



PROCESSING OF SULFURIC LIQUOR TO OBTAIN RARE EARTH CONCENTRATES AND SELECTIVE CERIUM REMOVAL BY THERMAL OXIDATION

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ABSTRACT

The mixed rare earth oxalates and carbonates were obtained from a sulfuric liquor purified in two consecutive steps: addition of limestone pulp 10% m/m up to a pH up to 3.5 and dosage of lime pulp 10% m/m up to a pH of 5.0. The REO (Rare Earth Oxides) losses were only of 8.3% m/m, all Fe^{3+} , PO_4^{3-} and Th^{4+} ions were removed and there was reduction of 99%, 87% and 37% in the Al^{3+} , UO_2^{2+} and SO_4^{2-} concentrations, respectively. The x-ray diffraction of the product from the calcination of the mixed rare earth oxalates, at 1100°C in a muffle, showed that the final product was a mixture of Ce_2O_3 and CeO_2 , represented by Ce_4O_7 . On the other hand, it was formed an intermediate crystalline structure in the oxides obtained by calcination of the mixed rare earth carbonates calcined in the same condition, which one was identified as $(\text{Nd}_{0.40}\text{Ce}_{0.60}\text{O}_{1.80}+\text{CeO}_2)$. The Ce_4O_7 was completely dissolved by a HCl solution 12 mol.L⁻¹, whereas the cerium from $(\text{Nd}_{0.40}\text{Ce}_{0.60}\text{O}_{1.80}+\text{CeO}_2)$ was not solubilized. Therefore, the x-ray diffractions of the cerium oxides, obtained by calcination of pure cerium oxalate and pure cerium carbonate at the same condition in the muffle, showed the formation of the crystalline structures identified as CeO_2 , which ones were not dissolved by HCl solution 12 mol.L⁻¹.

KEYWORDS: Sulfuric Liquor, Rare Earth Elements, Thermal Oxidation, Cerium.

PROCESSAMENTO DO LICOR SULFÚRICO PARA OBTENÇÃO DOS CONCENTRADOS DE TERRAS RARAS E REMOÇÃO SELETIVA DO CÉRIO POR OXIDAÇÃO TÉRMICA

RESUMO

Os oxalatos e os carbonatos mistos de terras raras foram obtidos a partir do licor sulfúrico purificado em duas etapas consecutivas: adição de polpa de calcário 10% m/m até pH 3,5 e dosagem de polpa de cal hidratada 10% m/m até pH igual a 5,0. A perda dos ETR_2O_3 (Óxidos de Terras Raras) foi de 8,3% e ocorreu remoção completa dos íons Fe^{3+} , PO_4^{3-} e Th^{4+} e reduções de 99%, 87% e 37%, respectivamente, nas concentrações dos íons Al^{3+} , UO_2^{2+} e SO_4^{2-} no licor purificado. As difratometrias de raios X dos produtos das calcinações, obtidos na temperatura de 1100°C e em mufla, do oxalato do cério puro e do carbonato de cério puro, mostraram a formação dos óxidos de Ce^{4+} (CeO_2), os quais não foram solubilizados em solução de ácido clorídrico 12 mol.L⁻¹. A difratometria de raios X mostrou que houve a formação de uma mistura dos óxidos Ce_2O_3 e CeO_2 , representado pelo Ce_4O_7 , na estrutura cristalina dos óxidos mistos de terras raras obtidos a partir dos oxalatos mistos, enquanto que foi formado uma mistura dos óxidos de neodímio e cério, identificado como $(\text{Nd}_{0,40}\text{Ce}_{0,60}\text{O}_{1,80}+\text{CeO}_2)$, após a decomposição térmica completa dos carbonatos mistos de terras raras. O Ce_4O_7 foi completamente solubilizado em solução de HCl 12 mol.L⁻¹. Enquanto que o cério presente na composição do $(\text{Nd}_{0,40}\text{Ce}_{0,60}\text{O}_{1,80}+\text{CeO}_2)$ e dos CeO_2 não solubilizou com solução de HCl 12 mol.L⁻¹.

PALAVRAS-CHAVES: Licor Sulfúrico; Terras Raras; Oxidação Térmica; Cério.

1. INTRODUCTION

Rare earth elements (REE) plays an important role in the global economy at present, due to the various applications in which those elements are used (Beltrani et al., 2015). REE are classified into two categories: light rare earth elements (LREE), which comprises La, Ce, Nd and Pr, and heavy rare earth elements (HREE) encompassing Sm to Lu, Sc and Y (Lucas et al., 2015). Rare earth-based materials are used in the electronics industry, steel industry, household batteries, fluorescent bulbs, permanent magnets and lasers applied in medical and nuclear technologies (Gupta and Krishnamurthy, 2005; Alonso et al., 2015).

The REE are still recovered mainly from natural minerals like monazite ((Ce,La,Nd,Th)PO₄), xenotime (YPO₄) and bastnasite ((La,Ce)CO₃F) (Alonso et al., 2015). In monazite the content of rare earth oxides (REO) ranges from 35% w/w to 71% w/w, whereas xenotime and bastnasite assign from 52% w/w to 54% w/w and 70% w/w to 74% w/w of REO, respectively (Kanazawa and Kamitani, 2005; Jordens et al., 2013). Monazite and bastnasite are extensively used in the production of rare earth products (Kanazawa and Kamitani, 2005). The CeO₂/REO mass ratio is approximately 50 wt% for bastnasite and 45-50 wt% in the case of monazite (Dan et al., 2014; Li et al., 2018). Additionally, cerium removal is usually the first step in REE purification, as the largest mass fraction of the concentrate lowers the throughput of the subsequent steps (Xie et al., 2014; McNeice and Ghanreman, 2018).

