99% of Fe (III) is also extracted with La and Ce that cause the poor purity of rare earth mixture.

In this present work, we continued studying the recovery of RE by solvent extraction. Our objective was to enhance both the RE extraction yields and the purity of the extracted RE mixture. Factors that could promote the extraction of RE such as time, pH, and D2EHPA/TBP ratio were analyzed, and their influences on Al extraction yield were also evaluated. Furthermore, the separation of impurity Fe from the leaching solution was studied in detail to improve the purity of the product RE mixture. Note that the spent FCC catalyst used in this present work is different from the previous one especially in iron content. Therefore, some previous experiments were performed again, including XRF analysis and acid leaching.

EXPERIMENTAL

1. Materials

The spent FCC catalyst was collected from Dzung Quat refinery located in the middle of Vietnam. The catalyst was dried at 140 °C for two days and stored in a desiccator. Nitric acid (Merck, 65%) was used as a leaching agent, and sodium hydroxide (Merck, ≥99%) was used for precipitation. The stock solutions of metals used in this study were prepared by dissolving analytical grade metal nitrites in distilled water. Di-2-ethylhexyl phosphoric acid (D2EHPA), tributyl phosphate (TBP), diisooctyl phosphinic acid (DiOPA), and 2-ethylhexylphosphonic mono-2-ethylhexyl ester (HEHEHP) were purchased from Sigma-Aldrich or TCI and used as extractants diluted in *n*-octane (VWR international GmbH) for solvent extraction.

2. Experimental Procedure

2-1. Acid Leaching

The optimum acid leaching conditions for the highest RE and lowest Al yields obtained from our previous study [19] were employed. These conditions were: 10 g of spent FCC catalyst was leached with 30 ml of 2 M HNO₃ at 80 °C in 1 h. The solid residue was filtered and washed three times with distilled water (10 ml of water for each time). The solution obtained after acid leaching and water washing was withdrawn, added with distilled water to reach 100 ml, and analyzed by an inductively coupled plasma (ICP-OES) spectrometer.

2-2. Model Solutions

Model solutions with pH < 1 containing 4 key elements Al(III), Fe(III), La(III), and Ce(III) as nitrates were prepared from 10,000 ppm Al(III); 1,000 ppm Fe(III); 5,000 ppm La(III); and 1,000 ppm Ce(III) stock solutions such that they have similar metals concentration with the obtained leach liquor, and the pH was adjusted by the addition of 1 M HNO₃ solution.

2-3. Precipitation

Each 50 ml of model solution with pH of 0.77 was added with

0.2 M NaOH solution under constant stirring to obtain a desired pH in a range of 2.5 to 6. The samples were then centrifuged at 5,000 rpm for 20 min, and the centrifugate was taken for ICP-OES analysis.

2-4. Solvent Extraction

All extraction tests were performed at room temperature in 2 ml microcentrifuge tubes by mechanical shaking with a defined contact time. The organic and aqueous phases were equal in volume (0.9 ml each). D2EHPA, TBP, DiOPA, and HEHEHP were extractants, while *n*-octane was used as an organic diluent. All samples were centrifuged after extraction, and the metal concentration in the aqueous phase before and after the extraction was analyzed by ICP-OES.

3. Analysis

The chemical composition of the spent FCC catalyst was determined by X-ray fluorescence (XRF) using S4 Pioneer instrument (Bruker) based on ASTM D 7085 [20]. The catalyst powders were heated in the oven at 600 °C for 3 h to remove carbon. The catalyst was then ground, mixed with binder and pelletized under pressure of about 630 atm for 3 min.

ICP-OES spectrometer OPTIMA 2000DV (PerkinElmer) was used to analyze the metal concentration in the aqueous solutions. The metal concentration in the organic phase was obtained from mass balance. The percentage of extraction (%E) was calculated from the distribution ratio (D_M) as follows:

$$D_M = C_{M(\text{organic})} / C_{M(\text{aqueous})}$$

$$\%E = 100 \cdot D_M / (D_M + 1)$$

RESULT AND DISCUSSION

1. Characterization of the Initial Spent FCC Catalyst and the Leaching Results

Table 1 shows the result of XRF analysis of the spent FCC catalyst collected from Dzung Quat refinery. Silicon and aluminum are the most major elements (27.15 wt% Al and 14.51 wt% Si). The total RE content only accounts for 1.88 wt% (1.82 wt% La and 0.06 wt% Ce). The iron content (0.51 wt% of Fe or 1.46 wt% of Fe₂O₃) in this spent FCC catalyst is higher than other sources [17,18,21]. The higher iron content in spent FCC would increase the difficulties of

