Purification of rare earth elements from monazite sulphuric acid leach liquor and the production of high-purity ceric oxide

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ABSTRACT

The present work describes the development of an efficient and relatively simple process to obtain high grade CeO_2 from sulphuric acid leach liquor. The liquor was obtained through acid digestion of monazite. The steps investigated in the process for obtaining ceric oxide were: (i) purification of the RE elements through their precipitation as rare earth and sodium double sulphate ($NaRE(SO_4)_2 \cdot xH_2O$), (ii) $NaRE(SO_4)_2 \cdot xH_2O$ conversion into RE-hydroxide ($RE(OH)_3$) through metathetic reaction and (iii) recovery of cerium and (iv) purification of cerium from the mixture of ceric hydroxide and manganese dioxide precipitate through dissolution of the solid with HCl and precipitation of the cerium through the addition of oxalic acid ($H_2C_2O_4$) or ammonium hydroxide (NH_4OH) solution. The X-ray diffraction spectra of the double sulphate obtained indicated the presence of monohydrated double sulphate. X-ray diffraction and chemical analysis indicated that the precipitation should be carried out at 70 °C and at 1.1 times the stoichiometric ratio of NaOH. An excess of 30% of $KMnO_4$ was necessary to separate cerium from the other RE elements. Both oxalic acid and ammonium hydroxide proved efficient in the precipitation of cerium from the mixture of Ce/Mn obtained in the cerium separation. Following purification, calcinated products were obtained, assaying between 99% and 99.5% CeO_2. The cerium recovery yield was greater than 98%.

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1. Introduction

Rare earth (RE) elements are a group of chemical elements that includes all the lanthanides, yttrium and scandium. Given their particular spectroscopic and magnetic properties, the RE elements play an important role in many fields of advanced materials science; therefore, industrial demand for them has increased (Martins and Isolani, 2005). The rare earth elements are found together in nature, in various minerals, such as bastnasite, monazite, xenotime, amongst others (Gschneidner, 1980; Sundaram, 1987).

Monazite is one of the most abundant rare earth (RE) minerals found in nature. The chemical treatment of monazite can be carried out via the alkaline route through sodium hydroxide addition or via the acid route by means of sulphuric acid digestion. The rare earth leach liquor produced through digestion with sulphuric acid also contains other elements such as, U, Th and Fe. The high commercial value of the rare earth elements depends on their purity and the quality of their compounds.

In order to purify the liquor, the RE elements are usually precipitated in the form of rare earths and sodium double sulphate ($NaRE(SO_4)_2 \cdot xH_2O$) through the addition of sodium sulphate according to Eq. (1):

$$Na^+ + RE^{+3} + 2SO_4^{2-} + xH_2O \Longleftrightarrow NaRE(SO_4)_2 \cdot xH_2O \qquad (1)$$
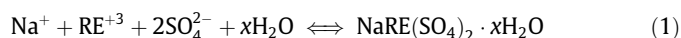
As the RE-Na double sulphate is only slightly soluble in acid solutions, in order to achieve its dissolution aiming at the separation of the RE into individual elements, the double sulphate is converted into a high soluble compound, such as RE-hydroxide (Gupta and Krishnamurthy, 1992).

The conversion of the RE-Na double sulphate into RE-hydroxide was carried out by metathetic reaction through the addition of NaOH according to Eq. (2):

$$NaRE(SO_4)_2 \cdot xH_2O + 3NaOH \Longleftrightarrow RE(OH)_3 + 2Na_2SO_4 + xH_2O \qquad (2)$$
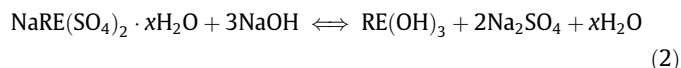
The influence of the process variables on the double sulphate precipitation and on its conversion into RE-hydroxide is rarely mentioned in literature. Kul et al. (2008) investigated the precipitation of the RE-Na double sulphate from a bastnasite sulphuric leach liquor. In their study, the Na_2SO_4 excess was smaller than that employed in the present research, however the yttrium recovery was also smaller.

