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Selective elimination of natural radionuclides during the processing of high grade monazite concentrates by caustic conversion method

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Abstract−This work is directed for removal of the nondesired species (^{228}Ra, ^{226}Ra, ^{223}Ra, ^{210}Pb, Th(IV) and Fe(III)) in the rare earth chloride ($RECl_3$) liquor before separation of Ln(III). The different factors affecting elimination of radium-isotopes, lead (^{210}Pb), Th(IV) and Fe(III) from the $RECl_3$ liquor, have been investigated and optimized. The results indicated that the activity concentration of radionuclides in $RECl_3$ liquor was above the safe limits required during the separation process of Ln(III). Adjustment of pH 3±0.1 leads to eliminate 14±1% of radionuclides and Th(IV), and 40±3% of Fe(III), while 12±1% of Ln(III) was lost. The developed method shows that more than 95% of the nondesired species was selectively removed when the liquor was eliminated by potassium sulfate or sulfuric acid solutions in presence of Ba/Pb-carrier (1 : 1). About 20-83% of Ln(III) was lost when the non-desired species removed by sodium or ammonium sulfate or potassium chromate solutions. Fe(III) interfered with Ln(III) when radionuclides and Th(IV) were eliminated by 2.6 M H_2SO_4 in presence of Ba/Pb-carrier. Finally, use of 0.23 M K_2SO_4 or 2.6 M H_2SO_4 was efficient to reduce level of ^{228}Ra, ^{226}Ra, ^{223}Ra and ^{210}Pb to the safe limits in viewpoint of radiation protection. In addition, the interfered Th(IV) and Fe(III) were also eliminated efficiently from $RECl_3$ liquor before the chemical processing of Ln(III).

Keywords: Monazite, Rare Earth Industry, TENORM, Radiation Protection, Treatment

INTRODUCTION

The presence of naturally occurring radioactive materials (NORM) in rare earth minerals in varying concentrations is quite often significant enough to result in occupational and environmental radiation exposures during their mining, milling and chemical processing for the extraction of the rare earth elements and compounds. The mining of the ores and further processing results in concentration/redistribution of the NORM in the process streams, product intermediaries, products and effluent wastes as technically enhanced naturally occurring radioactive materials (TENORM). Rare earth elements (Ln(III)) are chemically rather similar to uranium (U) and thorium (Th) and are often found in conjunction with these radionuclides. The production of Ln(III) has been accompanied by the production of large volumes of thorium hydroxide and residues containing radioactive lead and radium-isotopes [1,2]. The main minerals used as sources of Ln(III) can be extracted from placer deposits such as monazite or xenotime. Monazite contains 0.2-0.4% uranium as U_3O_8 and 4.5-9.5% thorium as ThO_2, depending on the region of origin/occurrence. Monazite is widely distributed, and many countries such as Australia, Brazil, China, Egypt, India, Malaysia, South Africa, Sri Lanka, Taiwan (China) and the United States of America are engaged in its production. Until recently, monazite was the most important resource for Ln(III) [3-5].

The chemical attack of the mineral based on NaOH separates sodium phosphate from a mixture called 'cake I', which is rich in heavy minerals. Cake I is further filtered, given that it yields a concentration of rare earth chlorides and a mixture called 'cake II' containing most of thorium and uranium originally present in monazite feedstock. The decay chain of U and Th is not in secular equilibrium in cake II: Th precipitates while radium remains in solution. The latter can reach very high activities (7 and 10 MBq/kg for ^{226}Ra and ^{228}Ra, respectively). In 2010, the extraction of monazite reached 1.3×10^5 tons and its processing has made 10% of cake II waste. This large amount of highly enhanced radioactivity NORM requires scrupulous monitoring and control [6-12]. Wastes from the mining and processing of radioactive ores are potential sources of radiological impact, both for those working in the industry and for members of the public who may be exposed if wastes are dispersed in the environment. These wastes are characterized by large volumes and low activity concentrations of materials containing radionuclides with very long half-lives [1,9-12].

In the literature, limited trials have been investigated to remove the undesirable species such as natural radionuclides (e.g., radium-isotopes, ^{210}Pb) from rare earth liquor during processing of monazite. In Australia, most production of rare earth elements comes from the digestion of monazite using caustic method. Long-lived radionuclides such as radium-226 (1,600 years) and lead-210 (22.3 years) were removed from the rare earth chloride liquor by precipitation as sulfate and sulfide, respectively [7,9]. In Malaysia, the rare earths are produced from monazite digested by hot and concentrated sulfuric acid (H_2SO_4). Most of the undesirable species of thorium associated with lanthanides were separated as thorium hydroxide from the obtained sulfate leach solution [13]. Recently, special atten-

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tion was directed to extraction of rare earth metals from the monazite ores available in Egypt. Consequently, we attempted to develop new chemical procedures for separation and purification of rare earth elements from monazite digested by the caustic method. We investigated some factors affecting the removal of radium-isotopes (^{228}Ra, ^{226}Ra, ^{223}Ra) and lead (^{210}Pb) before separation and purification of Ln(III) from the rare earth chloride ($RECl_3$) liquor to be safer.