Table 1. XRF analysis of the spent FCC catalyst powder

Component	Weight%
Al	27.15
Ca	0.18
Ce	0.06
Co	0.07
Fe	0.51
K	0.04
La	1.82
Na	0.10
Ni	0.54
Si	14.51
Ti	0.72
V	0.10

Table 2. Compositions of 100 ml leach liquor and the leaching yields by 30 ml 2 M HNO₃ at 80 °C in 1 h

Element	Concentration (mg/L)	Leaching yield (%)
Al	3238±10	12
Ca	44±0.4	25
Ce	15±0.03	25
Co	0	0
Fe	136±2	25
K	9±0.4	22
La	1608±3	88
Na	75±2	75
Ni	11±0.1	2
Si	55±1	0.4
V	21±2	21

purification step.

10 g of spent FCC catalyst was leached by 30 ml of 2 M HNO₃ at 80 °C in 1 h. The composition of 100 ml leach liquor collected after filtration and water washing as described in the acid leaching procedure is summarized in Table 2. The leaching yield of each metal is also included in this table. These data indicated that the selected leaching conditions were very efficient to extract La (almost 90% of La was leached out). Although Si and Al are the most dominant components in the initial material, their leaching yields are extremely low compared to other metal elements (only 0.4% for Si, and 12% for Al). However, Al still has the highest concentration in the leaching solution with 3,238±10 mg/L and needs to be removed in order to obtain a solution that is rich in RE. Other main impurities include Na (75±2 mg/L), Si (55±1 mg/L), and Ca (44±0.4 mg/L). With exception of Fe, the leaching of the present base metals, namely Fe, Co and Ni, is negligible. The determined concentrations are 11±0.1 mg/L and 0 mg/L for Ni and Co, respectively, whereas 25% of the Fe detected in the spent FCC catalyst powder is leached to give a concentration of 136±2 mg/L in the leach liquor.

Among other main impurities, Fe shares many similarities with RE as the common valence of Fe is also +3 [22]. Fe(III) was found to be extractable in organophosphorus acidic extractants (e.g., D2EHPA and HEHEHP) [23]. In our previous study [19], Fe was also extracted up to 99% by a mixture of 25% (v/v) D2EHPA and 25% (v/v) TBP in n-decane, while the extraction yields of the base metal Ni and the other impurities such as Si, Ca or Mg (which have

Table 3. Composition and pH of model solution compared to those of obtained leaching solution

Element	Concentration in model solution (mg/L)	Concentration in real solution (mg/L)
Al	2926±7	3238±10
Ce	15±0.4	15±0.03
Fe	130±2	136±2
La	1530±5	1608±3
pH values	0.77	0.79

ion valence of +2, and +4 in the case of Si) were 0%. Therefore, besides Al, it is also essential to study the methods to separate Fe from the leaching solution.

2. Solvent Extraction of RE from the Model Leaching Solution

The extraction experiments were started by using model solutions containing the four most important elements: Al, Ce, La, and Fe. The metals concentration and pH values of the used model solution are comparable with the real leach liquor (Table 3).

2-1. Effect of Type of Extractants

D2EHPA, TBP and a mixture of D2EHPA and TBP were selected to investigate in this study as these reagents are the two most common extractants used in RE extraction [24]. The results of comparable experimental conditions (pH=0.77, room temperature, extraction time of 10 min, n-octane as diluent) are shown in Table 4. The extraction for all studied metals is negligible by TBP. In contrast, D2EHPA is very efficient with high extraction yields for Ce (96%) and La (66%). However, significant quantity of Fe and Al was also extracted by D2EHPA, namely 32% Fe and 1.3% Al, respectively. Even though the extraction yield for Al is only 1.3%, the large amount of Al present (approximately 3,000 mg/L, see Table 3) in the leach liquor results in a considerable amount of Al being extracted. The application of a 1 : 1 mixture of D2EHPA and TBP has a lower RE extraction power (84% Ce and 55% La), but its selectivity towards RE is improved. The Fe extraction drops to 9%, whereas no Al is transferred into the organic phase. Therefore, a mixture of D2EHPA and TBP was selected for a further extraction investigation. Factors that could enhance RE extraction yields such as time, pH, and D2EHPA/TBP ratio were examined, and their influences on Al extraction yield were also evaluated.