A selective process path was developed for the extraction of the REO (Rare Earth Oxides) from a beneficiated low-grade rare earth ore (<74 μm) (Testa et al., 2016). This process route involves extraction of the REE from a fine-grain material using sulfuric acid with low acid consumption in comparison with the conventional process routes. Most importantly, a small extraction of impurities, such as iron, aluminum, phosphorus and thorium owe to the roasting step (Teixeira et al, 2019; Teixeira and Silva, 2015; Berni et al., 2013). Although this selective REO extraction represents a noticeable improvement, the product of this process, which is the rare earth sulfuric liquor, still contains small amounts of impurities, such as Ca²⁺, Mg²⁺, Mn²⁺, Fe³⁺, Al³⁺, Th⁴⁺, UO₂²⁺, SO₄²⁻ and PO₄³⁻. Most of these impurities should be removed to avoid losses of REO or degradation in the quality of the product in the downstream steps, which are usually either solvent extraction or ion exchange (Beltrani et al., 2015; Silva et al., 2018a; Silva et al., 2018b; Yun et al., 2016; Silva et al., 2019a). These process route will be used in this study to generate the purified rare earth sulfuric liquor and to produce high quality mixed rare earth oxalates, carbonates and hydroxides (Silva et al., 2019b; Silva et al., 2019c).

To this effect, the objective of this work is to shed light on the impact of the use of different reagents such as limestone, lime, magnesium oxide and sodium hydroxide in experiments involving the one single purification step method and two consecutive purification steps method in the selective removal or reduction of the impurities, such as Fe³⁺, PO₄³⁻, Th⁴⁺, Al³⁺ and UO₂²⁺ in the composition of rare earth liquor. The best purification condition observed in this study considered the minimum REE losses, reagent consumption and residue generation. Furthermore, this study addresses the use of thermal treatment, XRD patterns and hydrochloric acid leaching to selectively separate Ce from other rare earth elements and then shed light on the mechanisms involving in the thermal processes.

2. MATERIAL AND METHODS

2.1 Reagents and Analytical Methods

A 97.0% w/w sodium hydroxide supplied by Anidrol Produtos Laboratórios, as well as a 95.0% w/w magnesium oxide and 98.6% w/w calcium hydroxide supplied by Sigma Aldrich

were used in the experiments. Also, a commercial limestone (91.0% purity) was employed and its chemical composition is shown in Table 1.

Table 1. Limestone composition (% w/w)

CaO	Mg	Fe	Al	P	Si	Mn	LOI (*)	Others
50.8	1.76	0.12	0.19	<0.10	0.77	<0.10	43.4	3.00

(*) Loss on Ignition

HCl 37% w/w analytical reagent (A. R.) from Anidrol Produtos Laboratórios, CeO₂ A. R. (99.9% w/w) and Ce₂(C₂O₄)₃.xH₂O A. R. (99.9% w/w) from MERCK and Ce₂(CO₃)₃.xH₂O A.R. (99.9% w/w) from ALDRICH were used as reagents in this study.

The mixed rare earth oxalates and carbonates were obtained from a purified rare earth sulfuric liquor generated in the processing of a rare earth ore, having monazite as the main REE carrier. The REE components were precipitated from the sulfate liquor by using oxalic acid A.R. and sodium carbonate A. R. as reagents.

The concentrations of aluminum, iron, phosphorous, sulfur, lanthanum, praseodymium, neodymium and samarium in the liquid samples were determined by ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry), a Varian instrument model VISTA-PRO. Other rare earth elements and impurities were determined by ICP-MS (Inductively Coupled Plasma Mass Spectrometry), a PerkinElmer model NexION 300D. The Fe II concentrations were analyzed by titration with K₂Cr₂O₇. The contents of the elements in the solid samples were determined according the analytical methods described in Table 2. The solid samples were dried in an oven at 100°C for at least one hour and then pulverized to a condition where 95% of the total mass was below 74 µm.

Table 2. Methods used in the chemical analyses of solid samples

Elements	Procedure
REE, Th, U	Fusion with Li ₂ B ₄ O ₇ or H ₂ O ₂ , dilution in 2% (vol/vol) nitric acid and ICP-MS
Ca, Mg, Fe, Al, P, Mn	Fusion with Na ₂ CO ₃ and Na ₂ B ₄ O ₇ , dilution to 67% (v/v) HCl and ICP-OES
S	Direct combustion and infrared spectrometry

The pH and redox potential measurements were performed with a Mettler Toledo type M400, having a reference electrode InPro3250SG/325/Pt10. Dried samples for X-ray diffraction were ground to <74 µm and analyzed in a PANalytical X'PERT PRO MPD with θ/θ geometry and Cu anode under 2000W and 60kV.

2.2 Purification of Rare Earth Sulfuric Liquor

The pH of the rare earth sulfuric liquor was raised in the two consecutive purification steps method, first by raising the pH up to (3.5±0.2) using limestone (CaCO₃) 10% w/w pulp and then by raising the pH up to (5.0±0.2) by adding lime (Ca(OH)₂) pulps 10% w/w. The experiments carried out with the single purification step method was done by raising the pH straight to (5.0±0.2) using 10% w/w limestone, magnesium oxide (MgO) and lime pulps and 20% w/w sodium hydroxide (NaOH) solution. After the desired pH level was achieved, the pulps were stirred for 2 hours at a speed varying from 200 to 300 rpm and then filtered after resting for 1 one day. The cakes were washed with distilled water in a proportion of 25 wt% of not washed cake and 75 wt% of distilled water. Five liters of the rare earth liquor were used in each experiment.

2.3 Calcination of Mixed Rare Earth Oxalates and Carbonates

The procedure used in calcination experiments comprised the following steps: (i) weighing of approximately 100 g of precursor. A container made of zirconite was used, its height was approximately 10 cm, to prevent any mass losses during thermal decomposition; (ii) calcination in different temperatures (450°C, 700°C and 1100°C) and residence times (1h and 4h); (iii) cooling of the calcination products to room temperature (20°C) and (iv) weighing of the final mass and assaying the calcination products.