EXPERIMENTAL

1. Chemicals and Reagents

All chemical reagents used in this study were of analytical grade reagents with high purity ≥99%. The reagents were used without further purification. Arsenazo (III), Thoron (I) and potassium thiocyanate (KSCN) were supplied by Merck (Darmstadt), Germany.

2. Digestion of Monazite

The monazite samples used in this study were of high-grade brands (~92%) provided by the Egyptian Nuclear Materials Authority, Cairo, Egypt. The samples were ground mechanically and homogenized to obtain a fine powder below 100 μm to accelerate surface reaction. Monazite samples were digested by the caustic method using a hot sodium hydroxide solution through main two steps [4]. Initially, monazite was mixed with 40% NaOH assuming a solid/liquid ratio of 1 : 5 with stirring for four hours at 140±2 °C. In the second step, 20% NaOH was added again with stirring for one hour at the same temperature. Then, the solid phase was separated from the supernatant of sodium phosphate and excess of sodium hydroxide by decantation, and washed twice with hot double-distilled water. The produced hydroxide cake was dried at 110±2 °C, cooled to room temperature, crushed and sieved to below 100 μm.

3. Preparation of Samples for Radiometric Measurements

For nondestructive radiometric measurement by γ-ray spectrometer, 50 grams of the dried solid samples (e.g., monazite or hydroxide cake) were weighed and packed in cylindrical polyethylene bottles (150-cm^3). To assess the natural radionuclides in the rare earth chloride ($RECl_3$) liquors and effluents, 100 ml of solution was packed inside the bottles. The bottles were closed tightly and sealed by molten wax to prevent escape of radon gas. Then, the samples were kept and left for one month to establish a secular equilibrium between radionuclides of radium-isotopes of our interest (e.g., ^{228}Ra, ^{226}Ra and ^{223}Ra) and their respective decay progenies [5,14,15].

4. Non-destructive Radiometric Measurements

The radiometric analysis of samples was done using a high purity germanium (HPGe) detector supplied by Canberra Industries Inc., USA. The detector was a model GX1020-10863 and equipped with liquid nitrogen monitor (LN2), operating voltage of +3,500 V, relative efficiency of 10% and resolution (FWHM) of 2.0 keV at 1332.5 keV peak of ^{60}Co. The detector was also coupled to a data acquisition system with Giene-2000 multichannel analyzer, and was housed in a cylindrical Pb-shield with a fixed bottom to reduce the interference of background radiation [5]. The energy calibration of the detector was done by sealed point source containing 0.1 μCi (3,700 Bq) of ^{60}Co, ^{133}Ba and ^{137}Cs provided from Amersham, England. The efficiency calibration of the HPGe detector was also calibrated for measurement of the aquatic samples using certified reference solution containing radium-226 (37,040±154 Bq/L). For measurement of solid samples, the efficiency calibration was done by certified reference material (IAEA-314, stream sediment) containing natural ^{238}U, ^{232}Th and radium (^{226}Ra) provided from the AQCS/IAEA, Seibersdorf's laboratories, Vienna, Austria [16].

Activity concentration of ^{226}Ra ($t_{1/2}$ 1,600 y) isotope was calculated by average of ^{214}Pb (351.93 keV, 35.6%) and ^{214}Bi (609.3 keV, 45.5%), and ^{210}Pb (22.3 y) was measured at 46.5 keV (4.1%). Activity of ^{223}Ra (11.4 d) was quantified at 154.0 keV (5.2%). Activity concentration of ^{228}Ra (5.8 y) was quantified by average of γ-emissions of ^{228}Ac at 338.6 keV (12.1%) and 911 keV (29%). Activity of potassium (^{40}K) was measured at 1,460.8 keV (10.7%). The self-attenuation effects due to the interaction of the low γ-emissions (i.e., ^{210}Pb at 46.5 keV, ^{234}Th at 63.3 and 92.6 keV) in the samples containing high Z-elements were corrected as described by others [15,17-19]. For this purpose, samples of the study, solid certified reference material of IAEA-314 and 312 as well as standard solution containing ^{226}Ra and ^{210}Pb assuming equilibrium conditions, were counted at the same geometrical conditions such as measuring time, sample-to-detector distance, sample weight and the same sample container (i.e., G~1). Therefore, correction factors were calculated and used to minimize the coincidence-summing influence for the studied samples at low energy.