2-2. Effect of Contact Time and pH on the Extraction Performance of Mixture of 1 : 1 D2EHPA and TBP

The contact time was varied from 10-140 min, while the other

Table 4. % Extraction of selected metals by n-octane and various extractants and mixtures thereof in n-octane. T=23 °C, pH=0.77, t=10 min

Metal/ pH	n-Octane (75% v/v) D2EHPA (25% v/v)	n-Octane (75% v/v) TBP (25% v/v)	n-Octane (50% v/v) D2EHPA (25% v/v) TBP (25% v/v)
Al	1.3	0	0
Ce	96	0	84
Fe	32	2	9
La	66	0	55
pH	0.72	0.81	0.77

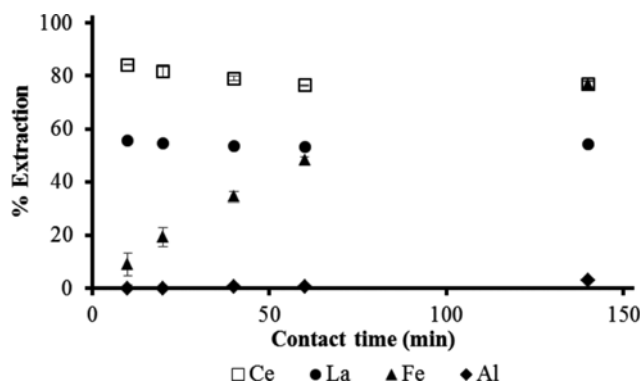


Fig. 1. Extraction of Ce, La, Al, and Fe in dependence of the contact time using a mixture of 25% (v/v) D2EHPA and 25% (v/v) TBP in n-octane. T=23 °C, pH=0.77.

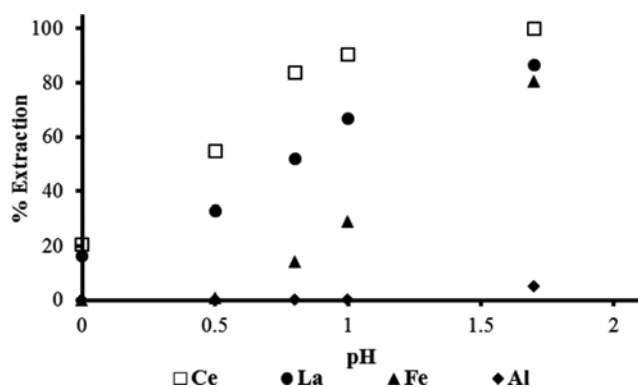


Fig. 2. Extraction of RE and Al, Fe impurities in dependence of the pH using 25% (v/v) D2EHPA and 25% (v/v) TBP in n-octane. T=23 °C, t=10 min.

parameters such as temperature, pH, ratio of organic and aqueous phases were kept constant. The effect of the applied contact time is shown in Fig. 1.

As contact time increases, the extraction yields of RE decrease while those of impurities (Al and Fe) increase. Interestingly, from the four metals Al, Ce, La and Fe, the extraction power of Fe depends on time most significantly, presumably due to a series of species and parallel steps occurring during the Fe complex formation at the interface [25–27]. Therefore, the best extraction time is 10 min to minimize the amount of impurities extracted together with RE (especially Fe), while the efficiency of rare earth extraction is highest.

Fig. 2 depicts the influence of pH on the extraction of Al, Ce, La and Fe. It is clearly shown that increasing pH enhances considerably the extraction of all metal ions. This is attributed to the presence of D2EHPA in the mixture of extractants. As organophosphorus acid D2EHPA can extract RE by cation exchange, hence the extraction by D2EHPA is strongly pH dependent. At pH>1, the mixture of 1:1 D2EHPA and TBP starts to extract Al along with RE and Fe. Up to 5% of Al is extracted at pH=1.7. Consequently, pH of the aqueous phase should be kept at 1 or lower for a 0% Al extraction.

2-3. Effect of D2EHPA/TBP Ratio

Volume ratio of D2EHPA/TBP was increased from 1:4 to 4:1, while the other conditions were kept constant (pH=0.77, room tem-

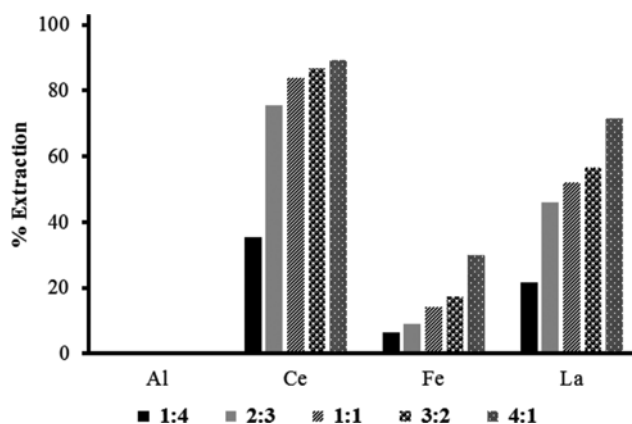


Fig. 3. Extraction of Ce, La, Al, and Fe in dependence of the D2EHPA/TBP ratio in 50% (v/v) n-octane. T=23 °C, pH=0.77, t=10 min.

perature, contact time=10 min, and n-octane=50% (v/v) of organic phase).

