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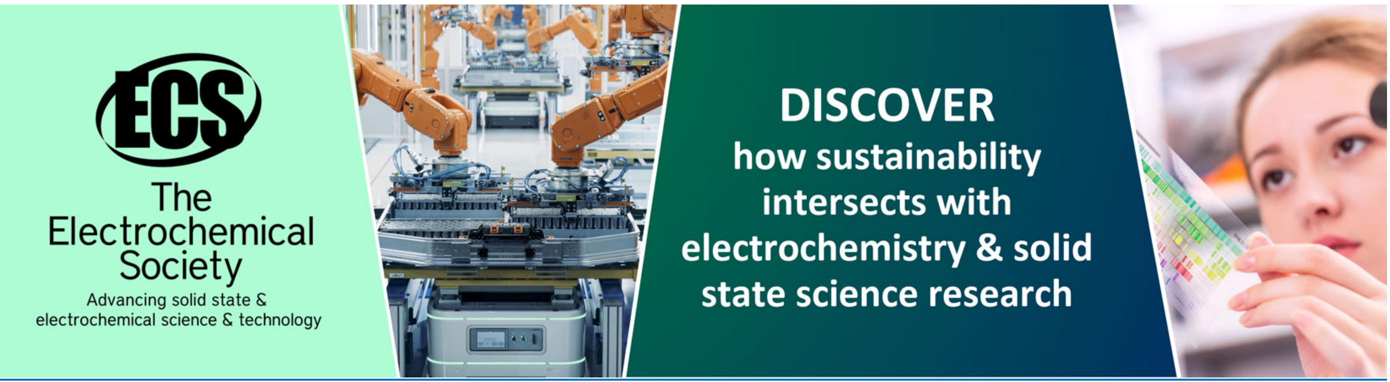

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Separation of Ce, La and Nd in rare earth hydroxide (REOH) by oxidation with potassium permanganate and precipitation

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Abstract. The present work describes the development of an efficient and relatively simple process to obtain high grade $Ce(OH)_4$ from REOH (Rare earth hydroxide). The Rare earth hydroxide was obtained through base digestion of monazite. The steps investigated in the process for obtaining $Ce(OH)_4$ were: (i) dissolution RE hydroxide (REOH) with HNO_3 and oxidation of Ce^{+3} to Ce^{+4}, (ii) selective precipitation of $Ce(OH)_4$ with Na_2CO_3, (iii) selective precipitation of $Nd(OH)_3$ with ammonium hydroxide (iv) precipitation of La with oxalic acid. The main variables affecting the cerium oxidation were: the ratio of the $KMnO_4$ /REOH, temperature and oxidation time. A ratio of 1.25/10 of $KMnO_4$ / REOH was necessary for full cerium recovery. The recovery of cerium increases as temperature and oxidation time rises, the purity of the product $Ce(OH)_4$ at the pH above 4. The process conditions were achieved in the use of 1.25/10, $KMnO_4$/REOH ratio, at the 120 °C and the oxidation time of 75 minutes. The composition of the final product $Ce(OH)_4$ was 97.98 wt.% $Ce(OH)_4$, in a process yielding a recovery of Ce greater than 93%, were obtained. The composition of the final product $Nd(OH)_3$ was 37 wt.% $Nd(OH)_3$, in a process yielding a recovery of Nd greater than 98%, were obtained. The composition of the final product $La_2(C_2O_4)_3$ was 90 wt.% $La_2(C_2O_4)_3$, in a process yielding a recovery of La greater than 93%, were obtained. The oxidation of Ce^{3+} to Ce^{4+} using $KMnO_4$ follows first order reaction. The value of reaction rate constant of Ce was 0.0291 $minutes^{-1}$.

***Keywords**: REOH, oxidation, $KMnO_4$, precipitation*

1. Introduction

The rare earth elements (REE) find application in many fields associated with modernity such as green energy, high performance magnets, lighting and consumer electronics, medical equipment as well as in more traditional industries including glass, ceramics and catalysis [1]. The supply of REE to the world market is predominantly from China, resulting from the processing of ionic clays and high grade mineral concentrates such as bastnasite, monazite and xenotime [2][3]. In recent years, a relatively high supply risk index has been assigned to the REE by a number of countries [4]. This has spurned interest in the production of REE from mineral concentrates of lower grade and varying sources. To satisfy the demands of these alternative resources the application of new separation methodologies is of interest.

The monazite ores are known to contain significant quantities of REEs and therefore processing of monazite ores for REEs has become more prominent recently [5]. Rare earths hydroxide (REOH) was a monazite process products containing REE elements namely Ce, La, Nd, Pr, Y, Sm and Gd [6]. Youcai et.al, 2017, studied extraction and recovery of cerium(IV) and thorium(IV) from sulphate medium by an α-aminophosphonate extractant to extract cerium(IV) and thorium(IV) from sulphate medium by an α-aminophosphonate extractant. A solvent extraction process to extract and recover cerium and thorium from bastnasite leaching was proposed, in which the purities of cerium and thorium products reached 99.9% and 99% with yield of 92% and 98%, respectively. Aminophosphonate extractant was very expensive, while the chemicals used in precipitation or in this process were very cheap [7].

In alkaline solutions, the trivalent cerium is readily oxidized to the tetravalent ceric ion either by bubbling oxygen during the RE-hydroxide precipitation or afterwards by drying the RE-hydroxide in the presence of air [8]. In acid solutions, the oxidation of Ce^{+3} to Ce^{+4} may occur by chemical oxidation with strong oxidants such as persulphate, permanganate, bismuth, lead dioxide or silver oxide are used; by electrochemical oxidation or by photochemical oxidation [9].

This study proposes a methodology which consists of: (i) dissolution RE hydroxide (REOH) with HNO_3 and oxidation of Ce^{+3} to Ce^{+4}, (ii) selective precipitation of $Ce(OH)_4$ with Na_2CO_3, (iii) selective precipitation of $Nd(OH)_3$ with ammonium hydroxide at pH 8.5. (iv) precipitation of La with oxalic acid to La oxalate. The effects of the main variables involved in the precipitation and purification of cerium, the process variables assessed were: molar of $KMnO_4$, time and temperature of oxidation reaction were investigated.