Sensitivity of the measurements can be evaluated by using the detection limit (L_D) described in [20], assuming the Gaussian probability distribution of the number of counts in the background (B) and rejecting the data not included in a range of 1.645σ (95% confidence level). The minimum detectable activity (MDA) concentration for the background was calculated by using L_D, according to the formula [21]:

$$\mathrm{MDA\ (Bq/L)\ or\ (Bq/kg)} = \frac{K_\alpha \cdot \sqrt{C_B}}{\varepsilon \cdot I_\gamma \cdot t \cdot V} \qquad (1)$$

where K_α, C_B, ε, I_γ, t and V are the statistical coverage factor equivalent to 1.645, the background counts, the photopeak efficiency, the probability of gamma emission, the counting time (s) and the sample volume (Liter), respectively. The MDA for radionuclides of interest (^{228}Ra, ^{226}Ra, ^{223}Ra, ^{210}Pb) was below 5 Bq/kg. For the quantify activity concentration of radionuclides, the samples were counted for a long enough counting period (7,200 seconds) to minimize the counting errors. This analysis considered that the statistical errors of the gamma-ray counting (<6%), detection efficiency errors (<3%) and errors from γ-ray intensity (<1%) accounted for the overall errors of the measured activities found to be less 10%. The specific activity concentration (A) of radionuclides in the studied samples was calculated by using the formula [22]:

$$\mathrm{A\ (Bq/L)\ or\ (Bq/kg)} = \frac{\mathrm{CPS}}{\varepsilon \cdot I_\gamma \cdot t \cdot V} \qquad (2)$$

where CPS refers to the net count per second for each sample investigated. The combined uncertainty (ΔU) of the activity concentration was estimated using Eq. (3) [23]:

$$\Delta U = u \cdot \sqrt{\left(\frac{\Delta \mathrm{CPS}}{\mathrm{CPS}}\right)^2 + \left(\frac{\Delta \varepsilon_\gamma}{\varepsilon_\gamma}\right)^2 + \left(\frac{\Delta I_\gamma}{I_\gamma}\right)^2 + \left(\frac{\Delta t_s}{t_s}\right)^2 + \left(\frac{\Delta V_s}{V_s}\right)^2} \qquad (3)$$

where ΔCPS, $\Delta\varepsilon_\gamma$, ΔI_γ, Δt_s and ΔV_s are the uncertainties of the count rate, detector efficiency, γ-ray emission probability, counting time

Table 1. Activity concentration of radionuclides in TENORM residues of monazite, hydroxide cake and rare earth chloride ($RECl_3$) liquor

Sample type	N	Activity concentration (mean±SD (CV, %))*				
		Ra-isotopes:			Lead (^{210}**Pb**), ^{238}U-series	^{40}**K**[d]
		^{228}**Ra** (^{232}Th-series)	^{226}**Ra** (^{238}U-series)	^{223}**Ra** (^{235}U-series)		
Monazite (Bq/kg)	10	142,850±1,940 (1.3)	36,530±290 (0.8)	18,620±360 (1.9)	2,890±160 (5.5)	<MDA
H. Cake (Bq/kg)[a]	8	117,700±500 (0.4)	21,920±1,850 (8.4)	16,640±540 (3.2)	1,990±80 (4.0)	<MDA
RE-liquor (Bq/L)[b]	8	10,700±350 (3.3)	1,860±70 (3.8)	1,350±20 (1.5)	2,280±60 (2.1)	<MDA

[a] Hydroxide cake

[b] Rare earth chloride ($RECl_3$) liquor

N: number of samples

[*]: SD: standard deviation, CV: coefficient of variance

[d] Minimum detectable activity (MDA<5 Bq/kg)

and sample volume (Liter), respectively.

In the elimination process, the total counts due to γ-emissions of radionuclides (e.g., ^{228}Ra (^{228}Ac), ^{226}Ra, ^{223}Ra, ^{214}Pb, ^{214}Bi, ^{212}Pb, ^{212}Bi, ^{210}Pb, ^{208}Tl) in rare earth liquor before and after treatment by precipitating agents were measured by a high efficiency scintillation detector. The detector is an NaI(Tl) model 3M3/3-X (3″×3″) with operating voltage fixed at +1,100 volts obtained from Canberra Industries Inc., USA. Measurement of each liquor sample was repeated three times for 1,000 seconds with coefficient of variance below 10%.

5. UV-visible Spectrophotometric Measurements

Absorbance of total rare earth elements (ΣLn(III)), thorium (IV) and iron (III) was measured in the liquor phase using double beam UV-Visible spectrometer (model Cintra 2.2, Australia). Total rare earth elements (ΣLn(III)) in solutions were measured by the Arsenazo III method at wavelength (λ_{max}) of 650±2 nm, while Th(IV) was measured by the Thoron I method at 540±2 nm. Fe(III) was measured by thiocyanate method at 495±2 nm [24].