Fig. 3 shows that the extraction of all studied metals, except for Al, increases with rising D2EHPA proportion in the applied D2EHPA/TBP mixture. As demonstrated in section 2.1 D2EHPA is more efficient than TBP in extracting trivalent metals, and hence will improve the observed extraction power. The highest extraction power of 89% for Ce and 72% for La is observed for a mixture of 40% (v/v) D2EHPA and 10% (v/v) TBP in n-octane. This is comparable to the observed extraction power towards the RE for D2EHPA only (25% (v/v) in n-octane: 96% Ce and 66% La extraction, respectively). However, the extraction power for Fe is also rising with the rising D2EHPA proportion in the D2EHPA/TBP mixture reaching 30% for the 4:1 mixture.

Apparently, choosing a suitable contact time, pH and D2EHPA/TBP volume ratio can promote a high RE extraction power while keeping the extraction of Al at 0%. The remaining problem is to remove Fe(III) impurity. According to the above presented extraction results, Fe(III) is always co-extracted with RE with a substantial extraction efficiency in a range of 9% to 80%. Therefore, it is essential to remove Fe(III) prior to RE extraction by D2EHPA or a mixture of D2EHPA and TBP.

3. Removal of Fe(III) from the Model Leaching Solution

Two methods to remove Fe(III) from the model leaching solution were studied: precipitation and solvent extraction.

3-1. Precipitation Method

Based on the solubility product constant values, K_{sp} of $\text{Al}(\text{OH})_3$ [28], Ce [29], La [30], $\text{Fe}(\text{OH})_3$ [28] at 25 °C and their concentrations in the model solution (Table 3), the calculated pH range in which Fe(III), Al(III), La(III) and Ce(III) precipitated as metal hydroxides are pH 2-3, 3.1-4.1, 8.3-9.3 and 8.8-9.8, respectively. Therefore, Fe(III) can be theoretically separated from La and Ce by hydroxide precipitation. However, hydroxide precipitation of Fe(III) is problematic due to two reasons. First, the separation of the RE from the main impurity Al by the developed solvent extraction method should be performed at pH=1 or below; thus, precipitation of iron hydroxide requires increase of the pH followed by a readjustment of the pH to approximately 1 to perform the RE extraction. Secondly, iron hydroxide is prone to form metastable col-

loids which require a posttreatment, such as an hour-long boiling stage, flocculation, or the addition of surfactants to enhance settling [23]. To ensure that the removal of Fe(III) by a simple precipitation is challenging, simple bench scale precipitation experiments were performed.

The adjustment of the pH from initial 0.77 to a pH of 2.5, 3.5, 3.9, 4.5 and 5.6 upon the addition of 0.2 M NaOH to 50 mL of the model solution indeed gives colloidal solution from which the iron hydroxide cannot be separated by filtration, even though an almost complete precipitation of Fe(III) at this examined pH range is known [31,32]. Attempts to perform a liquid-solid separation by centrifugation at 5,000 rpm for 20 min failed, too. It was observed, that the initial colorless solution started changing to orange-yellow color at pH=3.5, suggesting the presence of iron hydroxide species in solution or as colloids. However, even after centrifuging, the liquid kept this orange-yellow color. To probe if the observed color was caused by the presence of iron hydroxide colloids, two sets of experiments were performed: The supernatant liquid of the sample with pH of 4.5 was transferred to another tube and was observed to be clear of solid. Upon the addition of a few drops of a concentrated HNO₃ (65%) the color of the solution vanished, indicating that iron hydroxide colloids were still present in the supernatant liquid. In addition, the Fe concentration of the supernatant liquids was analyzed by ICP-OES. The determined Fe concentrations are listed in Table 5 and displayed with the calculated Fe content for the case that no precipitation of iron hydroxide occurred. The results show that both values are approximately equal, which demonstrates that iron hydroxide forms metastable colloids, which could not be separated from the leach liquor by centrifugation or filtration without further treatment. Thus, a removal of Fe from the leaching solution by hydroxide precipitation method under the conditions studied is not possible and hence removal of the impurity by solvent extraction will be applied.