2.4 Hydrochloric Acid Leaching

The procedure used in hydrochloric acid leaching experiments of calcination products comprised the following steps:

- Weighing of approximately 50 g of the calcination product in a beaker;
- Adding about 65 wt% of distilled water (about 33 g) and dispersing the calcination product in order to form a paste.
- Transferring the paste to a round-bottom flask connected to a heating mantle attached to a top condenser;
- Adding a HCl solution 37% w/w slowly until the pulp reached 25% w/w of the calcination product and 75% w/w of HCl solution (37 % w/w);
- Maintaining the heating at 90°C and stirring the pulp at a speed fast enough to keep the solids in suspension for 4 hours;
- Addition of about 200 mL of distilled water in order to dilute the pulp;
- Stirring for about 30 minutes at a speed fast enough to maintain the solids in suspension. Heating is not necessary in this step;
- Filtering the pulp;
- Washing the cake preparing a pulp containing 25 wt% of not washed wet cake and 75 wt% of distilled water. Stirring for about 30 minutes at a speed fast enough to maintain the solids in suspension;
- Filtering the pulp.
- The rare earth hydrochloric liquor was generated. A sample of the liquor was assayed;
- Drying the washed wet cake at 75°C until it reaches a constant weight. A sample of the dry cake was assayed.

3. RESULTS AND DISCUSSION

3.1 Chemical Analyses of Rare Earth Sulfuric Liquor

The chemical analysis of the rare earth sulfuric liquor is presented in Table 3. Table 4 shows the concentration of individual rare earth elements in the liquor.

Table 3. Composition of rare earth sulfuric liquor (g/L)

REO	REE ³⁺	Ca ²⁺	Mg ²⁺	Mn ²⁺	Fe ³⁺	Al ³⁺	PO ₄ ³⁻	Th ⁴⁺	UO ₂ ²⁺	SO ₄ ²⁻
4.49	3.74	0.89	0.41	0.94	2.12	0.36	1.06	0.0079	0.0034	16.2

Table 4. Concentration of individual rare earth elements in the rare earth sulfuric liquor (mg/L)

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sc
874	1857	196	645	66	16	44	4.32	7.91	0.88	1.42	<0.20	0.41	<0.20	17.7	5.98

The highest mass ratio found in the rare earth sulfuric liquor was SO₄²⁻/REO=3.7 kg/kg, followed by Fe/REO=0.47 kg/kg. The Mn/REO, PO₄³⁻/REO and Ca/REO mass ratios were close

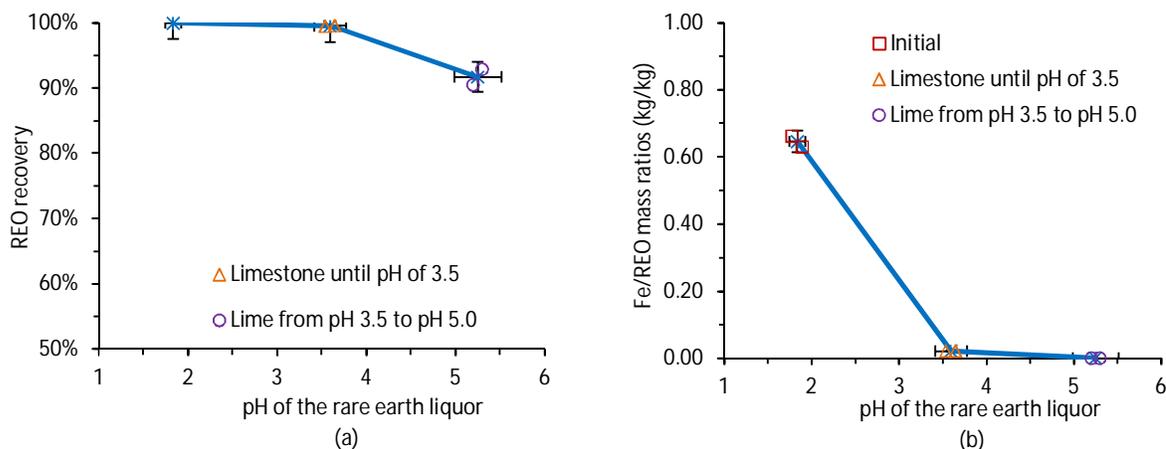
to 0.24 kg/kg. The Mg/REO mass ratio was 0.09 kg/kg, while for Al/REO, the mass ratio was below 0.09 kg/kg. Likewise, the Th/REO and U/REO mass ratios were high, 1750 mg/kg and 665 mg/kg respectively. These mass ratios will be evaluated throughout this study, as they are important parameters in the definition of the quality of the rare earth oxides or carbonates that can be produced from the purified rare earth sulfuric liquor by precipitation with either oxalic acid or sodium carbonate.

The pH of the rare earth sulfuric liquor was 1.7. The presence of the cation Fe^{+2} in the liquor was not detected. This is expected as any un-oxidized iron will dissolve during acid leaching and remain in the solution as Fe^{+2} only when the pH values are 6-8 (Onal et al., 2015). No presence of Fe^{2+} is beneficial to the process proposed in this study because in a high pH, the rare earth elements hydrolyze, forming insoluble rare earth hydroxides. For instance, the rare earth hydroxides such as $\text{Nd}(\text{OH})_3$, $\text{La}(\text{OH})_3$ and $\text{Ce}(\text{OH})_3$ precipitate under a relatively alkaline condition, which means that the elimination of the ions Fe^{+2} from the liquor will result in the loss of a large amount of REE (Zhang et al., 2014; Kim and Osseo, 2012). As can be seen, the LREE/REE and HREE/REE and (Pr+Nd)/REE mass ratios are 95.6%, 4.4% and 22.5% w/w, respectively. Therefore, the rare earth sulfuric liquor is rich in LREE and poor in HREE, containing a significant amount of Pr+Nd.