The separation of natural RE mixtures into individual elements is very difficult to achieve, due to the similarity of their chemical and physical properties. In aqueous solutions, the RE elements present as trivalent cations. Cerium is the most likely to oxidize to its tetravalent state and, given this property, its separation is

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generally the easiest. In the tetravalent form, cerium ions exhibit markedly a different chemical behaviour if compared to the other trivalent rare earth ions (Gupta and Krishnamurthy, 1992; Topp, 1965). 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 (Gupta and Krishnamurthy, 1992; Callow, 1967).

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 (Topp, 1965; Fritz et al., 1963; Kedari et al., 1999; Donohue, 1979; Hirai and Komasawa, 1996).

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 (Gupta and Krishnamurthy, 1992; Donohue, 1979; Callow, 1967). 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 ($K_{sp} \sim 10^{-22}$) (Topp, 1965).

Oxidation through permanganate solution leads to simultaneous precipitation of $Ce(OH)_4$ and MnO_2 (Eq. (3)). After precipitation, the solids need to be purified if a high purity product is desired (Morais et al., 2003).

$$3Ce^{3+} + MnO_4^- + 4H^+ \iff 3Ce^{4+} + MnO_{2(s)} + 2H_2O$$
$$\Delta E^\circ_{298\,K} = 0.24\,V \tag{3}$$
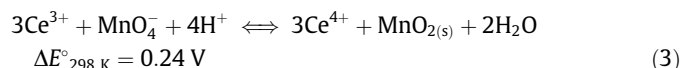
This study proposes a methodology which consists of: (i) purification of the RE elements through $(NaRE(SO_4)_2 \cdot xH_2O)$ precipitation, (ii) conversion of $NaRE(SO_4)_2 \cdot xH_2O$ into RE-hydroxides $(RE(OH)_3)$ through metathetic reaction, (iii) selective precipitation and (iv) purification of cerium.

The effects of the main variables involved in the precipitation of the double sulphate and its conversion into RE-hydroxide, such as nature and excess of the precipitation agent, temperature and reaction time, were investigated. In the precipitation and purification of cerium, the process variables assessed were: final pH, molar ratios of $KMnO_4/Na_2CO_3$, $KMnO_4$ excess and precipitation reaction time.

2. Experimental

2.1. Reagents and solutions

The RE liquor used in this experiment – supplied by INB (Indústrias Nucleares do Brasil) – was produced through monazite digestion with sulphuric acid. Prior to the processes investigated in the present study, uranium and thorium were removed from the liquor by solvent extraction (Amaral and Morais, in press). Table 1 presents the chemical composition of the leach liquor.

The compositions of the feed and intermediate products used in this study are presented in Table 1; they are sulphuric liquor after

the removal of thorium and uranium, double sulphate obtained from the sulphuric liquor, rare earth hydroxide obtained from the double sulphate and chloride solution obtained from the rare earth hydroxide. The content of the RE elements in the sulphuric liquor are presented.

In the double sulphate precipitation experiments, Na_2SO_4 and NaCl were added as solids and NaOH was used as an aqueous solution. In the cerium recovery step, the RE chloride solution was prepared by dissolving the RE-hydroxide in a hydrochloric acid solution (2.0 mol L^{-1}). The mixture of potassium permanganate and sodium carbonate (both at 0.2 mol L^{-1}) was prepared by dissolving the two salts in distilled water. In the cerium purification, the precipitate contaminated with manganese was dissolved with the addition of a 3.0 mol L^{-1} hydrochloric acid solution at 70 °C.

All reagents used in this work were of analytical grade and their solutions were prepared with distilled water. In all the stages of the experiment, the concentration of the rare earth elements were determined by an energy-dispersive X-ray spectrometer (Kevex system) (Morais and Ciminelli, 2001, 2004), X-ray diffraction and chemical analysis.

2.2. Experimental procedure

2.2.1. Double sulphate precipitation

The double sulphate precipitation experiments were carried out in beakers placed in a water bath for temperature control, mechanical agitation and pH control. The precipitate was then filtered, washed with distilled water and dried at 100 °C.