3-2. Solvent Extraction Method

There are several possibilities to separate iron from rare earth concentrates by solvent extraction methods [23]. For example, the application of amines, such as trioctylamine (TOA) or other tertiary amines enables the extraction of iron at low pH [33-35]. However, the formation of a third phase is sometimes limiting the performance of these process [36]. For an iron removal at pH of up to 2.5 the application of tertiary amines in the presence of phosphonic acid or phosphinic acid, respectively, is reported [37]. Also, mixed alkyl/aryl phosphonic acid or alkyl phosphinic acid, such as diisooctyl phosphinic acid (DiOPA) are suggested for the extraction of Fe(III) impurities [38,39]. The phosphinic acids have no ester-O

Table 6. % Extraction of selected metals by DiOPA with various % vol in n-octane. T=23 °C, pH=0.77, t=10 min

Metal	n-Octane (75% v/v) DiOPA (25% v/v)	n-Octane (50% v/v) DiOPA (50% v/v)
Al	0	0
Ce	0	0
Fe	24	20
La	0	0

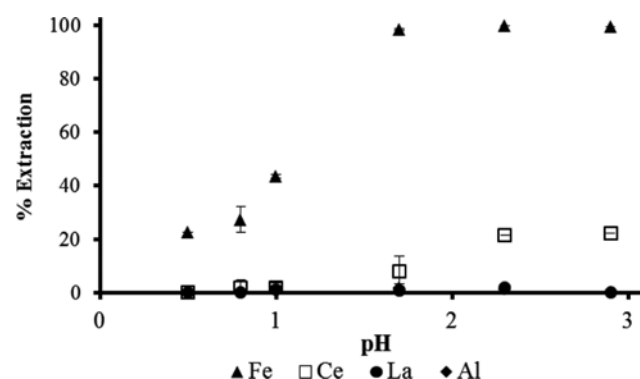


Fig. 4. Extraction of Ce, La, Al, and Fe by 25% (v/v) DiOPA in n-octane in dependence of the pH. T=23 °C, t=10 min.

atoms in their structures, and hence are weaker acid than D2EHPA [40]. As a result, their RE (e.g., La and Ce) extraction is less effective than D2EHPA. Therefore, it is predicted that dialkyl phosphinic acids are potential extractants for separation of Fe(III) from the mixture of La and Ce. Diisooctyl phosphinic acid (DiOPA) was chosen to investigate in this study.

The results in Table 6 show, that DiOPA does not extract RE or Al at pH=0.77, room temperature, and a contact time of 10 min. However, DiOPA extracts 24% Fe. At increased volume of DiOPA to 50% in n-octane, the extraction of Fe slightly decreases to 20%. Thus, DiOPA (25% (v/v) in n-octane) was further examined for Fe extraction. To tune the Fe extraction yield, the influence of the pH (Fig. 4) and the contact time (Fig. 5) was investigated. As depicted in Fig. 4, the extraction efficiency of Fe increases markedly with increasing pH, reaching a quantitative Fe extraction at pH=1.7 or higher. Whereas, notable extraction of Ce was observed for a pH of 1.5 (8%) and above (22% at pH=2.9). Thus, the pH of the aqueous phase should be less than 1.5 to minimize loss of Ce

Table 5. Concentration of Fe(III) in case of no precipitation and in supernatant liquid after centrifugation

Volume of NaOH added (ml)	Total liquid volume (ml)	pH	Calculated Fe concentration (no precipitation) (mg/L)	Concentration of Fe in the supernatant liquid after centrifugation (mg/L)
0	50	0.77	130	130
48	98	2.5	63	61
57	107	3.5	57	49
88	138	3.9	45	37
115	165	4.5	37	37
125	175	5.6	35	35

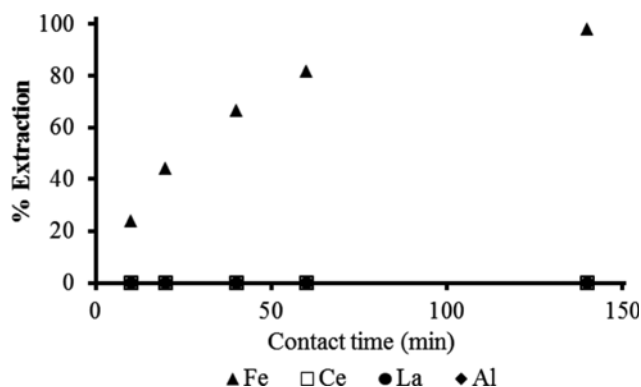


Fig. 5. Extraction of Ce, La, Al, and Fe by 25% (v/v) DiOPA in n-octane in dependence of the contact time. T=23 °C, pH=0.77.

during Fe removal. At pH=1.5, about 80% Fe is removed from the solution containing RE.