6. Elimination Procedures

The different parameters affecting the elimination of radionuclides (e.g., ^{228}Ra, ^{226}Ra, ^{223}Ra, ^{210}Pb), Th(IV) and Fe(III) before separation and purification of Ln(III) were studied and optimized. These factors included i) influence of hydrogen ion concentration, ii) type of carrier solution (Ba^{2+}, Pb^{2+} or mixture), iii) precipitating agent used to eliminate the non-desired species. The elimination efficiency of the undesirable species was quantified and expressed as a removal percentage (R, %) of certain species from the investigated rare earth chloride ($RECl_3$) liquor. Thus, the R % was calculated using the formula:

$$R\ (\%) = \left(\frac{A_1 - A_2}{A_1}\right) \times 100 \qquad (4)$$

where A_1 and A_2 represent the radiometric or colorimetric (UV-visible) measurements of $RECl_3$ liquor before and after treatment by the precipitating reagent, respectively.

RESULTS AND DISCUSSION

1. Activity Concentration of Radionuclides in IAEA-312 and TENORM Residues

For quality control and quality assurance purposes, activity concentration of the naturally occurring radionuclides of ^{238}U, ^{232}Th and ^{226}Ra in certified reference material (AQCS/IAEA-312 stream sediment, Seibersdorf's Laboratories, Austria) [25] was examined as unknown sample. It is observed that the activity concentration of the tested radionuclides was in fairly good agreement between the standard and measured values with relative error not exceeding 7%. Consequently, the nondestructive radiometric measurement herein was adequate and accurate in the further investigations.

In the present work, the natural radionuclides of radium-isotopes (^{228}Ra, ^{226}Ra, ^{223}Ra) and lead (^{210}Pb) were identified and quantified in monazite, hydroxide cake (H. cake) and rare earth chloride ($RECl_3$) liquor. The results are summarized in Table 1. In monazite samples before digestion, activity concentration of radionuclides was 142,850±1,940, 36,530±290, 18,620±560 and 2,890±260 Bq/kg for ^{228}Ra, ^{226}Ra, ^{223}Ra and ^{210}Pb, respectively (Table 1). In samples of hydroxide cake (monazite digested by hot 20-40% NaOH), activity concentration decreased to 117,700±500, 21,920±11,850, 16,640±540 and 1,990±80 Bq/kg for radionuclides of ^{228}Ra, ^{226}Ra, ^{223}Ra and ^{210}Pb, respectively (Table 1). Thereafter, hydroxide cake was converted to $RECl_3$ liquor by concentrated HCl till pH~0.4 to produce a solution containing rare earth elements in chloride form as Ln(III). Radionuclides attributed mainly to ^{228}Ra, ^{226}Ra, ^{223}Ra and ^{210}Pb were identified and quantified in this liquor (Table 1). It was found that the mean activity concentration of radionuclides was 10,700±350, 1,860±70, 1,350±20 and 2,280±4 Bq/L for ^{228}Ra, ^{226}Ra, ^{223}Ra and ^{210}Pb, respectively. Thus, the activity concentration of all radionuclide found in all samples was high and above the worldwide safe limits [26-30]. In addition, the majority of the enhanced radioactivity in all TENORM residues (monazite, H. Cake and $RECl_3$ liquor) was attributed mainly to γ-emissions of ^{228}Ra progenies (i.e., ^{228}Ac, ^{212}Pb, ^{212}Bi, ^{208}Tl), whereas the rest was due to ^{226}Ra radiation or its progenies (i.e., ^{214}Pb, ^{214}Bi) as well as radionuclides of ^{223}Ra and ^{210}Pb. For instance, 66.1% of the enhanced total radioactivity in $RECl_3$ was attributed to ^{228}Ra radiation, while 33.9% is due to radiation of ^{226}Ra (11.5%), ^{223}Ra (8.3%) and ^{210}Pb (14.1%), Fig. 1. Subsequently, special attention was considered for removal the enhanced radionuclides present in the $RECl_3$ liquor before the chemical processing of Ln(III).

2. Elimination Studies

In this section we aimed to remove the enhanced naturally occurring radionuclides attributed mainly to radium-isotopes (^{228}Ra, ^{226}Ra, ^{223}Ra) as well as radioisotopes of lead (^{210}Pb) in Ln(III) chlo-

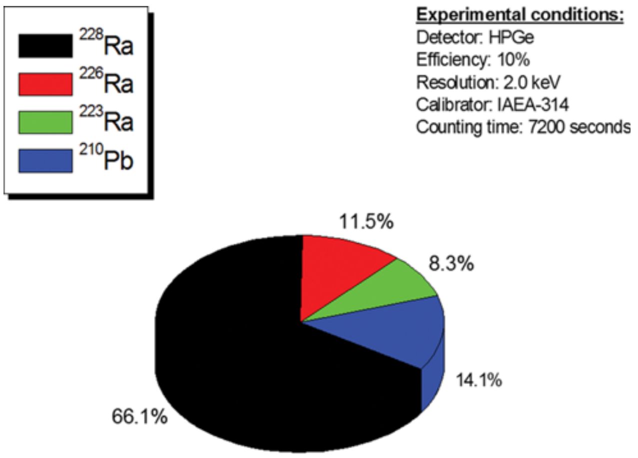

Fig. 1. Contribution of radionuclides in the rare earth chloride ($RECl_3$) liquor.