1.1. Theory

The separation of cerium from the RE elements can be carried out by selective dissolution of the trivalent RE-hydroxides, by keeping the cerium (IV) hydroxide in its insoluble form or through its selective precipitation from the acid solution. In either case, the cerium separation occur given the solubility difference between the Ce(IV)-hydroxide ($K_{sp} \sim 10^{-54}$) and the RE(III)-hydroxide ($K_{sp} \sim 10^{-22}$) Oxidation through permanganate solution leads to simultaneous precipitation of $Ce(OH)_4$ and MnO_2, as we see in equations (1) (2) and (3).

$$RE(OH)_3 + 3\ HNO_3 \rightarrow RE(NO_3)_3 + 3\ H_2O \tag{1}$$
$$Ce(OH)_3 + 3\ HNO_3 \rightarrow Ce(NO_3)_3 + 3\ H_2O \tag{2}$$
$$2\ KMnO_4 + 2\ Ce(NO_3)_3 + 2\ HNO_3 \rightarrow K_2O + 2\ MnO_2 + 2\ Ce(NO_3)_4 + H_2O \tag{3}$$

Mixing of $KMnO_4$ and Na_2CO_3 at the oxidation process has been done by Renata, et al. (2010). In this work, Na_2CO_3 was used as a precipitating agent after oxidation [10]. The reaction of Na_2CO_3 with $Ce(NO_3)_4$ was following Equation (4) and Equation (5).

$$Na_2CO_3 + 2H_2O \rightarrow 2NaOH + CO_2\uparrow + H_2O \tag{4}$$
$$Ce(NO_3)_4 + 4NaOH \rightarrow Ce(OH)_4\downarrow + 4NaNO_3 \tag{5}$$

Separation of La and Nd by precipitation with NH_4OH at pH 8,5. In the hydroxide form the value of pK_{sp} of $La(OH)_3$ ~22.3, the pK_{sp} of $Ce(OH)_3$ ~ 19.82 and pK_{sp} of $Nd(OH)_3$ ~23.3.

$$(Nd.\ La)\ (NO_3)_3 + NH_4OH \rightarrow Nd(OH)_{3\ (s)} + NH_4NO_3 + La(NO_3)_{3\ (liquid)} \tag{6}$$

The last filtrate was La Nitrate, when oxalic acid was added, La oxalate ($La_2(C_2O_4)_3$) was precipitated. Reaction of La Nitrate with oxalic acid solution according to Equation (7).

$$2\ La(NO_3)_3 + 3\ H_2C_2O_4 \rightarrow La_2(C_2O_4)_3\ (s) + 3HNO_{3\ (liquid)} \tag{7}$$

1.2. Kinetics of oxidation reaction
As shown by the stoichiometric reaction, full oxidation of one mole of a target compound requires N moles of potassium permanganate. Typically, second-order reaction rate constants for the oxidation of VOC compounds by permanganate have been obtained using a pseudo-first-order approach by assuming that either the contaminant or permanganate concentration is constant.

2. Methodology
2.1. Materials & Equipment
The materials used were rare hydroxide (REOH) product from PTBGN, technical HNO_3, water, filter paper, $KMnO_4$, oxalic acid and ammonium hydroxide. All reagents used in this work were of technical grade and their solutions were prepared with distilled water.

Glass equipment, analytic scales, Ikamag heater stirrers, thermometers, ovens, and x-ray spectrometers (XRF) are used in this study.

2.2. Cerium Recovery
In the cerium recovery step, the RE nitrate solution was prepared by dissolving the RE-hydroxide in a nitric acid solution (14 mol L^{-1}). Solution sodium carbonate was prepared by dissolving the two salts in distilled water.

The experiments were carried out in beakers, under magnetic agitation, at 25 ± 1 °C temperature. A volume of 100 mL of a rare earth nitrate solution was used (10 grams of RE hydroxide in 25 mL HNO_3). The oxidation of Ce(III) to Ce(IV) through the addition of $KMnO_4$ (0.25 – 1.25 grams). The time of reaction was 15 – 75 minutes and temperature of reaction was 90 – 120 °C.

The precipitation of Ce(IV) was accomplished with Na_2CO_3 solution (15 wt.%). The pH control (pH = 4) throughout the experiment was carried out through manual addition of a Na_2CO_3 solution (15 grams /100 L). After precipitation, the solid was filtered and was washed with distilled water and then dried at 105 °C.

2.3. Separation of Nd and La
The neodymium was selectively precipitated from the filtrate as neodymium hydroxide with the addition of an ammonium hydroxide solution (15 wt.%) at a controlled pH 8,5. After precipitation, the solid was filtered and the filtrate was precipitated as lanthanum oxalate through the addition of an oxalic acid solution (15 wt.%). The neodymium hydroxide and lanthanum oxalate then dried at 105 °C. In all the stages of the experiment, the concentration of the rare earth elements was determined by X-ray spectrometer. In all the stages of the experiment, the concentration of the rare earth elements was determined by X-ray spectrometer.

3. Results and Discussion
The results of the composition of REOH (Feed) using XRF were presented in Table 1. In general the largest element content in REOH was Ce, followed by La and Nd.

Table 1. Composition of the rare earth hydroxide present in the samples

Component	Y^{3+}	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Gd^{3+}	Dy^{3+}
wt. %	2.14	17.12	31.15	0.36	11.38	6.72	1.01	0.47

3.1. Effect of $KMnO_4$/REOH ratio
3.1.1. Recovery of cerium hydroxide. The recovery of cerium through the investigated technique comprises two phenomena, namely, the oxidation of Ce(III) to Ce(IV) by MnO^{4-} (Eq. (3)), and the precipitation of Ce(IV) as hydroxide. As a strong oxidant agent, in nitrate medium, MnO_4^- is capable of oxidizing the nitric ion to NO_2 according to Equation (8):

$$2KMnO_4 + 2HNO_3 \Leftrightarrow K_2O + 2NO_2 + 2MnO_2 + H_2O + 4\ On \quad (8)$$

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To avoid competition between this reaction and the cerium oxidation reaction represented by Equation (5), the pH and the NO^{3-} concentration in the RE Nitrate solution must be controlled. At this point of the study, the influence of the weight of $KMnO_4$ or, the $KMnO_4$/REOH ratio and the reaction time and temperature of the cerium oxidation were investigated.

$$\text{Recovery of element}\,(\%) = \frac{\text{weight of element in the product}}{\text{weight of element in the feed}}\,x100\% \tag{9}$$

Element : Ce, La and Nd
Product : $Ce(NO_3)_4$, $Nd(OH)_3$ concentrate and $La_2(C_2O_4)_3$

Weight of element in the feed = wt,% x weight of REOH (10)
Weight of element in the product = wt,% x weight of product (11)