3.2 Selective Impurities Removal from Rare Earth Sulfuric Liquor

3.2.1 Two consecutive purification steps method

The REO recoveries and impurities/REO mass ratios are presented in Figure 1 and the compositions of the rare earth liquors are shown in the Table 5. Table 6 shows the concentration of individual rare earth elements in the rare earth sulfuric liquors after to be treated with limestone to pH of 3.5 and after to be treated with lime from a pH of 3.5 to a pH of 5.0.



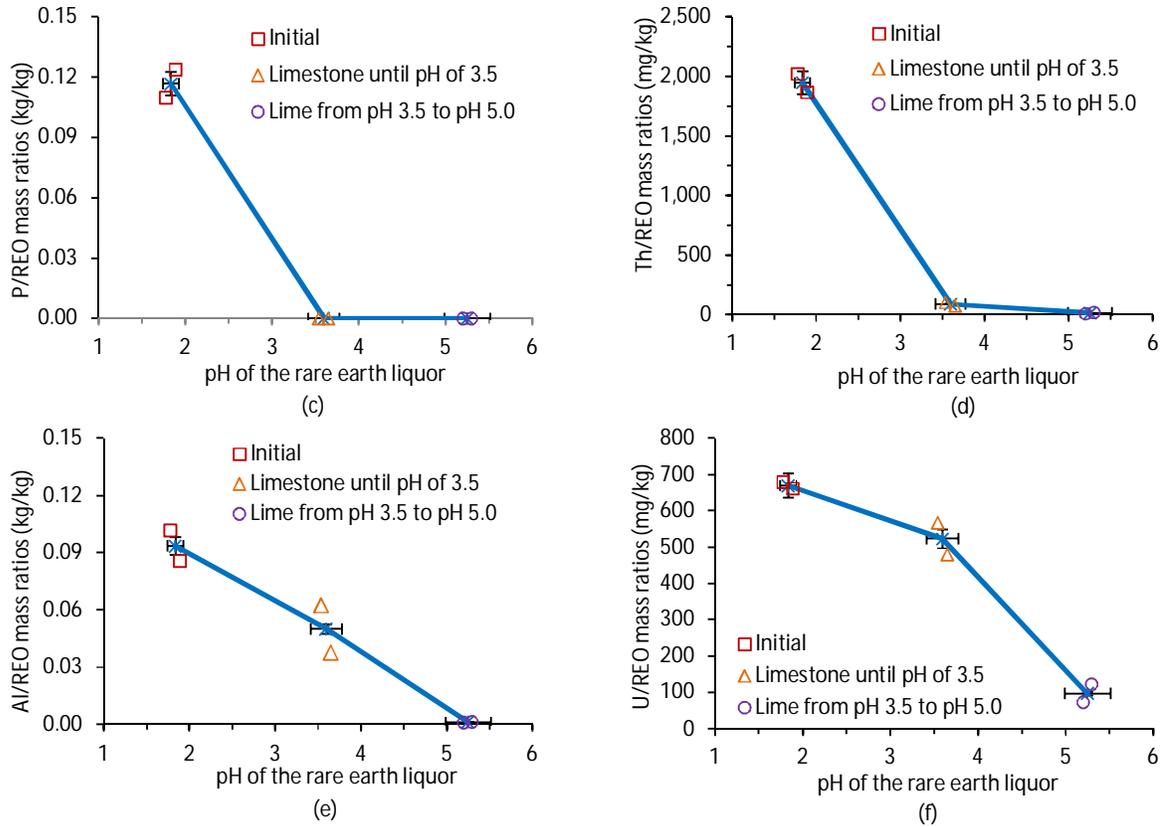


Figure 1. REO recovery (a) and Fe/REO (b), P/REO (c), Th/REO (d), Al/REO (e) and U/REO (f) mass ratios in the initial rare earth sulfuric liquors and after to be treated in two consecutive purification steps

Table 5. Composition of the rare earth sulfuric liquor after to be treated in two consecutive steps (g/L)

Condition of purification/ Elements	REO	REE ³⁺	Ca ²⁺	Mg ²⁺	Mn ²⁺	Fe ³⁺	Al ³⁺	PO ₄ ³⁻	Th ⁴⁺	UO ₂ ²⁺	SO ₄ ²⁻
Limestone pH of 3.5	4.32	3.59	1.00	0.46	0.95	0.09	0.22	0.00	0.0004	0.0026	11.9
Lime from a pH of 3.5 to pH of 5.0	4.07	3.39	1.05	0.47	0.95	0.00	0.00	0.00	0.0001	0.0004	10.6

Table 6. Concentration of individual rare earth elements in the rare earth sulfuric liquors after to be treated in two consecutive steps (mg/L)