2.2.2. Conversion to RE-hydroxide

The conversion of the double sulphate into hydroxide was carried out in beakers, under mechanical agitation for 1 h. Then, the RE-hydroxide was filtered, washed with distilled water and dried at 100 °C. The RE-hydroxide conversion experiments were carried out at 25 and 70 °C using different stoichiometric ratios of NaOH.

2.2.3. Cerium recovery

The experiments were carried out in beakers, under magnetic agitation, at 25 ± 1 °C. A volume of 100 mL of a rare earth chloride solution was used. The oxidation of Ce(III) to Ce(IV) and the precipitation of Ce(IV) was accomplished through the addition of a mixture of $KMnO_4$ and Na_2CO_3 (both 0.2 mol L^{-1}). The pH control throughout the experiment was carried out through manual addition of a Na_2CO_3 solution (0.25 mol L^{-1}). After precipitation, the solid was filtered in a vacuum Buchner filter and was washed with distilled water and then dried at 100 °C.

2.2.4. Cerium purification

The solid composed of ceric hydroxide and manganese dioxide was then dissolved in a 3.0 mol L^{-1} HCl solution at 70 °C using 5% of solids, in one hour of mechanical agitation. The cerium was selectively precipitated as cerium oxalate through the addition of an oxalic acid solution (10 wt.%) or as cerium hydroxide with the addition of an ammonium hydroxide solution (3.0 mol L^{-1}) at a

Table 1
Composition of the main species present in the samples used in this study.

Sample/content	RE_2O_3[a]	Ce^{+3}	Fe^{+3}	PO_4^{-3}	SO_4^{2-}	Na^+	Cl^-
Sulphuric liquor (g L^{-1})[b]	37.8	14.8	0.54	20.2	94.0	–	–
Double sulphate (wt.%)	43.6	17.5	<0.001	0.95	50.6	6.0	–
RE-hydroxide (wt.%)	80.2	31.7	<0.001	0.08	0.80	0.13	–
Chloride solution (g L^{-1})	40.6	16.0	<0.001	0.04	0.40	0.08	26.2

[a] RE_2O_3 = total rare earth oxide.
[b] Density = 1.122 g mL^{-1}.

controlled pH. Finally, the product was calcinated in a porcelain crucible for one hour at 900 °C to produce the cerium oxide (CeO_2).

3. Results and discussion

3.1. Precipitation of the RE and Na double sulphate

3.1.1. Effect of the precipitation agent

The efficiency of the precipitation of RE elements from sulphuric liquor was investigated with the use of three different reagents: sodium chloride (NaCl), sodium sulphate (Na_2SO_4) in its solid form and a 2 mol L^{-1} sodium hydroxide (NaOH) solution, at room temperature (25 ± 1 °C). The amount of the reagents added was two times the stoichiometric ratio and the reaction time was 2 h. The RE recovery was 93.7%, 91.2% and 86.5%, respectively when NaOH, Na_2SO_4 and NaCl was used, thus indicating higher efficiency of the NaOH and Na_2SO_4.

3.1.2. Effect of the amount of reagents on the RE precipitation

The amount of the reagent added ranged from 1.5 to 11 times the stoichiometric amount, at 70 ± 1 °C. Fig. 1a presents the RE recovery through an added amount of the reagents NaOH and Na_2SO_4. Fig. 1b shows the relation between the soluble RE elements and the amount of Na_2SO_4 added.

The ratio of RE elements recovery is almost the same when either NaOH or Na_2SO_4 is used (Fig. 1a). The RE recovery was approximately 98% when the stoichiometric amount of the reagent was two times as high. However, under this condition the content of yttrium in the filtrate is 0.5 g L^{-1} and its recovery was only 31% (Fig. 1b). This low recovery occurs due to the higher solubility of the heavy RE when compared with the light and medium RE. In order to reach an yttrium recovery of over 99%, the stoichiometric amount of NaOH and Na_2SO_4 had to be raised to values 8.5 times as high (Fig 1a). One may also observe that when the stoichiometric amount of the reagents increases from 2 to 8 times, the improvement on the recovery of the total RE is insignificant (from 98.5% to 99.5%). The increase in the amount of the reagent added is only justifiable if the recovery of yttrium is of concern.