The effect of the $KMnO_4$ / REOH ratio was investigated in the range between 0.25/10 and 1.25/10. In this range, the weight ratio of $KMnO_4$ in the oxidant solution is affect the cerium recovery or purity. The use of Na_2CO_3 in the precipitant solution enhances the stability of the permanganate solution, which is more stable in basic medium, when compared with its stability in acid or neutral medium.
The composition (% weight) of cerium hydroxide ($Ce(OH)_4$) ranged from 70% to 94% when the $KMnO_4$/REOH ratio increased at the interval considered. The impurities in $Ce(OH)_4$ are $La(OH)_3$, $Nd(OH)_3$, water etc (Y, Dy, Gd, Mn). Thus, after an $KMnO_4$/REOH ratio 1.25/10, only a marginal rise was observed in the cerium recovery. However, the ratio of $KMnO_4$/REOH will did not affect the purity of the cerium (Figure 1). The amount of $KMnO_4$ not too much because the formed MnO_2 will contaminate $Ce(OH)_4$.

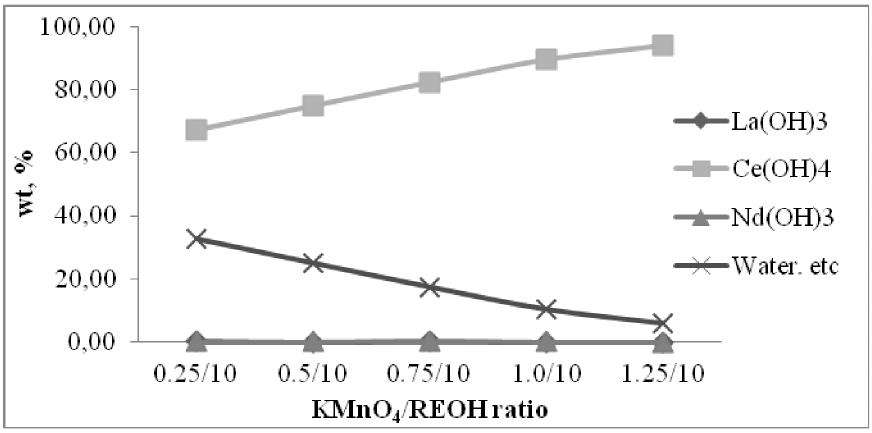

Figure 1. Influence of the $KMnO_4$/REOH ratio on the purity of the $Ce(OH)_4$

The recovery of cerium ranged from 47% to 89.0% when the $KMnO_4$/REOH ratio increased at the interval considered (Figure 2). The stoichiometric amount of $KMnO_4$ was 1.17 grams for 10 grams REOH or $KMnO_4$/REOH ratio was 1.17/10.

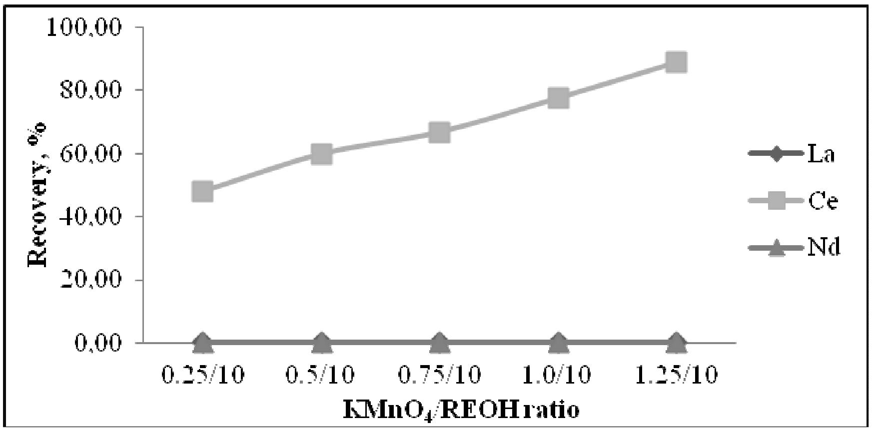

Figure 2. Influence of the $KMnO_4$/REOH ratio on the recovery of the cerium in $Ce(OH)_4$

Renata, et al. (2010), the recovery of cerium ranged from 40% to 99.9% when the excess of permanganate increased at the interval considered. Thus, after an excess of 30%, only a marginal rise was observed in the cerium recovery [10]. However, the excess of permanganate did not affect the purity of the cerium.

3.1.2. Recovery of neodymium hydroxide concentrate. The neodymium was selectively precipitated from the filtrate as neodymium hydroxide with the addition of an ammonium hydroxide solution (15 wt.%) at a controlled pH 8,5. The filtrate was RE (La, Nd) Nitrate. Reaction of RE (La, Nd) with ammonium hydroxide solution at pH 8,5 according to Equation (9).

The lanthanum was till in the filtrate. Figure 3 shows the composition (% weight) of neodymium hydroxide ($Nd(OH)_3$) concentrate ranged from 20% to 25% when the $KMnO_4$/REOH ratio increased at the interval considered. The impurities in $Nd(OH)_3$ concentrate are $La(OH)_3$, $Ce(OH)_3$, water etc. (Y, Ce, La, Dy, Gd, Mn). Thus, $KMnO_4$/REOH ratio, only a marginal rise was observed in the cerium recovery. However, the ratio of $KMnO_4$/REOH will did not affect the purity of the neodymium (Figure 3). The cerium recovery in $Ce(OH)_4$ was not perfect so it precipitated in $Nd(OH)_3$. The % weight of cerium in $Nd(OH)_3$ concentrate was decrease with increase of $KMnO_4$/REOH ratio.

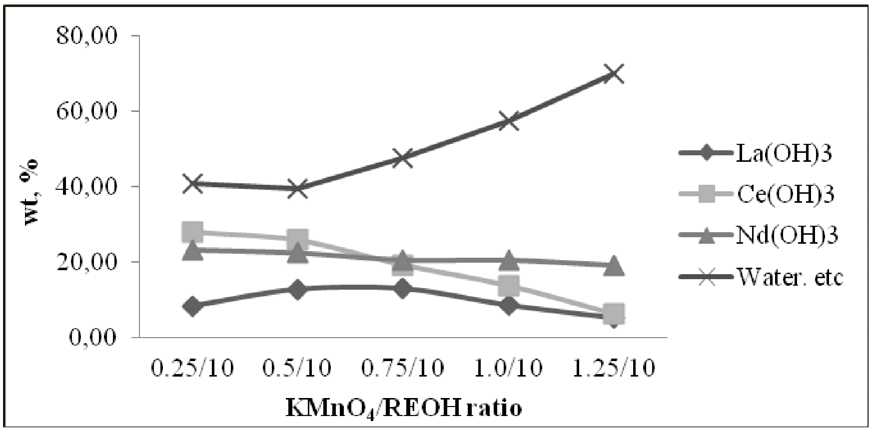

Figure 3. Influence of the $KMnO_4$/REOH ratio on the purity of the $Nd(OH)_3$ concentrate

The recovery of neodymium ranged from 85% to 93% when the $KMnO_4$/REOH ratio increased at the interval considered (Figure 4).