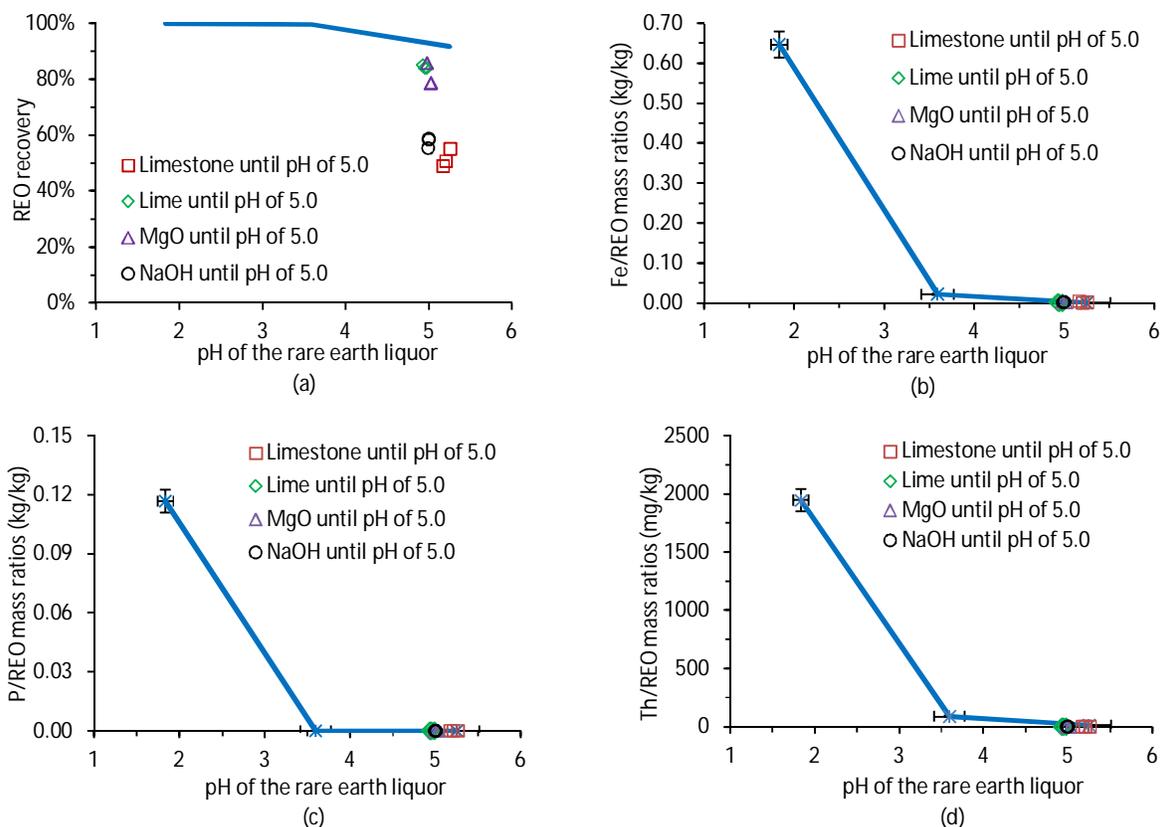
La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sc
Liquor after to be treated with limestone to pH of 3.5															
83	1,80	185	61	63	14	43	3.91	7.01	0.81	1.22	<0.20	0.47	<0.20	17.0	1.26
Liquor after to be treated with lime from a pH of 3.5 to a pH of 5.0															
81	1,71	172	56	55	12	37	3.42	5.52	0.63	0.93	<0.20	0.26	<0.20	14.5	0.02

The LREE/REE, HREE/REE and (Pr+Nd)/REE mass ratios in the liquors changed slightly, in comparison to figures verified in the rare earth sulfuric liquor, being 95.8%, 4.2% and 20.4% w/w respectively in the partially purified rare earth sulfuric liquor (pH=3.5) and 96.2%, 3.8% and 21.6% w/w respectively in the purified rare earth sulfuric liquor (pH=5.0). Scandium (Sc) was the rare earth element which was mostly affected by a rise in pH because 79.0% of its initial amount precipitated with addition of limestone in a pH of 3.5, whereas 20.6% of the element precipitated with dosing lime in pH 5.0, totalizing a total Sc removal of 99.6% in two consecutive purification steps. This occurred due to the lower basicity of the scandium, in comparison to other rare earth elements (Bauer and Lindstrom, 1968).

According to the results, it can be observed that the purification of the rare earth sulfuric liquor in the two consecutive purification steps proved to be efficient because the loss of REO was only $(8.3 \pm 2.3\%)$, which implies that the recovery was $(91.7 \pm 2.4\%)$ of the REO fed. Most of the impurities in the rare earth sulfuric liquor fed were eliminated. The REO recoveries with the addition of limestone in pH 3.5 and with lime in pH 5.0 were $(99.6 \pm 0.1\%)$ and $(92.1 \pm 2.4\%)$ respectively. The removal of uranium was lower due to a U/REO mass ratio of approximately 100 mg/kg remained in the purified rare earth sulfuric liquor. A significant reduction in the concentration of sulfate occurred in the liquors ($\text{SO}_4^{2-}/\text{REO}=2.6 \text{ kg/kg}$), which is expected to be highly beneficial to the downstream step, since a high sulfate content in the rare earth concentrates has a negative impact on the performance of the solvent extraction due to the formation of a third phase.

3.2.2 Single purification step method

Three experiments were carried out with the addition of different reagents such as CaCO_3 , $\text{Ca}(\text{OH})_2$, MgO and NaOH aiming at raising the pH from 1.7 to pH to 5.0. The REO recoveries and the impurities/REO mass ratios are presented in Figure 2. The composition of the respective purified rare earth liquors is shown in Table 7. The results obtained in the two consecutive purification steps are also presented in Figure 2 for comparison reasons.



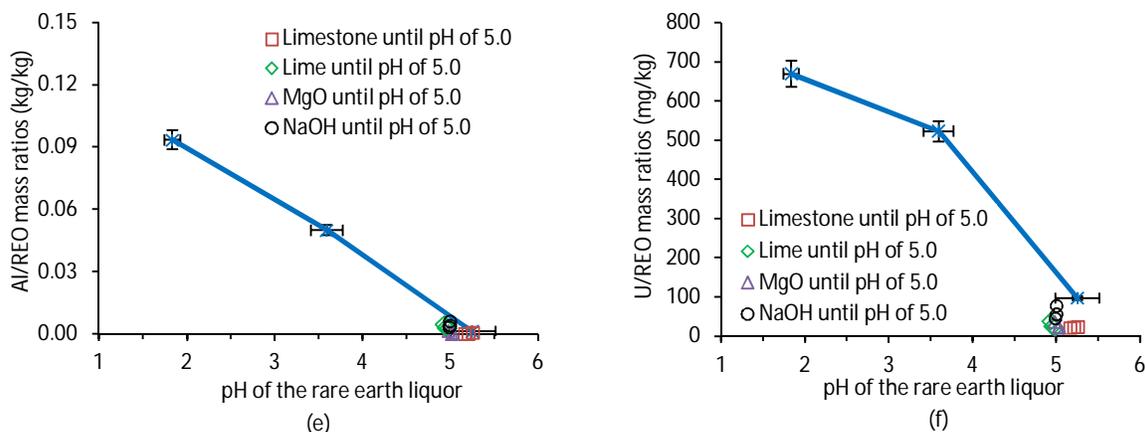


Figure 2. REO recovery (a) and Fe/REO (b), P/REO (c), Th/REO (d), Al/REO (e) and U/REO (f) mass ratios in the initial, partially (pH=3.5) and purified (pH=5.0) rare earth sulfuric liquors obtained with different reagents in a single purification step method and two consecutive purification steps method