The contamination of the double sulphate with iron was observed in the NaOH experiments. The Fe concentration was 90 μg g^{-1} when 1.5 times the stoichiometric amount of NaOH was used and 3200 μg g^{-1} for 8.5 times the stoichiometric amount of the added NaOH. For the Na_2SO_4 reagent the Fe concentration was 70 μg g^{-1} for any added amount.

As this paper concerns academic research, the following experiments to obtain the RE double sulphate were carried out with the Na_2SO_4 stoichiometric ratio 8.5 times as high.
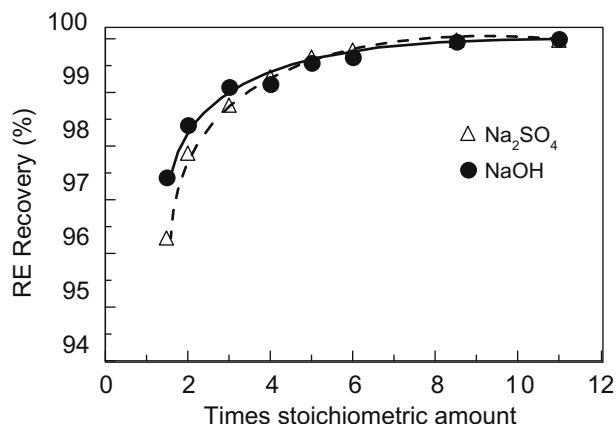
Fig. 1a. Effect of the amount of NaOH and Na_2SO_4 added in the RE elements recovery.
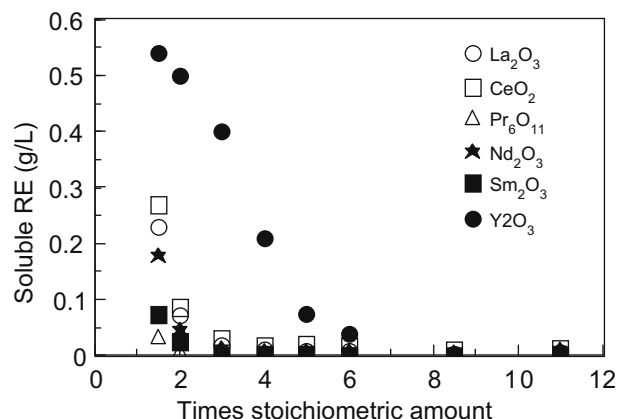
Fig. 1b. Concentration of the soluble RE elements in the filtrate when Na_2SO_4 is used.

3.1.3. Effect of temperature

The effect of the temperature was investigated at temperature variations from (25 ± 1 °C) to (80 ± 1 °C) through the addition of Na_2SO_4 at 8.5 the stoichiometric ratio. Over the temperature range investigated, apart from yttrium recovery, no significant influence of temperature on the recovery of the other RE elements is observed. If a complete precipitation of yttrium is pursued, 70 ± 1 °C is the optimum temperature. For a smaller amount of Na_2SO_4, e.g. three times the stoichiometric ratio, a temperature of 70 °C would also be required for the precipitation of all rare earth elements.

3.1.4. Effect of time

The effect of time was investigated at the interval between 0.5 and 3 h, at 70 ± 1 °C at 8.5 times the stoichiometric amount of Na_2SO_4. The lanthanides recovery was 99.2% after a period of 1 h; however the yttrium recovery was only 67%. After a period of 2 h the lanthanides and yttrium recovery was 99.9% and 99.4%, respectively.