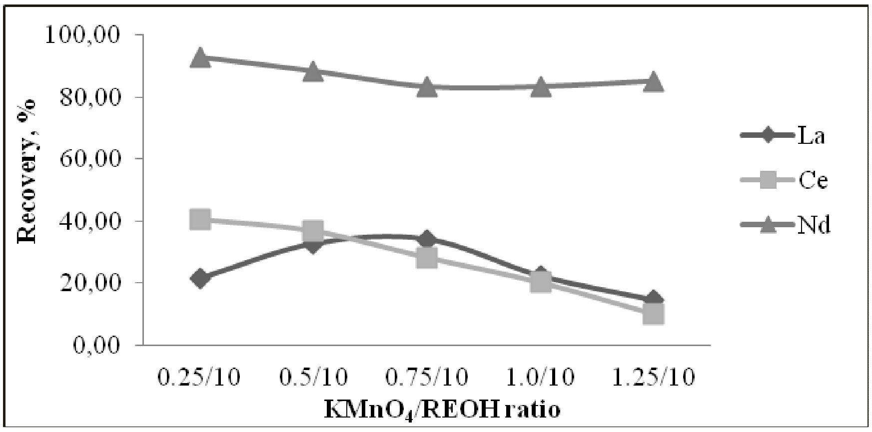

Figure 4. Influence of the $KMnO_4$/REOH ratio on the recovery of $Nd(OH)_3$

3.1.3. Recovery of lanthanum oxalate. The composition (% weight) of lanthanum oxalate ($La_2(C_2O_4)_3$) ranged from 60% to 90% when the $KMnO_4$/REOH ratio increased at the interval considered. The impurities in $La_2(C_2O_4)_3$ are $Ce_2(C_2O_4)_3$, $Nd_2(C_2O_4)_3$, water etc. (Y, Dy, Gd, Mn). Thus, $KMnO_4$/REOH ratio, only a marginal rise was observed in the cerium recovery. However, the ratio of $KMnO_4$/REOH will did not affect the purity of the neodymium (Figure 5).

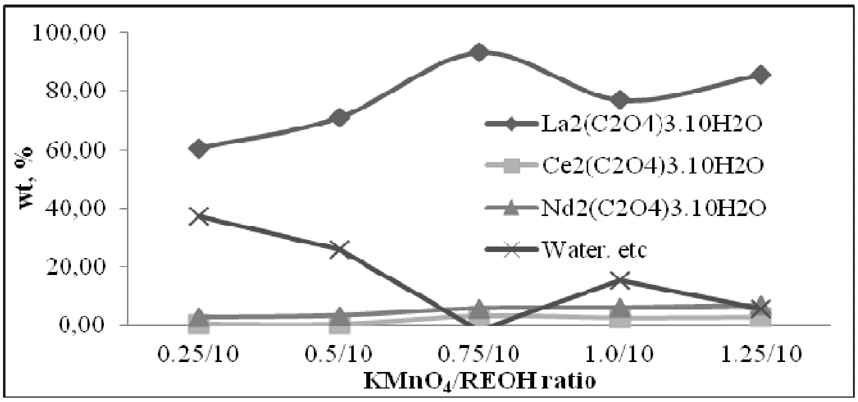

Figure 5. Influence of the $KMnO_4$/REOH ratio on the purity of the lanthanum oxalate

The recovery of lanthanum ranged from 53% to 70% when the $KMnO_4$/REOH ratio increased at the interval considered. (Figure 6).

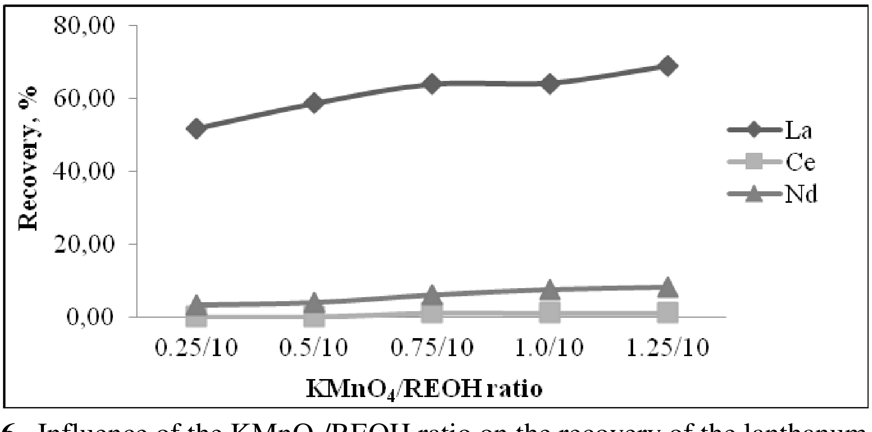

Figure 6. Influence of the $KMnO_4$/REOH ratio on the recovery of the lanthanum oxalate

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3.2. Effect of the oxidation reaction temperature

3.2.1. Recovery of cerium hydroxide. The effect of the temperature was investigated at temperature variations from 90°C to 120°C through the addition of $KMnO_4$/REOH ratio at 1/10. The highest temperature reached at the boiling point of 120°C. The composition (% weight) of cerium hydroxide ($Ce(OH)_4$) ranged from 70% to 90% when the temperature increased at the interval considered. The impurities in $Ce(OH)_4$ are $La(OH)_3$, $Nd(OH)_3$, water etc (Y, Dy, Gd, Mn). The oxidation reaction was complete when the temperature increased. The effect of temperature increased to the composition (% weight) of cerium hydroxide ($Ce(OH)_4$) was presented in (Figure 7).