Table 7. Composition of the rare earth sulphuric liquors obtained after purification with limestone, lime, MgO and NaOH in a single purification step (g/L)

Reagent / Elements	REO	REE ³⁺	Ca ²⁺	Mg ²⁺	Mn ²⁺	Fe ³⁺	Al ³⁺	PO ₄ ³⁻	Th ⁴⁺	UO ₂ ²⁺	SO ₄ ²⁻
Limestone pH of 5.0	2.02	1.68	0.72	0.40	0.77	0	0.00	0	0	0.0001	7.09
Lime pH of 5.0	3.64	3.04	0.81	0.43	0.89	0	0.01	0	0	0.0001	9.47
MgO pH of 5.0	3.59	2.99	0.82	2.50	0.89	0	0.00	0	0	0.0001	18.1
NaOH pH of 5.0	2.39	1.99	0.70	0.39	0.89	0	0.01	0	0	0.0002	15.8

As expected, the impurities Fe³⁺, PO₄³⁻, Th⁴⁺ and Al³⁺ were completely removed with addition of other reagents in pH of 5.0. Furthermore, the REO recovery was very low in comparison with experiments carried out in two consecutive purification steps (Figure 2a). The mean REO recovery in the two consecutive purification steps method was (91.7±2.4%), but in the single purification step method when limestone was used, this value was only (51.6±3.2%), however with the use of lime it was (84.4±0.6%), and by employing MgO the recovery was (80.9±4.7%) and NaOH assigned (57.5±1.8%), which means that the REO loss with the use of limestone was 48.4%. Lime resulted in a 15.6% loss, the loss with MgO was 19.1% and NaOH assigned a loss of 42.5%. The lower sulfate concentrations in the liquors produced by the addition of limestone and lime, occurred due to the formation of insoluble CaSO₄. On the other hand, soluble sodium and magnesium sulfates formed in the experiments carried out with addition of NaOH and MgO, resulting in a high concentration of sodium, magnesium and sulfate in the respective liquors. The sodium and magnesium concentrations in the purified rare earth liquor were 3.32 g/L and 2.50 g/L, respectively. The removal of uranium was higher when limestone, lime and MgO was used, resulting in a U/REO mass ratio in the liquor below 30 mg/kg.

3.2.3 Consumption of reagents and residues generation

Table 8 shows the consumption of reagents and generation of dry residues in the two consecutive purification steps and in the single purification step experiments with the use of CaCO₃, Ca(OH)₂, MgO and NaOH.

Table 8. Reagents consumption and dry residues generations in different condition of purification of rare earth sulfuric liquor

Condition of purification	kg of reagent or kg of dry residue per m ³ of rare earth sulfuric liquor	
	Reagent	Dry residue
Limestone pH of 3.5	3.48	5.00
Lime pH of 3.5 to pH of 5.0	0.86	2.51
Total	4.34	7.51
Limestone pH of 5.0	26.3	43.2
Lime pH of 5.0	7.22	25.1
MgO pH of 5.0	4.28	11.1
NaOH pH of 5.0	6.82	13.6

The lowest dry residue generation (7.51 kg/m³) occurred in the two consecutive purification steps experiment, while the lowest reagent consumption was observed in the experiments with MgO, however presenting a slight difference when compared with the total amount of reagents consumed in the two consecutive purification steps method. Additionally, the highest reagent consumption and residue generation occurred when limestone was used in the single purification step method.

3.3 Chemical Analyses of Mixed Rare Earth Oxalates and Carbonates

The purified rare earth liquor obtained in two consecutive steps was used to produce the mixed rare earth oxalates and carbonates. The Table 9 presents the composition of the mixed rare earth oxalates and carbonates used in this study and the Table 10 shows the individual REE mass ratios for both products.

Table 9. Chemical compositions of mixed rare earth oxalates or carbonates (% w/w)

Type of mixed rare earth	REO	REE	C	Sulfate	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	MnO ₂	P ₂ O ₅	Na ₂ O	Water (*)
Oxalates	53.8	44.7	12.1	0.19	<0.11	<0.03	<0.68	<0.09	<0.03	<0.05	<0.05	8.03
Carbonates	68.3	56.9	6.20	1.45	0.13	0.12	<0.68	<0.09	0.46	<0.05	0.08	5.00

(*) Crystallization water

Table 10. Individual rare earth elements mass ratios in the composition of mixed rare earth oxalates or carbonates (% w/w)

Type of mixed rare earth	La/ REE	Ce/ REE	Pr/ REE	Nd/ REE	Sm/ REE	Eu/ REE	Gd/ REE	Tb/ REE
Oxalates	18.0	49.7	5.84	22.3	1.96	0.35	1.03	0.10
Carbonates	19.0	48.1	5.38	23.5	1.87	0.34	0.98	0.09

Type of mixed rare earth	Dy/ REE	Ho/ REE	Er/ REE	Tm/ REE	Yb/ REE	Lu/ REE	Y/ REE	Sc/ REE
Oxalates	0.15	0.02	0.03	0.010	0.007	0.010	0.45	0.0
Carbonates	0.15	0.02	0.02	0.010	0.007	0.010	0.43	0.0