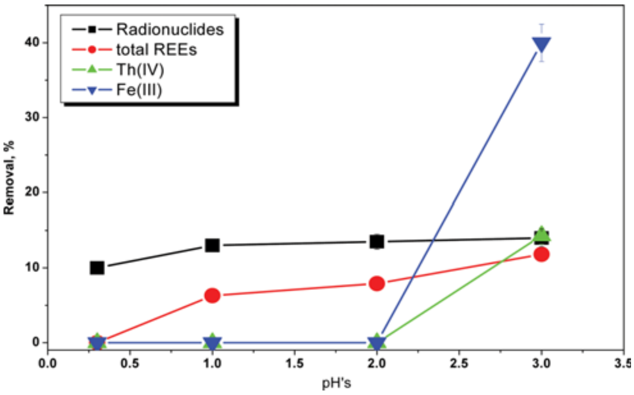

Fig. 2. Influence of pH on removal of radionuclides in the RE-chloride liquor.

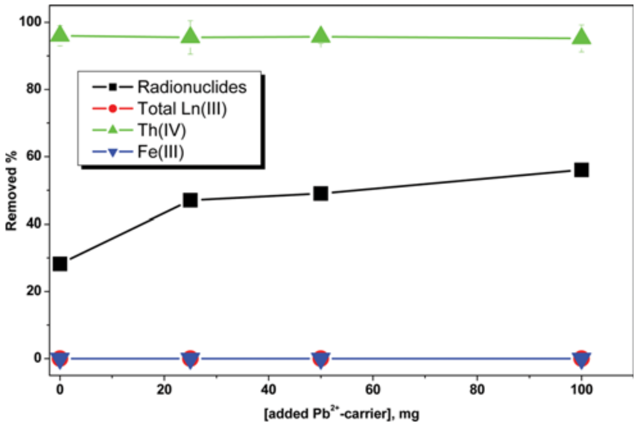

Fig. 3. Influence of Pb-carrier additions on removal of radionuclides, Th(IV) and Fe(III) from rare earth chloride (RE-Cl_3) liquor.

ride liquor, to produce eliminated Ln(III)-chloride (free radioactivity) to be safer during the separation and purification of the individual Ln(III). In this concern, we studied the influence of some factors affecting radionuclide removal.

2-1. Influence of pH

The hydrogen ion concentration of Ln(III) chloride liquor was adjusted at different pH's (0.4-3) using ammonium hydroxide solution (25%). The precipitate formed in solution was left overnight (20 hrs) and filtered off. The removal % of the total radioactivity level attributed mainly to the natural radionuclides of Ra-isotopes (^{228}Ra, ^{226}Ra, ^{223}Ra) and ^{210}Pb, as well as the loss in total Ln(III) and Th(IV) are presented in Fig. 2. It is observed that the removal % of radionuclides and Ln(III) increased with the pH alteration. At the significant pH of 3, the amount of the total radionuclides removed and Ln(III) lost from the RE-chloride liquor reached 14±1 and 12±1%, respectively, while removal % of Th(IV) and Fe(III) was 14±1 and 40±3%, respectively. This means that ~86% of total radionuclides still remained with 88% of Ln(III) in presence of Th(IV) and Fe(III) in the RE-chloride liquor. The removal % of radionuclides, Th(IV), Fe(III) and Ln(III) may be attributed to a coprecipitation or adsorption mechanisms with hydrous and/or hydroxides of some metals within the studied pH range. The metal oxides and/or hydroxides that may be acting as collector radionuclides have a low solubility product (K_{SP} at 25 °C) in acidic medium [31,32], Table 2.