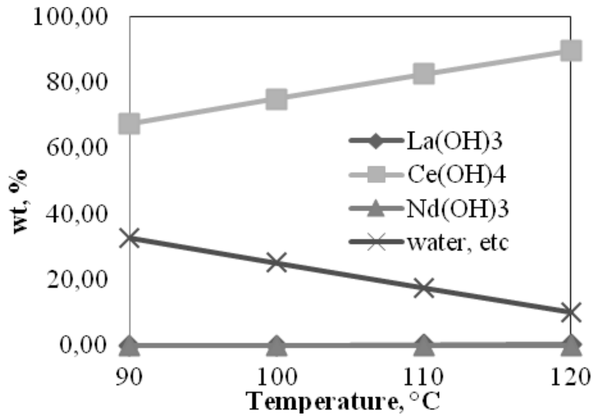

Figure 7. Influence of the temperature on the purity of the cerium hydroxide

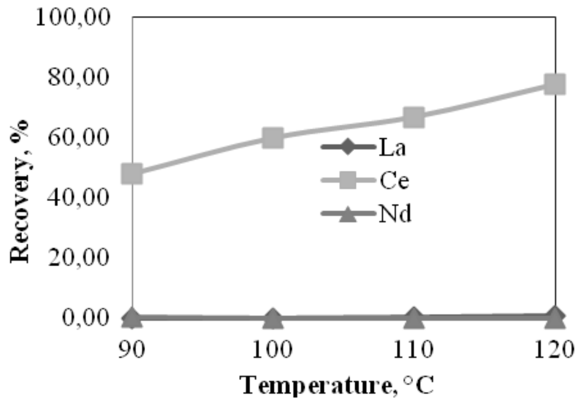

Figure 8. Influence of the temperature on the recovery of the cerium hydroxide

The recovery of cerium ranged from 47% to 80.0% when the temperature increased at the interval considered. (Figure 8).

3.2.2. Recovery of neodymium hydroxide. The composition (% weight) of neodymium hydroxide ($Nd(OH)_3$) concentrate ranged from 20% to 25% when the temperature increased at the interval considered. The impurities in $Nd(OH)_3$ concentrate are $La(OH)_3$, $Ce(OH)_3$, water etc (Y, Ce, La, Dy, Gd, Mn). Thus, the temperature, only a marginal rise was observed in the cerium recovery. However, the temperature will did not affect the purity of the neodymium (Figure 9). The cerium recovery in $Ce(OH)_4$ was not perfect so it precipitated in $Nd(OH)_3$. The % weight of cerium in $Nd(OH)_3$ concentrate was decrease with increase of temperature.

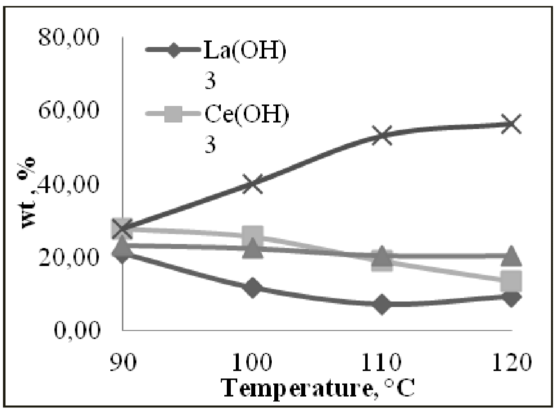

Figure 9. Influence of the temperature on the purity of the $Nd(OH)_3$ concentrate

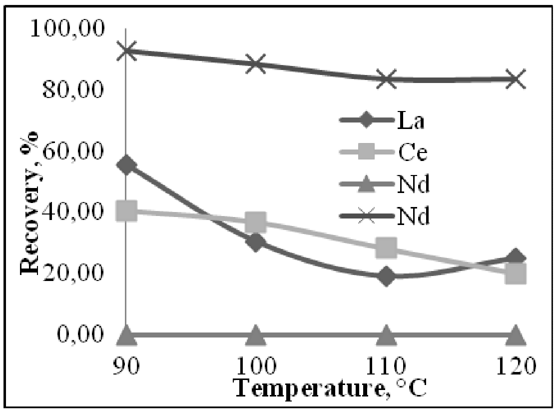

Figure 10. Influence of the temperature on the recovery of $Nd(OH)_3$ concentrate

The recovery of neodymium is ranged from 95% to 90% when the temperature increased at the interval considered. (Figure 10).

3.2.3. Recovery of lanthanum oxalate. The composition (% weight) of lanthanum oxalate ($La_2(C_2O_4)_3$) ranged from 60% to 95% when the temperature increased at the interval considered. The impurities in $La_2(C_2O_4)_3$ are $Ce_2(C_2O_4)_3$, $Nd_2(C_2O_4)_3$, water etc (Y, Dy, Gd, Mn). Thus, temperature only a marginal rise was observed in the cerium recovery. However, the ratio of KMnO4/REOH will did not affect the purity of the lanthanum (Figure 11).

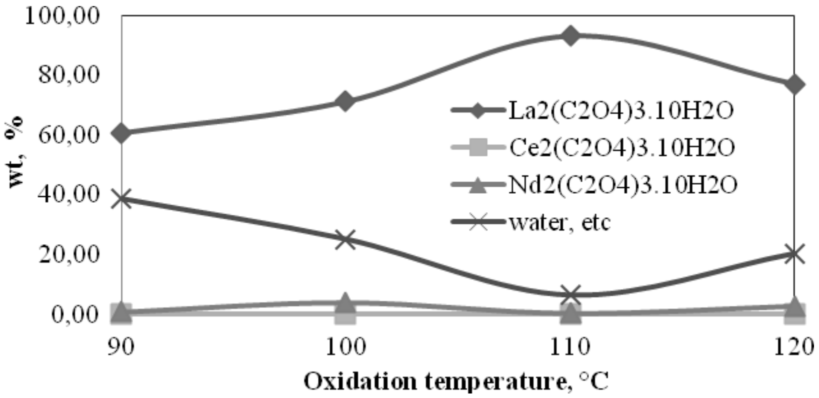

Figure 11. Influence of the temperature on the purity of the $La_2(C_2O_4)_3$

The recovery of lanthanum ranged from 51% to 65% when the temperature increased at the interval considered. (Figure 12).