3.1.5. Characterization of the RE-Na double sulphate

The double sulphate, obtained by precipitation with Na_2SO_4, was characterized by X-ray diffraction and chemical analysis. The X-ray diffraction spectra indicated the presence of monohydrated double sulphate, mainly $CeNa(SO_4)_2·H_2O$ and $LaNa(SO_4)_2·H_2O$. The chemical analysis indicated 50.6 wt.% of SO_4^{2-} and 6.0 wt.% of Na^+. As the density of the sulphuric liquor is 1.122 g mL^{-1}, the RE elements, which were 3.37% (37.8 g L^{-1}) in the sulphuric liquor, increased to 43.6% in the double sulphate. The content of iron, which was 0.54 g L^{-1} (0.048%) in the sulphuric liquor, was reduced to values lesser than 0.001% in the double sulphate, while the phosphate dropped from 20.2 g L^{-1} (1.8%) to 0.95%, indicating the efficiency of the process (Table 1). The yield of the process depends on the excess of Na_2SO_4 used – around 98% for two times the stoichiometric amount of Na_2SO_4 and higher than 99.9% for eight times its stoichiometric amount. In the latter case, the concentration of the RE elements remaining in the solution was 0.023 g L^{-1} (see Table 2).

3.2. Conversion of double sulphate into RE-hydroxides (RE(OH)₃)

The conversion of double sulfate into hydroxide was carried out by metathetic reaction through NaOH addition. In this experiment the temperature and the excess of NaOH were investigated. The effect of the temperature was checked at the interval between 25 °C (room temperature) and 70 °C using a 2.0 mol L^{-1} NaOH solution. The amount of NaOH ranged from amounts smaller than the stoi-

Table 2
Content of the RE elements in the sulphuric liquor.

| RE elements	La	Ce	Pr	Nd	Sm	Gd	Tb	Dy	Y
Content (g L^{-1})	6.76	14.8	1.71	6.08	0.87	0.56	0.03	0.13	0.57

chiometric (0.6 times) to 1.25 times the stoichiometric value and the reaction time was 1 h.

The solids obtained in this study were characterized by X-ray diffraction and chemical analysis. Table 3 shows the influence of the stoichiometric amount of NaOH and the temperature on the conversion of the double sulphate.

The study found that the best results were achieved when the conversion was carried out at 70 °C, 1.05–1.25 times the stoichiometric amount of NaOH, when a smaller content of sulphate was achieved. The best crystalline phase was obtained when the experiment was carried out at 70 °C and 1.10 times the stoichiometric amount NaOH. According to the chemical analyses and considering the sulphate and sodium content, around 2% of the solid remains as double sulphate after the conversion, indicating a conversion yield of 98%. The sulphate content, which was 50.6% in the double sulphate, dropped to 0.80% in the RE(OH)$_3$, while the sodium fell from 6.0% to 0.13% and phosphate dropped from 0.91% to 0.04% (Tables 1 and 3). The content of rare earths in the solution was lesser than 0.001 g L^{-1}, indicating no solubilisation of the RE elements in this step of the process.

3.3. Recovery of cerium

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 chloride medium, MnO$_4^-$ is capable of oxidizing the chloride ion to Cl$_2$ according to Eq. (4):

$$2MnO_4^- + 8H^+ + 6Cl^- \iff 3Cl_2 + 2MnO_{2(s)} + 4H_2O$$
$$\Delta E°_{298\ K} = 0.32\ V \tag{4}$$
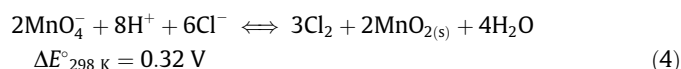
To avoid competition between this reaction and the cerium oxidation reaction represented by Eq. (3), the pH and the Cl$^-$ concentration in the RE chloride solution must be controlled. At this point of the study, the influence of the initial and final pH, the excess of KMnO$_4$, the KMnO$_4$/Na$_2$CO$_3$ ratio and the reaction time of the cerium oxidation/precipitation were investigated.
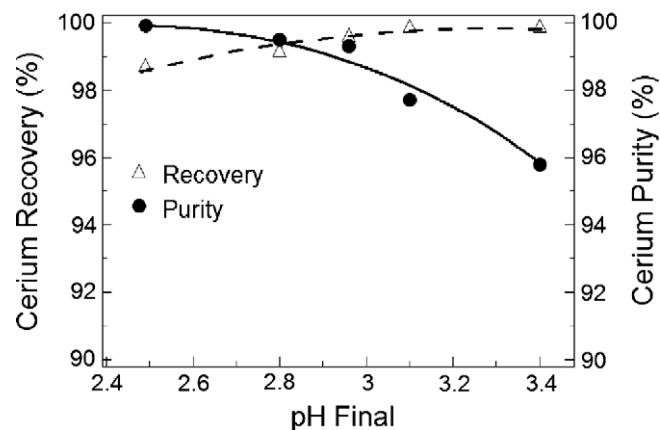
3.3.1. KMnO$_4$/Na$_2$CO$_3$ molar ratio