2-2. Influence of Carrier Metal Ions

Two different carrier solutions containing Ba^{2+} or Pb^{2+} (25 mg/mL) were examined to eliminate the technically enhanced natural radioactivity attributed to radium-isotopes and ^{210}Pb present in the Ln(III) chloride liquor. The radionuclides were eliminated by coprecipitation process using the constant addition of sulfuric acid (2.6 mol/L) in the presence of Ba- or Pb-carrier alone, and as a synergistic admixture of both carriers (Ba/Pb). Figs. 3-5 demonstrate the effect of carrier on the removal % of the total radionuclides of Ra-isotopes and ^{210}Pb from Ln(III) in the RE-chloride liquor. Before addition of Ba and/or Pb-carrier, the addition of H_2SO_4 led to decrease in concentration of radionuclides and Th(IV), while concentration of Ln(III) and Fe(III) remained constant. It was found that the removed amount of radionuclides and Th(IV) without carrier addition was ~28 and 95%, respectively. The removed species can be attributed to a coprecipitation for radionuclides of Ra-isotopes (^{228}Ra, ^{226}Ra, ^{223}Ra) and ^{210}Pb as a low soluble sulfates of Ca^{2+} and/or Sr^{2+} (Table 2) already present in monazite sample used according to:

Table 2. The solubility product (K_{SP}) of some hydroxides, sulphates and chromates [31,32]

M-hydroxides	K_{SP} at 25 °C	M-sulphates	K_{SP} at 25 °C	M-chromates	K_{SP} at 25 °C
$Al(OH)_3$	3.00×10^{-34}	$CaSO_4$	4.93×10^{-5}	$SrCrO_4$	4.00×10^{-5}
$Fe(OH)_3$	2.79×10^{-39}	$SrSO_4$	3.44×10^{-7}	$BaCrO_4$	1.17×10^{-10}
$Pb(OH)_2$	1.43×10^{-20}	$BaSO_4$	1.08×10^{-10}	$PbCrO_4$	3.00×10^{-13}
$Zn(OH)_2$	3.00×10^{-17}	$RaSO_4$	3.66×10^{-11}	/	/

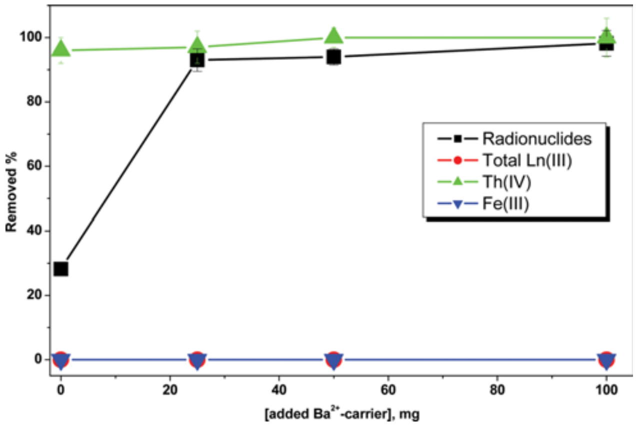

Fig. 4. Influence of Ba-carrier additions on removal of radionuclides, Th(IV) and Fe(III) from rare earth chloride (RE-Cl$_3$) liquor.

$$Ca^{2+}_{(aq)}+\mathbf{Ra}^{2+}_{(aq)}+\mathbf{Pb}^{2+}_{(aq)}+\mathbf{Th}^{4+}_{(aq)}+5SO_4^{2-}{}_{(aq)} \rightarrow [Ca(\mathbf{Ra,Pb,Th})(SO_4(s))_5]\downarrow \quad (5)$$

$$Sr^{2+}_{(aq)}+\mathbf{Ra}^{2+}_{(aq)}+\mathbf{Pb}^{2+}_{(aq)}+\mathbf{Th}^{4+}_{(aq)}+5SO_4^{2-}{}_{(aq)} \rightarrow [Sr(\mathbf{Ra,Pb,Th})(SO_4(s))_5]\downarrow \quad (6)$$

In case of Pb-carrier, the high removal % obtained during the elimination process was 56% and 95% for radionuclides (Ra-isotopes and ^{210}Pb) and Th(IV), respectively, in the presence of 100 mg of Pb, Fig. 3. With the addition of Ba-carrier (0.0-100 mg), a significant increase in the removal % of radionuclide from the Ln(III) was observed. The maximum removal % of radionuclides and Th(IV) reached ~98% in the presence of 100 mg Ba-carrier, Fig. 4.

In both cases, the concentrations of Ln(III) and Fe(III) remained constant in the RE-chloride liquor without loss. The decrease in levels of radionuclides and Th(IV) was due to co-precipitation with the added carriers, Ba and Pb to form low soluble sulfates as:

$$Ba^{2+}_{(aq)}\text{-carrier}+\mathbf{Ra}^{2+}_{(aq)}+\mathbf{Pb}^{2+}_{(aq)}+\mathbf{Th}^{4+}_{(aq)}+5SO_4^{2-}{}_{(aq)} \rightarrow [Ba(\mathbf{Ra,Pb,Th})(SO_4(s))_5]\downarrow \quad (7)$$

$$Pb^{2+}_{(aq)}\text{-carrier}+\mathbf{Ra}^{2+}_{(aq)}+\mathbf{Pb}^{2+}_{(aq)}+\mathbf{Th}^{4+}_{(aq)}+5SO_4^{2-}{}_{(aq)} \rightarrow [Pb(\mathbf{Ra,Pb,Th})(SO_4(s))_5]\downarrow \quad (8)$$