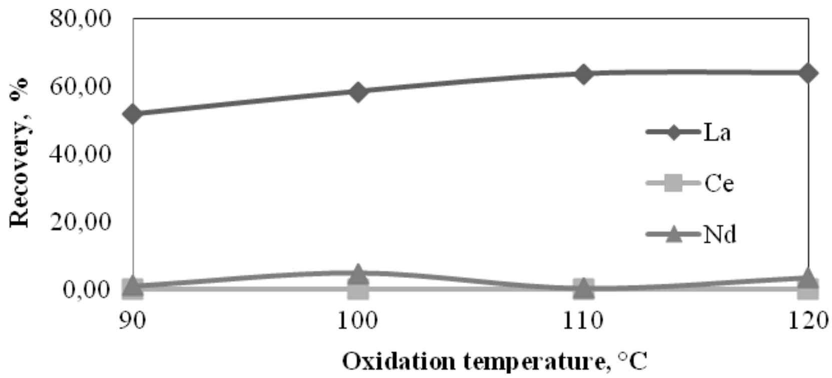

Figure 12. Influence of the temperature on the purity of the $La_2(C_2O_4)_3$

3.3. Effect of the oxidation time

3.3.1. Recovery of cerium hydroxide. The effect of oxidation time was investigated at the interval between 15 and 75 minute, at 120 °C at amount of $KMnO_4$/REOH ratio 1/10. The composition (%weight) of cerium hydroxide ($Ce(OH)_4$) ranged from 60% to 99% when the oxidation time increased at the interval considered. The impurities in $Ce(OH)_4$ are $La(OH)_3$, $Nd(OH)_3$, water etc (Y, Dy, Gd, Mn). The oxidation reaction was complete when the oxidation time increased. The effect of oxidation time increased to the composition (% weight) of cerium hydroxide ($Ce(OH)_4$) was presented in (Figure 13).

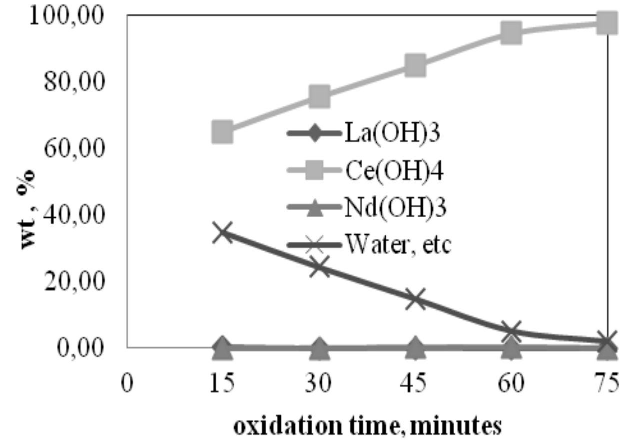

Figure 13. Influence of the oxidation time on the purity of the cerium hydroxide

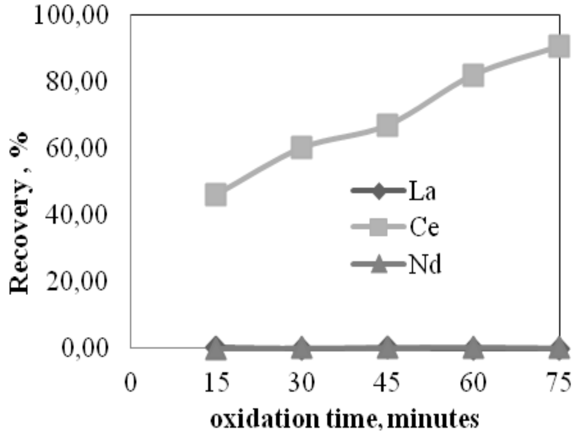

Figure 14. Influence of the oxidation time on the recovery of the cerium hydroxide

The recovery of cerium ranged from 47% to 93% when oxidation time increased at the interval considered. (Figure 14). A cerium precipitation yield higher than 99% takes the oxidation time need 150 minutes [10]. After drying the precipitate at 110°C, the chemical composition was determined as: 69.2% CeO_2, 14.5% MnO_2, 0.05% Pr_6O_{11}, 0.06% Nd_2O_3 and 16.0% H_2O. The content of cerium in the solution was 0.008 g L^{-1}, indicating a cerium precipitation yield higher than 99%. In this the chemical composition was determined 65.95% Ce element or 97.98% $Ce(OH)_4$, 0.04% Nd element or 0.05% $Nd(OH)_3$ and 1.97% H_2O etc.

3.3.2. Recovery of neodymium hydroxide. The composition (% weight) of neodymium hydroxide ($Nd(OH)_3$) concentrate ranged from 30% to 35% when the oxidation time increased at the interval considered. The impurities in $Nd(OH)_3$ concentrate are $La(OH)_3$, $Ce(OH)_3$, water etc (Y, Ce, La, Dy, Gd, Mn). Thus, the oxidation time, only a marginal rise was observed in the cerium recovery. However, the oxidation time will affect the purity of the neodymium (Figure 15). The cerium recovery in $Ce(OH)_4$ was not perfect so it precipitated in $Nd(OH)_3$. The % weight of cerium in $Nd(OH)_3$ concentrate was decrease with increase of temperature.

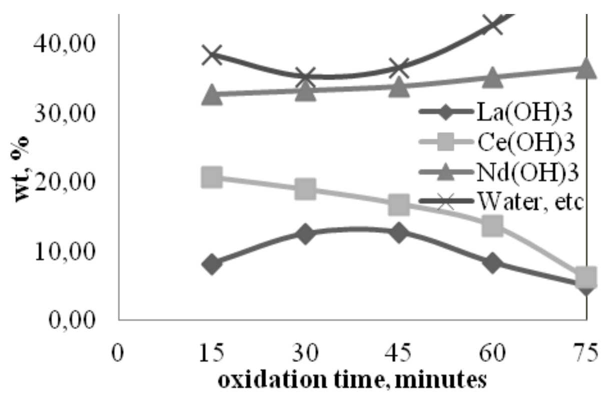

Figure 15. Influence of the oxidation time on the purity of the $Nd(OH)_3$ concentrate

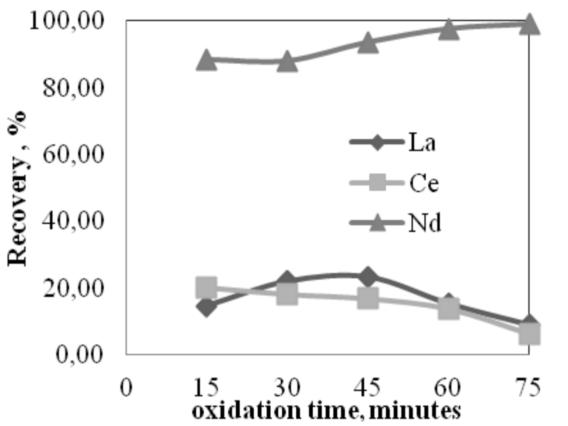

Figure 16. Influence of the oxidation time on the recovery of the $Nd(OH)_3$ concentrate

The recovery of neodymium ranged from 95% to 90% when the oxidation time increased at the interval considered. (Figure 16).