It is possible to see that the mixed rare earth oxalates contain lower REO and sulfate content, whereas the mixed rare earth carbonates presented a higher sulfate, Fe₂O₃, Al₂O₃, MnO₂ and Na₂O content. The total amount of impurities was about 0.20% w/w in the mixed rare earth oxalates and 2.25% w/w in the mixed rare earth carbonates. The main impurity

presented in the mixed rare earth oxalates is sulfate (0.19% w/w), perhaps due to the coprecipitation of some sulfate salts, where the main impurities in the mixed rare earth carbonates are sulfate, iron oxide, aluminium oxide, manganese oxide and sodium oxide. A low purity mixed rare earth carbonate occurred due to the coprecipitation of some sulfate salts or hydroxides containing Mn, Fe and Al, and the formation of sodium and rare earth double sulfate or $\text{NaREE}(\text{SO}_4)_2$ (Morais et al., 2010; Silva et al., 2018b; Silva et al., 2019a). During the precipitation of REE with oxalic acid, sulfuric acid was generated, resulting in the fall in the pH of the filtrate to pH~1.4, whereas when the REE was precipitated with sodium carbonate, the pH of the filtrate rose (pH~6.5) due to the formation of basic character salt (Na_2SO_4). A rise in pH favours the hydrolysis of some ions, such as, Fe^{3+} and Al^{3+} ions, causing their precipitation (Silva et al., 2018a). According to what was expected, there was no a significant variation in the mass ratios of individual rare earth elements/REE (i.e. La/REE, Ce/REE, etc.) in the mixed rare earth oxalates and carbonates. The sum of the mass ratios of La/REE, Ce/REE, Pr/REE and Nd/REE is above 96% w/w in both cases, while the mass ratio for Ce/REE being about 48.9% w/w.

3.4 XRD Patterns Comparison of Calcination Products

Figure 3 shows XRD patterns (30° to 70° 2Theta) of CeO_2 99.9% w/w A.R. and of the products obtained by calcination in muffle at 1100°C and residence time of 1h of pure cerium oxalate, pure cerium carbonate, mixed rare earth oxalates and mixed rare earth carbonates as precursors.

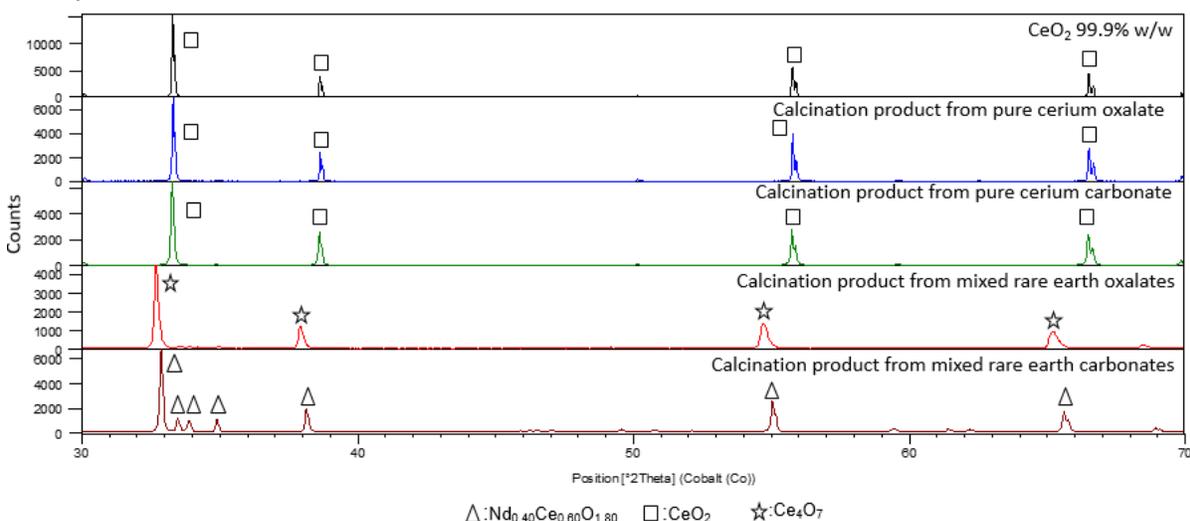


Figure 3. XRD patterns of CeO_2 A.R. 99.9% w/w and calcination products obtained from pure cerium oxalate, pure cerium carbonate, mixed rare earth oxalates and mixed rare earth carbonates as precursors in muffle at temperature of 1100°C and residence time of 1h (30° to 70° 2Theta)

It is observed that the crystalline structures formed by the calcination of pure cerium oxalate and pure cerium carbonate were CeO_2 , with peaks corresponding CeO_2 A.R peaks. On the other hand, different crystalline structures are formed when mixed rare earth oxalates or carbonates were calcined under the same condition. A crystalline structure formed between Ce_2O_3 (Ce^{3+}) and CeO_2 (Ce^{4+}), represented by Ce_4O_7 , when the mixed rare earth oxalates were calcinated, and ($\text{Nd}_{0.40}\text{Ce}_{0.60}\text{O}_{1.80} + \text{CeO}_2$) was formed when the mixed rare earth carbonates were calcinated. The mass proportion is of approximately 80% w/w of $\text{Nd}_{0.40}\text{Ce}_{0.60}\text{O}_{1.80}$ and 20% w/w of CeO_2 .

The present study unveils the identification of the crystalline structure Ce_4O_7 , which is a great breakthrough, which complements the endothermic transformation that triggered at 400°C . However, the formation of $Nd_{0.40}Ce_{0.60}O_{1.80}$ as a crystal structure, was previously identified by Horlait et al. (2012). According to Horlait et al. (2012), a crystal structure with $x=0.40$, $Nd_xCe_{1-x}O_{2-x/2}$, has low solubility in mineral acids such as sulfuric, hydrochloric and nitric acids.

3.5 Hydrochloric Acid Leaching Experiments

Figure 4 shows all results obtained in the hydrochloric leaching experiments with mixed rare earth oxalates, pure cerium oxalate, mixed rare earth carbonates and pure cerium carbonate.