The variation in the removal % of radionuclides from the Ln(III) chloride liquor in the presence and absence of Ba or Pb carrier can be attributed to the larger solubility product (K_{SP}) of Ca and Sr sulfate compared with Ba or Ra sulfate [31,32]. Consequently, the elimination of the enhanced activity concentration due to Ra-isotopes and/or ^{210}Pb by co-precipitation method as sulfate was more efficient and selective in the presence of Ba-carrier rather than the Pb-carrier. This can be attributed to the low solubility product of Ba and/or Ra sulfate compared with Pb sulfate as:

$$PbSO_4\ (K_{SP}.\ 2.53\times10^{-8}) > BaSO_4\ (K_{SP}.\ 1.08\times10^{-10}) > RaSO_4\ (K_{SP}.\ 3.66\times10^{-11}).$$

On the other hand, different series of a synergistic admixture of the carriers used (Ba^{2+} with Pb^{2+}) are investigated in a trial to improve the elimination process of the undesirable species associated with Ln(III) in RE-chloride liquors. The results were represented in Fig. 5. It can be seen that the removal % of radionuclides with the synergistic additions was significant within the ratios ranged from 3 : 1 till 1 : 3 (Ba/Pb). The maximum removal % of Ra-isotopes and ^{210}Pb within this range was ~93%. Within synergistic admixture range of Ba/Pb carrier, it is found that more than 95% of Th(IV) was removed, whereas all Ln(III) and Fe(III) remained soluble in the RE-chloride liquor. This means that, the elimination process for radionuclides of Ra-isotopes and ^{210}Pb in Ln(III) chloride liquor was achieved without loss of Ln(III). It can be seen that use of Ba^{2+} as a carrier for the elimination of Ra-isotopes (^{228}Ra, ^{226}Ra, ^{210}Ra) as sulfate from RECl$_3$ liquor is efficient and economic regarding to Pb^{2+}. Despite of these advantages, addition of Pb^{2+} as the carrier is significantly improved the selective co-precipitation and elimination of ^{210}Pb associated with Ra-isotopes in the liquor. Therefore, a synergistic admixture of Ba/Pb carrier solution (1 : 1 v/v, 25 mg/ml for each) was chosen as a suitable carrier in the further investigations for elimination of radium-isotopes and ^{210}Pb present in the Ln(III) chloride liquor.

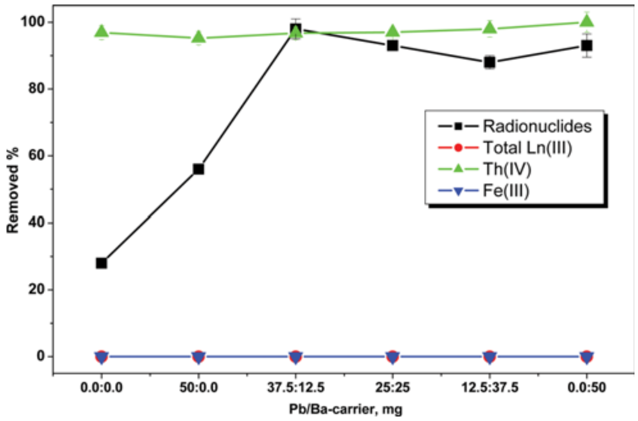

Fig. 5. Influence of Pb/Ba-carrier admixture on removal of radionuclides, Th(IV) and Fe(III) from rare earth chloride (RE-Cl$_3$) liquor.

2-3. Influence of Precipitating Agent

For this purpose, different five precipitating agents are suggested and examined for elimination of radionuclides contributed to Ra-isotopes (^{228}Ra, ^{226}Ra, ^{223}Ra) and ^{210}Pb, Th(IV) and Fe(III). The studied reagents include solutions of sulfuric acid, sodium sulfate, ammonium sulfate, potassium sulfate and potassium chromate. To perform these experiments, the RECl$_3$ liquor is filtered off to remove the non-dissolved or suspended matters. Then, the acidity of the clear supernatant of liquor is adjusted to pH 3±0.1 and left for overnight. The liquor is filtered off again to remove the formed possible metal oxides and/or hydroxides. Then, the precipitating agents were tested in the presence of admixture of Ba/Pb-carrier (1 : 1) for removal of the undesirable materials such as Ra-isotopes and ^{210}Pb, Th(IV) and/or Fe(III).