3.3.3. Recovery of lanthanum oxalate. The composition (% weight) of lanthanum oxalate ($La_2(C_2O_4)_3$) ranged from 63% to 97% when the oxidation time increased at the interval considered. The impurities in $La_2(C_2O_4)_3$ are $Ce_2(C_2O_4)_3$, $Nd_2(C_2O_4)_3$, water etc (Y, Dy, Gd, Mn). (Figure 17).

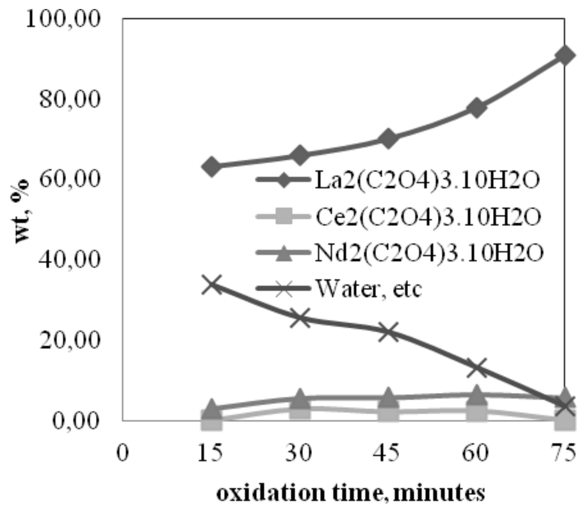

Figure 17. Influence of the oxidation time on the purity of the $La_2(C_2O_4)_3$

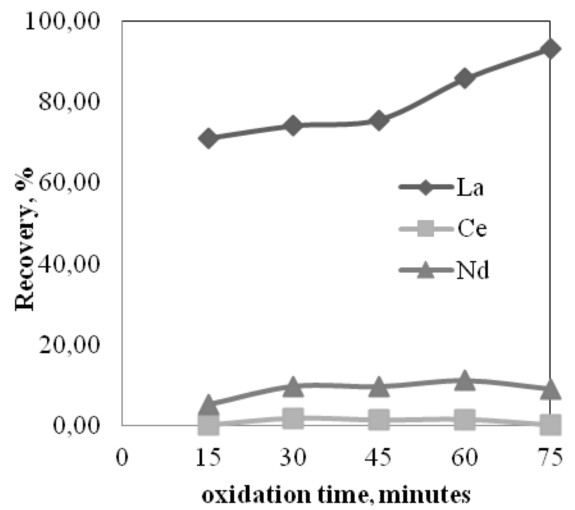

Figure 18. Influence of the oxidation time on the recovery of the $La_2(C_2O_4)_3$

The recovery of lanthanum ranged from 70% to 90% when the oxidation time increased at the interval considered. (Fig. 18).

3.4. Reaction order and rate reaction constant determination

The general form of a first and second-order reaction rate equation, as a function of the target compound and potassium permanganate concentrations in the aqueous phase, can be written as follows [11].

$$\frac{dC_A}{dt} = -kC_A C_B \tag{12}$$

We now reformulate Equation (12) in terms of consumed fraction of reactants, $X_A = (C_{A0} - C_A) / C_{A0}$) and $X_B(=(C_{B0} - C_B) / C_{B0})$. Here, C_{A0} is the initial concentration of target compound (M). The definition of P (= C_{B0} / C_{A0}), we have: $X_B = NX_A / P$. Substitution of these definitions into:

$$\frac{dX_A}{dt} = kC_{A0}(1 - X_A)(P - NX_A) \tag{13}$$

Integration of Equation (13) gives the following general formula for the variation of X_A with time:

$$\frac{1}{C_{A0}(P-N)} \ln\left[\frac{P - NX_A}{P(1-X_A)}\right] = kt \qquad \text{where } P \geq N \tag{14}$$

According to Equation (14), a plot of $[1/C_{A0}(P - N)]\ln[(P - NX_A) / P(1 - X_A)]$ vs. time should yield a straight line, with its slope being the second-order reaction rate constant k. The solution for X_B follows from Eq. (15) by substituting $X_A = PX_B / N$ to obtain:

$$\frac{P}{C_{B0}(P-N)}\ln\left[\frac{N(1-X_B)}{(N-PX_B)}\right]=kt \qquad \text{where } N \geq PX_B \tag{15}$$

The assumption for the commonly used pseudo-first-order approach of constant concentration of one of the reactants is only valid if the amount of the target compound or permanganate is sufficiently high to neglect any change in the concentration during the course of an experiment. If permanganate is in excess, this means that P/N is much larger than unity. Therefore, Equation (16) for such conditions may be simplified to yield:

$$\frac{1}{C_{B0}}\ln\left[\frac{C_A}{C_0)}\right]=-kt \qquad \text{where } P \geq N \tag{16}$$

To estimate k using the pseudo-first-order approach, Eq. (16) can be used with a constant concentration of permanganate, equal to its initial value.

In the calculation of reaction rate constant with first order reaction, it was needed the graph of time correlation with –ln (1-X) where X was conversion (mole) or recovery. Based on the equation (13), first order reaction was experimented for finding the reaction constants. The reaction rate was the overall reaction rate constant with the assumption that the concentration of HNO_3 was constant because its amount tends to approach 1, therefore it could be mentioned that the occurring reaction was first order. The calculation results could be seen in Figure 19. Calculation of the second order reaction rate constant required the time versus $[1/C_{A0}(P-N)]\ln[(P-NX_A)/P(1-X_A)]$ correlation graph in Figure 20.