In contrast, an increase of the contact time enhances the extraction power for Fe only and does not affect the extraction of other elements such as Al, Ce, and La (Fig. 5). At 140 min, 98% of Fe is extracted, while no extraction of the other metals ions is observed. Apparently, DiOPA cannot extract Al, Ce and La at this low pH of 0.77. Therefore, increasing the contact time will be more effective towards a complete removal of the Fe impurities without losing rare earths compared to increasing the pH.

Comparable experiments were performed employing 2-ethylhexylphosphonic mono-2-ethylhexyl ester (HEHEHP) as extract in n-octane. The obtained extraction power for Al, Ce, Fe and La in dependence of the pH of the aqueous phase is depicted in Fig. 6. The results show that a high Fe extraction is achieved at all studied pH values, ranging from 94% at pH=0.5 to quantitative extractions for pH=0.9 and 2.0. However, at these conditions notable extraction of Al (2% at pH=0.5; 9% at pH=2.7), as well as La (8% at pH=0.5; 70% at pH=2.7) and Ce (17% at pH=0.5; 89% at pH=2.7) was observed. Thus, a Fe removal is not achievable using HEHEHP under the conditions chosen in this study and not further experiments were performed.

4. Solvent Extraction of RE from the Real Leaching Solution

Based on the results achieved from the model solution, the ap-

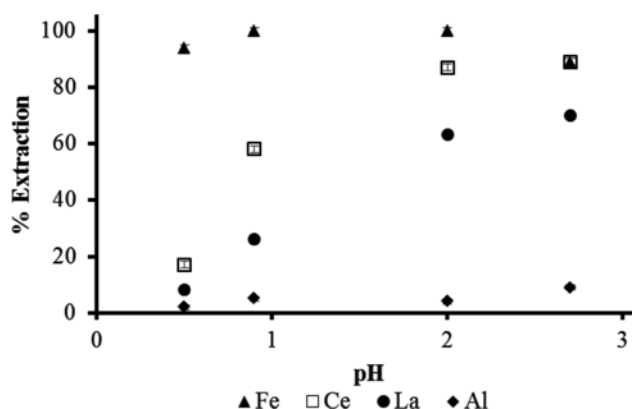


Fig. 6. Extraction of Ce, La, Al, and Fe by 2 mol/L HEHEHP in n-octane in dependence of the pH. T=22 °C, t=10 min.

plication of a mixture of D2EHPA and TBP allows high extraction yields of RE while 0% of Al is extracted. Additionally, DiOPA is very effective in removing Fe impurity when the contact time is increased to 140 min. As a result, a two-step solvent extraction process was constructed to obtain a RE mixture of high purity from the leach liquor: (1) removing Fe by using 25% (v/v) DiOPA in n-octane at pH=0.79, applying a contact time of 140 min; (2) extracting RE from the solution obtained from step (1) by a mixture of D2EHPA and TBP at pH≤1 with a contact time of 10 min. The corresponding results for a mixture of 1:1 D2EHPA and TBP at pH=0.79 are given in Table 7. DiOPA separates almost completely Fe (98%) from the leaching solution, which is in a good agreement with the obtained results from the model solution. Other elements that can be extracted by DiOPA include K, Na, Si and V. A small amount of Ce (3%) is also extracted, whereas the quantity of La is preserved in the aqueous phase.

After step (2) extraction, a significant amount of La and Ce is transferred into the organic phase (73% Ce and 52% La), while none of the major impurities, such as Al, Fe, Na, and Ni, are extracted. The analysis shows that a very high purity of a concentrate of La and Ce are extracted by this two-step extraction process (99.6 wt%). The stripping process to transfer this RE concentrate back to the aqueous phase was not performed in these series of

Table 7. Extraction of metals in the actual leaching solution by a two-step solvent extraction. T=23 °C, pH=0.79

Element	Content in a leaching solution (mg/L)			% Extraction	
	Before extraction	After step (1) extraction	After step (2) extraction	Step (1)	Step (2)
Al	3238±10	3272±21	3328±2	0	0
Ca	44±0.4	45±0.04	44±0.8	0	0
Ce	15±0.03	14±0.4	3±0.4	3	73
Fe	136±2	1±0.1	1±0.2	99	0
K	9±0.4	8±0.1	9±0.3	7	0
La	1608±3	1634±15	768±21	0	52
Na	75±2	67±10	80±7	11	0
Ni	11±0.1	11±0.05	12±0.02	0	0
Si	55±1	53±0.7	52±1	4	2
V	21±2	13±0.6	11±1	38	9

experiments.