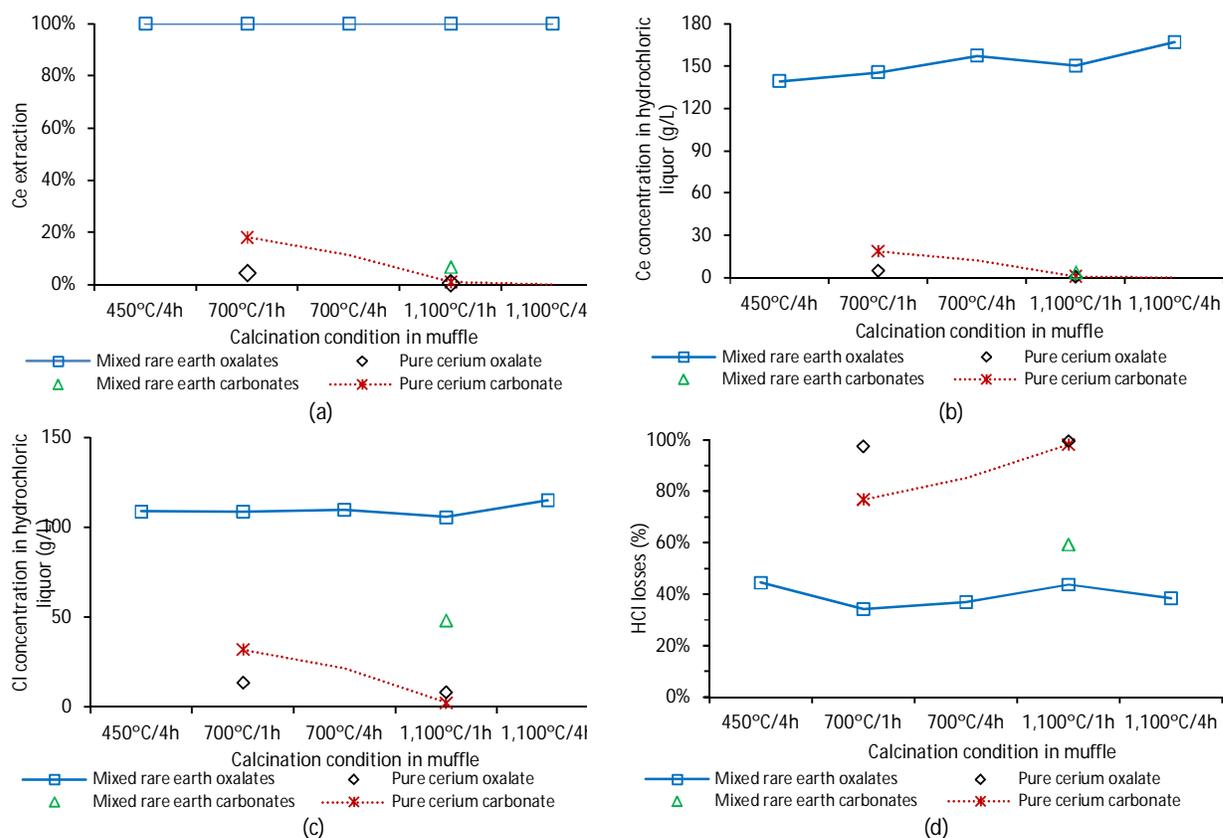


Figure 4. Results obtained in hydrochloric leaching experiments with mixed rare earth oxalates, pure cerium oxalate, mixed rare earth carbonates and pure cerium carbonate

The highest cerium extractions and cerium and chloride concentrations in the hydrochloric liquors and also the lowest HCl losses were observed in the experiments carried out with calcination products obtained when mixed rare earth oxalates were used as precursor. On the other hand, the lowest cerium extractions and cerium and chloride concentration in the hydrochloric liquors were noticed in the experiments done with calcination products generated with pure cerium oxalate, mixed rare earth carbonates and pure cerium carbonate. The highest HCl losses occurred in the experiments using pure cerium oxalate and pure cerium carbonate as precursors, whereas intermediate HCl losses were observed in the experiments with mixed rare earth carbonates.

4. CONCLUSION

The experiments show that the purification of rare earth sulfuric liquor by raising the pH in the two consecutive steps, one with CaCO_3 to pH up to 3.5 and the other with Ca(OH)_2 to pH up to 5.0, were more efficient in the selective removal of some impurities present in a rare earth sulfuric liquor in comparison with the use of the reagents CaCO_3 , Ca(OH)_2 , MgO and NaOH in the single purification step method by raising the pH directly to pH up to 5.0. In two consecutive steps, a total removal of Fe^{3+} , PO_4^{3-} and Th^{4+} ions were achieved and a reduction of 99% in the Al^{3+} ions, 87% in the UO_2^{2+} ions and 37% in the SO_4^{2-} ions concentrations was attained. Furthermore, the REO losses and the consumption of reagent was the lowest, being 8.3% (REO recovery of 91.7%) and 4.3 kg per m^3 of rare earth sulfuric liquor, respectively. Additionally, a low generation of residue was noticed, about 7.5 kg per m^3 of rare earth sulfuric liquor, making the product of this treatment seemingly suitable for use in the production of marketable rare earth products.

The XRD patterns presented by the calcination of the mixed rare earth oxalates and carbonates, as well as, the pure cerium oxalate and carbonate, depicted the formation of a crystalline structure between Ce_2O_3 and CeO_2 , represented by Ce_4O_7 , when the precursor was the mixed rare earth oxalates. When the precursor was the mixed rare earth carbonates, the crystalline structure formed was mixture of 80% w/w of $\text{Nd}_{0.40}\text{Ce}_{0.60}\text{O}_{1.80}$ and 20% w/w of CeO_2 . In the case when the precursors were pure cerium oxalate and carbonate, the crystalline structure identified was CeO_2 . Cerium was not selectively removed by hydrochloric acid solution (12 mol.L^{-1}) only when the precursor was the mixed rare earth oxalates. On the other hand, the cerium was not solubilized from the remaining rare earth elements when the precursor was the mixed rare earth carbonates. As expected, the CeO_2 , formed through calcination of the pure cerium oxalate and also by the pure cerium carbonate was not dissolved by a hydrochloric acid solution (12 mol.L^{-1}).

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