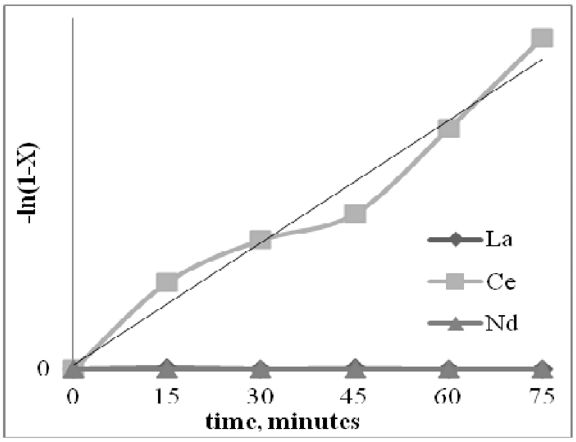

Figure 19. Correlation between time and - ln(1-X) for determining of k value and linearity of first order reaction

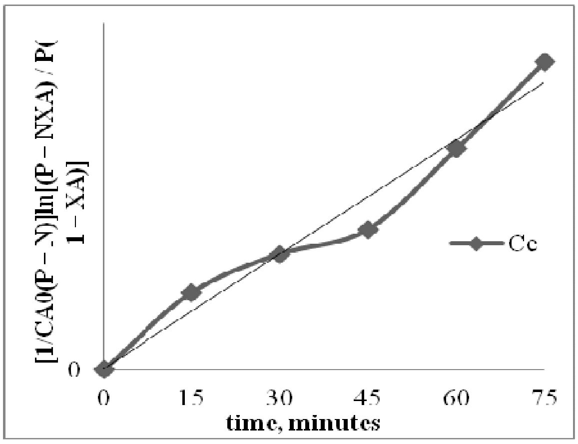

Figure 20. Correlation between time and $[1/C_{A0}(P-N)]\ln[(P-NX_A)/P(1-X_A)]$ for determining k value linearity of second order

Linear regression values were obtained from square root of R^2 as shown in Table 2.

Table 2. The equation and the value of linearity (R^2) in the first order reaction

	First order reaction	Second order reaction
La	y = 0 R² = #N/A	y = 0 R² = #N/A
Ce	y = 0.0291x + 0.0288 R² = 0.9697	y = 0.0879x + 0.0237 R² = 0.9674
Nd	y = 0 R² = #N/A	y = 0 R² = #N/A

Linearity values (R^2) of first order reaction (Table 2) were greater when compared to the linearity values (R^2) of second order reaction (Table 3), so it could be stated that the reaction was first order. The value of reaction rate constant of Ce was 0.0291 minutes^{-1}, the value of reaction rate constant of La and Nd were not applicable. The results showed that the oxidation rate of ethanol and toluene by permanganate, rather than employing the common pseudo-first-order kinetic analysis, we used a more realistic and accurate second-order formulation for the oxidation of target

Ferdowsi et al, 2017, did and optimizing and kinetics of leaching process of cerium, lanthanum and neodymium elements of apatite using nitric acid. The maximum leaching efficiency of which were 66.1%, 56.8% and 51.7% respectively for Ce, La and Nd, achieved under the optimum leaching conditions with nitric acid concentration of 18%, 0.06 ratio of solid to liquid and leaching time of 38 minutes, the activation energy of Ce of 6.54 kJ/mole [12].

4. Conclusion

The potassium permanganate as strong oxidator could be used to oxidize Ce^{+3} to Ce^{+4} The main variables affecting the cerium oxidation were: the ratio of the $KMnO_4$ /REOH, temperature and oxidation time. A ratio of 1.25/10 of $KMnO_4$ / REOH was necessary for full cerium recovery. The recovery of cerium increases as temperature and oxidation time rises, the purity of the product $Ce(OH)_4$ at the pH above 4. The process conditions were achieved in the use of 1.25 / 10 $KMnO_4$ / REOH ratio, at the 120^{o}C and the oxidation time of 75 minutes. The composition of the final product $Ce(OH)_4$ was 97.98 wt.% $Ce(OH)_4$, in a process yielding a recovery of Ce greater than 93%, were obtained. The composition of the final product $Nd(OH)_3$ concentrate was 37 wt.% $Nd(OH)_3$, in a process yielding a recovery of Nd greater than 98%, were obtained. The composition of the final product $La_2(C_2O_4)_3$ was 90 wt.% $La_2(C_2O_4)_3$, in a process yielding a recovery of La greater than 93%, were obtained. The oxidation of Ce^{3+} to Ce^{4+} using $KMnO_4$ follows first order reaction. The value of reaction rate constant of Ce was 0.0291 minutes^{-1}.

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References

[1] Stefania M and Marcello Ruberti 2013 "Rare earth elements as critical raw materials: Focus on international markets and future strategies"*Resour. Policy* **38** 36–43

[2] Koen B, Peter T J, Bart B, Ton V G, Yongxiang Y, Allan W and Matthias B 2013 “Recycling of rare earths : a critical review” *J. Clean. Prod* **51** 1–22

[3] Chen Z 2011 “Global rare earth resources and scenarios of future rare earth industry” *J. Rare Earths* **29** 1–6

[4] Tanushree D, Ki-Hyun K, Minori U, Eilhann E K, Byong-Hun J, Akash D and Seong-Taek Y 2016 “Global demand for rare earth resources and strategies for green mining” *Environ. Res.* **150** 182–190

[5] Farzaneh S, Fereshteh R and Ahmad A 2017 “Hydrometallurgical digestion and leaching of Iranian monazite concentrate containing rare earth elements Th, Ce, La and Nd” *Int. J. Miner. Process.* **159** 7–15

[6] L Berry, J Galvin, V Agarwal and M S Safarzadeh 2017 “Alkali pug bake process for the decomposition of monazite concentrates” *Miner. Eng.* **109** 32–41

[7] Lu Y, Zhang Z, Li Y and Liao W 2017 “Extraction and recovery of cerium (IV) and thorium (IV) from sulphate medium by an α -aminophosphonate extractant” *J. Rare Earths* **35** 34–40

[8] Chiranjib K G and Nagaiyar K 2005 *Extractive Metallurgy of Rare Earths*, first edition (Florida, Boca Raton: CRC Press)

[9] C S Kedari, S S Pandit and A Ramanujam 1999 "Studies on the in situ electrooxidation and selective permeation of cerium (IV) across a bulk liquid membrane containing tributyl phosphate as the ion transporter" *Separation Science and Technology* **34** 1907–1923

[10] Renata D A and Carlos A M 2010 "Purification of Rare Earth Elements from Monazite Sulphuric Acid Leach Liquor and The Production of High-purity Ceric Oxide" *Minerals Engineering* **23** 536–540

[11] Mojtaba G M, S Majid H and Niels H 2014 "Evaluation of the kinetic oxidation of aqueous volatile organic compounds by permanganate" *Science of The Total Environment* **485–486** 755-763

[12] Ferdowsi A, Yoozbashizadeh H 2017 "Process Optimization and Kinetics for Leaching of Cerium, Lanthanum and Neodymium Elements from Iron Ore Waste's Apatite by Nitric acid" *Transactions of Nonferrous Metals Society of China* **27** 420–428