The effect of the KMnO$_4$/Na$_2$CO$_3$ molar ratio was investigated in the range between 0.2/0 and 0.2/0.4. In this range, the molar ratio of KMnO$_4$/Na$_2$CO$_3$ in the oxidant solution does not affect the cerium recovery or purity. The use of Na$_2$CO$_3$ in the oxidant 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.

Fig. 2. Influence of the final pH on cerium recovery and purity–purity in relation with the RE elements.

3.3.2. Effect of pH

Another important variable affecting the cerium recovery is the pH. The initial and final pH was investigated. The final pH was tested in the range between 2.5 and 3.5. For initial pH lesser than 1, the KMnO$_4$ consumption increases due to the oxidation of the chloride ions (Eq. (4)). In the final pH control, it was verified that when the pH rises from 2.5 to 3.5, the cerium recovery rises, however the purity of the cerium decreases (Fig. 2). In accordance with the graph, the ideal pH is 3.0.

3.3.3. Effect of excess permanganate

In the present study, the excess of permanganate was investigated in the range between 10% and 50%. 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. However, the excess of permanganate did not affect the purity of the cerium (Fig. 3).

3.3.4. Effect of the reaction time on the oxidation and precipitation of cerium

The process was investigated in various experiments with duration between 15 and 150 min. The time recording started when all of the content of the oxidation agent was added and the final pH was set to a desired level. Fifteen minutes was sufficient to lead the cerium to a full precipitation. This was therefore the time adopted.

According to the X-ray diffraction patterns, only amorphous precipitates were obtained, regardless of the time. The precipitate was analysed through XPS in order to identify the presence of Mn(IV). Mn 2p XPS measurements allowed the determination of MnO$_2$ in the precipitate. After drying the precipitate at 110 °C, the chemical composition was determined as: 69.2% CeO$_2$, 14.5% MnO$_2$, 0.05% Pr$_6$O$_{11}$, 0.06% Nd$_2$O$_3$ and 16.0% H$_2$O. The content of cerium in the solution was 0.008 g L^{-1}, indicating a cerium precipitation yield higher than 99%.

Table 3
Experimental conditions and characterization of the conversion product by X-ray diffraction and chemical analysis.

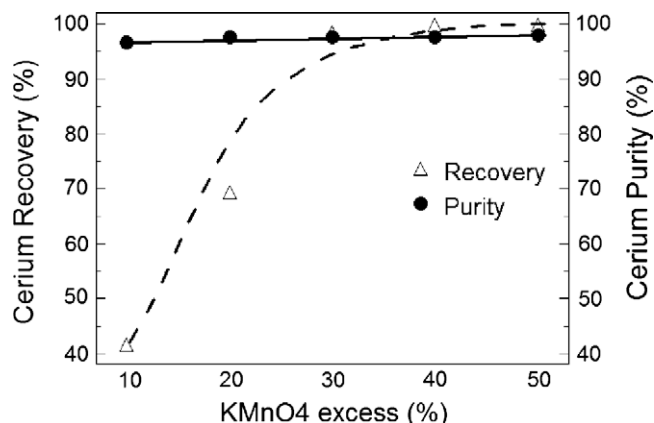| Stoichiometric amount of NaOH	Temperature (°C)	X-ray data	Chemical analysis (wt.%)	
			Na	SO$_4^{-2}$
0.6–0.8 times	25 ± 1	Amorphous phases and RE$_2$SO$_4$(OH)$_4$·2H$_2$O	0.6	21.8
0.6–0.8 times	70 ± 2	Amorphous phases, RE(OH)$_3$ and RE$_2$SO$_4$(OH)$_4$·2H$_2$O	0.3	22.4
1.05–1.25 times	25 ± 1	Amorphous phases and RE(OH)$_3$	0.14	9.8
1.05–1.25 times	70 ± 2	RE(OH)$_3$	0.13	0.80

Fig. 3. Influence of the excess of permanganate on the recovery and purity of the cerium–purity in relation with the RE elements.