CONCLUSION

Hydrometallurgical recovery of RE from the spent FCC catalyst from Dzung Quat Refinery was developed to achieve an RE mixture of high purity. The initial spent FCC catalyst contained two most major components, which were Al (27.15 wt%) and Si (14.51 wt%), whereas RE only accounted for 1.88 wt% (1.82 wt% La and 0.06 wt% Ce). Almost 90% of La while only 12% of Al was transferred from the spent FCC catalyst solid to the solution under the leaching conditions of 2 M HNO₃ at 80 °C and a solid-to-liquid ratio of 1/3 for 1 h.

Solvent extraction with D2EHPA, TBP and their 1 : 1 (v/v) mixture in n-octane was first performed on a model solution consisting of four key metal ions (Al, Ce, La and Fe) with metal concentrations and pH similar to those obtained in the leaching solution. The results showed that the mixture 1 : 1 of D2EHPA and TBP was less effective than D2EHPA in extracting rare earths (84% Ce and 55% La are extracted). However, its extraction power for Al (the most major impurity) was 0%. Therefore, a mixture of D2EHPA and TBP was further investigated for the effect of time, pH, and D2EHPA/TBP ratio on the extraction of RE and Al. Increasing time reduced the extraction of RE while facilitating that of impurities (Al and Fe). Therefore, 10 min was the optimum time to obtain a high RE extraction yield while minimizing the co-extraction of impurities. Increasing pH enhanced the extraction of all elements, and hence, the pH should be kept at 1 or below for no co-extraction of Al. The extraction of RE was also improved by rising the D2EHPA/TBP ratio. Interestingly, none of Al was co-extracted even at D2EHPA/TBP ratio of 4/1. At this D2EHPA/TBP ratio with pH=0.77 and contact time of 10 min, the extraction power for La, Ce, and Fe was 72%, 89%, and 30% respectively.

To remove Fe from the leaching solution two methods were studied: precipitation and solvent extraction. Under the studied conditions, Fe could not be separated by hydroxide precipitation. However, Fe was removed almost completely by 25% (v/v) DiOPA in n-octane using a contact time of 140 min. Most importantly, no RE was lost during the removal of Fe by this solvent extraction method. From that, a two-step solvent extraction method was developed: (1) removing Fe by 25% (v/v) DiOPA in n-octane applying a contact time of 140 min; (2) extracting RE by a mixture of D2EHPA and TBP at pH≤1 with a contact time of 10 min. This two-step solvent extraction was applied to a real leaching solution using a mixture of 1 : 1 D2EHPA/TBP at pH=0.79. A very high purity of a concentrate of La and Ce was extracted to the organic phase (99.6 wt%). This procedure can be applied for another type of spent FCC catalyst with high iron content and have high potential practical implications.

ACKNOWLEDGEMENTS

This research was funded by the Ministry of Industry and Trade of the Socialist Republic of Vietnam, funding number NĐT.09.GER/15 and the German Federation of Industrial Research Associations (AIF/ZIM projects KF2807202RH3 and 3027402RH3). MW grate-

fully acknowledges financial support from Max Buchner Foundation (MBFSt 3558).

CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

REFERENCES

1. T. Chiranjeevi, N. Ravichander, D. T. Gokak, V. Ravikumar and N. V. Choudary, *Petrol. Sci. Technol.*, **32**, 470 (2014).
2. M. I. M. Chou, L. M. Chen and S. F. J. Chou, *Int. J. Environ. Sust.*, **8**, 19 (2013).
3. F. Ferella, V. Innocenzi and F. Maggiore, *Res. Conserv. Recy.*, **108**, 10 (2016).
4. C. T. Nguyen, H. M. Nguyen and M. Q. Ta, *PetroVietnam J.*, **11**, 43 (2013).
5. X. Gao and W. T. Owens, US Patent, US20120156116 A1 (2012).
6. A. Jordens, Y. P. Cheng and K. E. Waters, *Miner. Eng.*, **41**, 97 (2013).
7. K. Binnemans, P. T. Jones, B. Blanpain, T. V. Gerven, Y. Yang, A. Waltone and M. Buchert, *J. Clean. Prod.*, **51**, 1 (2013).
8. P. F. Duby, Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons Inc. (2000).
9. L. Li, S. Xu, Z. Ju and F. Wu, *Hydrometallurgy*, **100**, 41 (2009).
10. P. Zhang, T. Yokoyama, O. Itabashi, Y. Wakui, T. M. Suzuki and K. Inoue, *J. Power Sources*, **77**, 116 (1999).
11. L. Pietrelli, B. Bellomo, D. Fontana and M. R. Monteverdi, *Hydrometallurgy*, **66**, 135 (2002).
12. P. Zhang, T. Yokoyama, O. Itabashi, Y. Wakui, T. M. Suzuki and K. Inoue, *Hydrometallurgy*, **50**, 61 (1998).
13. Y. Jiang, A. Shibayama, K. Liu and T. Fujita, *Hydrometallurgy*, **76**, 1 (2005).
14. Y. Jiang, A. Shibayama, K. Liu and T. Fujita, *Can. Metall. Q.*, **43**, 431 (2004).
15. C. H. Lee, H. Y. Yen, C. H. Liao, S. R. Popuri, E. I. Cadogan and C. J. Hsu, *J. Mater. Cycles Waste Manage.*, **19**, 102 (2017).
16. C. H. Lee, Y. J. Chen, C. H. Liao, S. R. Popuri, S. L. Tsai and C. E. Hung, *Metall. Mater. Trans. A.*, **44**, 5825 (2013).
17. V. Innocenzi, F. Ferella, I. D. Michelis and F. Vegliò, *J. Ind. Eng. Chem.*, **24**, 92 (2015).
18. Z. Zhao, Z. Qiu, J. Jang, S. Lu, L. Cao, W. Zhang and Y. Xu, *Hydrometallurgy*, **167**, 183 (2016).
19. M. Wenzel, K. Schnaars, N. Kelly, L. Götzke, M. S. Robles, K. Kretschmer, P. N. Le, D. T. Tung, N. H. Luong, N. A. Duc, D. V. Sy, K. Gloe and J. J. Weigand, Rare Metal Technology, John Wiley & Sons Inc., NJ (2016).
20. ASTM D7085, Standard Guide for Determination of Chemical Elements in Fluid Catalytic Cracking Catalysts by X-ray Fluorescence Spectrometry (XRF) (2010).
21. J. Wang, Y. Xu, L. Wang, L. Zhao, Q. Wang, D. Cui, Z. Long and X. Huang, *J. Environ. Chem. Eng.*, **5**, 3711 (2017).
22. T. Moeller, The Chemistry of the Lanthanides, Reinhold Publishing, New York (1963).
23. C. Xia, A review on iron separation in rare earths hydrometallurgy using precipitation and solvent extractions method, I. M.

- London, J. R. Goode, G. Moldoveanu, M. S. Rayat Eds., Canad. Institute of Mining, Metallurgy and Petroleum, Westmont (2013).
24. C. K. Gupta and N. Krishnamurthy, *Extractive metallurgy of rare earths*, CRC Press, Florida (2005).
25. J. W. Roddy, C. F. Coleman and S. Arai, *J. Inorg. Nucl. Chem.*, **33**, 1099 (1971).
26. T. Sato, T. Nakamura and M. Ikeno, *Hydrometallurgy*, **15**, 209 (1985).
27. H. Matsuyama, Y. Miyake, Y. Izumo and M. Teramoto, *Hydrometallurgy*, **24**, 37 (1990).
28. M. S. Silberberg, Principles of general chemistry, McGraw-Hill, U.S.A. (2010).
29. G. Avgouropoulos, Environmental Catalysis over Gold-Based Materials, RSC (2013).
30. D. L. Reger, S. R. Goode and D. W. Ball, Chemistry: Principles and Practice, Brooks/Cole, U.S.A. (2010).
31. V. L. Snoeyink and D. Jenkins, Water Chemistry, John Wiley & Sons, New York (1980).
32. E. Y. Seo, Y. W. Cheong, G. J. Yim, K. W. Min and J. N. Geroni, *Catena*, **148**, 11 (2017).
33. J. Tian, R. Chi, G. Zhu, S. Xu and Z. Zhang, *Nonferrous Met.*, **2**, 57 (2000).
34. K. Liu, Y. Wang, M. Wei, X. Tang and P. Zhang, China Patent, CN 107130120 A (2017).
35. M. Maeda, H. Narita, C. Tokoro, M. Tanaka, R. Motokawa, H. Shiwaku and T. Yaita, *Sep. Purif. Technol.*, **177**, 176 (2017).
36. M. Liu and Y. Zhou, *The Chinese J. Nonferrous Met.*, **15**(10), 1648 (2005).
37. S. Yu and J. Chen, *Hydrometallurgy*, **22**, 183 (1989).
38. A. F. Osaka, I. M. Nara and M. T. Osaka, US Patent, US 4582691 A (1986).
39. D. Nucciarone, B. Jakovljevic, B. A. Fir Medeiros, J. Hill-house, M. DePalo, in: K. C. Sole, P. M. Cole, J. S. Preston, D. J. Robinson (Eds.), *Proceedings of the International Solvent Extraction Conference ISEC*, **1**, 402 (2002).
40. L. Lin-yan, X. Sheng-ming, J. Zhong-jun, Z. Zhang, L. Fu-hui and L. Guo-bao, *Trans. Nonferrous Met. Soc. China*, **20**, 205 (2010).