3.4. Cerium purification

The precipitate from the cerium recovery process, containing cerium and manganese was dissolved by addition of 3 mol L^{-1} HCl at 70 °C, using 5% of solids.

During dissolution, the chloride ions (Cl$^-$) were oxidized to Cl^0 with liberation of Cl$_2$, according to Eq. (5):

$$2Ce^{4+} + 2Cl^- \iff 2Ce^{3+} + Cl_{2(g)} \quad \Delta E°_{298\ K} = 0.08\ V \tag{5}$$
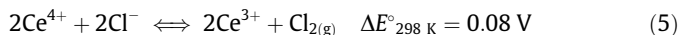
After dissolution, the cerium was selectively precipitated as cerium oxalate with the addition of a 10 wt.% oxalic acid solution, using an excess of 10% of the reagent, or cerium hydroxide with the addition of a 3.0 mol L^{-1} ammonium hydroxide solution at controlled pH.

The cerium precipitation experiments with ammonium hydroxide were conducted within a pH range between 5.0 and 8.0. For ammonium hydroxide at pH 5.0 and 7.0, no cerium hydroxide was precipitated. At pH 8.0 the yield was 99.8% and the manganese concentration in the cerium hydroxide precipitate was 0.42 wt.%. For oxalic acid, the yield was 98.1% and the manganese concentration in the precipitate was 0.07 wt.%.

Finally, the product was calcinated in a porcelain crucible for one hour at 900 °C in order to produce the cerium oxide (CeO$_2$). The chemical composition of the calcinated products was: cerium hydroxide – 99% CeO$_2$, 0.81% MnO$_2$, 0.10% Pr$_6$O$_{11}$, 0.10% Nd$_2$O$_3$; cerium oxalate – 99.5% CeO$_2$, 0.11% MnO$_2$, 0.10% Pr$_6$O$_{11}$, 0.10% Nd$_2$O$_3$. The cerium recovery yield for the overall process was greater than 98%.

4. Conclusions

The study of the main variables of the process of achieving double sulphate precipitation and its conversion into RE-hydroxide was an important step in the selection of the ideal conditions for the experiments. Amongst the precipitating agents studied, Na$_2$SO$_4$ turned out to be the most efficient. The precipitation of the lanthanides may be carried out using 2–3 times the stoichiometric ratio of the sodium sulphate at 70 °C. In such case, the yttrium precipitation reached only about 40 wt.%. In order to precipitate all the yttrium, eight times the stoichiometric amount of the sodium sulphate was required and the optimum temperature necessary was around 70 °C. The X-ray diffraction spectra detected the presence of monohydrated double sulphate. X-ray and chemical analysis indicated that the conversion of NaRE(SO$_4$)$_2$·H$_2$O to RE(OH)$_3$ should be carried out at 70 °C at 1.1 times the stoichiometric ratio of the NaOH.

The main variables affecting the cerium oxidation/precipitation were: the acidity of the rare earth chloride solution, the pH of the cerium precipitation and the KMnO$_4$ excess. An excess of 30% of KMnO$_4$ was necessary for full cerium recovery. The recovery of cerium increases as the final pH rises, however the purity of the final product (CeO$_2$) decreases as the pH rises above 3. Both oxalic acid and ammonium hydroxide proved efficient in the purification of cerium from Ce/Mn solutions. Following purification, calcinated products assaying 99 and 99.5 wt.% CeO$_2$, in a process yielding a recovery greater than 98%, were obtained.

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