2-3-1. Treatment by Sulfuric Acid Solutions (H$_2$SO$_4$)

The radioactive contaminants were removed from Ln(III) chloride liquor by the precipitation process to form insoluble sulfates using solutions of sulfuric acid and its salts such as sodium sulfate, ammonium sulfate and potassium sulfate. Fig. 6 demonstrates the influence of sulfuric acid (H$_2$SO$_4$) solutions within the concentration range of 0.33-3.85 mol/L on elimination of radionuclides in

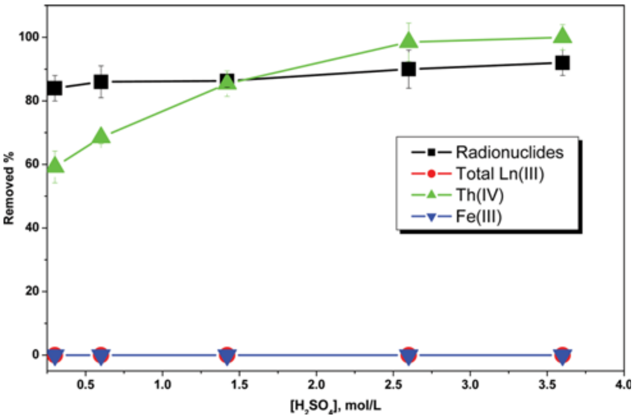

Fig. 6. Influence of H_2SO_4 solutions on removal of radionuclides, Th(IV) and Fe(III) from rare earth chloride (RE-Cl_3) liquor.

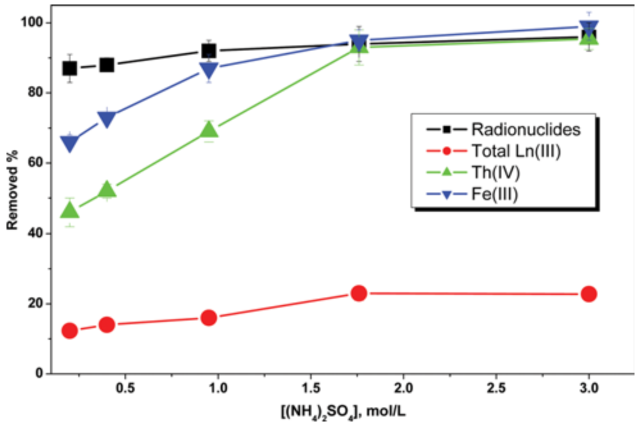

Fig. 8. Effect of ammonium sulphate solutions on removal of radionuclides, Th(IV) and Fe(III) from rare earth chloride (RE-Cl_3) liquor.

$RECl_3$ liquor. It is observed that the removal % of total radionuclides increase slightly with the increase of H_2SO_4 concentration, while removal of Th(IV) was significant increases. The high removal % was observed at H_2SO_4 concentration ≥2.6 mol/L. The high removal % of the undesired species were 90% and 98% for radionuclides and Th(IV), respectively. Whereas, the removal % of Ln(III) and Fe(III) were too low (zero). This means that Ln(III) and Fe(III) were remained completely soluble without radionuclides of Ra-isotopes, ^{210}Pb or Th(IV).

2-3-2. Elimination by Sodium Sulfate Solutions (Na_2SO_4)

The enhanced natural radionuclides in Ln(III) liquor solution were also eliminated using sodium sulfate (Na_2SO_4) solutions within concentration ranging from 0.02 to 0.26 mol/L. The results obtained are represented in Fig. 7. It was found that there are two basic varieties for the removal of the interested species by Na_2SO_4 solutions; one is advantageous while the other creates a problematic effect in the elimination process. The advantage was noticed in the removal of a significant amounts of Fe(III) with radionuclides of Ra-isotopes and ^{210}Pb as well as Th(IV). The removal % of the undesirable species was ~99, 80 and 97% for radionuclides (Ra-isotopes and ^{210}Pb), Th(IV) and Fe(III), respectively. While the problematic effect was related to loss in the amount of total Ln(III) in RE-chloride liquor associated with the elimination process. The amount of the Ln(III) lost ranged from 12 to 20% within the studied concentration range of Na_2SO_4 used.

2-3-3. Elimination by Ammonium Sulfate Solutions ($(NH_4)_2SO_4$)

Fig. 8 demonstrates the results obtained for the influence of ammonium sulfate $(NH_4)_2SO_4$) solutions on elimination of the undesired species in the RE-chloride liquor. The results indicated that the effect of $(NH_4)_2SO_4$ on elimination of Ln(III) is similar to that observed in the case of Na_2SO_4 (Fig. 7). The removal % of radionuclides and the lost % of Ln(III) increased slightly with concentration of ammonium sulfate, while the removal % of Th(IV) and Fe(III) increased significantly.

At steady state, the high removal % of the undesired species was obtained at ~1.8 mol/L of ammonium sulfate solution. The removal % obtained was ~94% for each species (radionuclides, Th(IV) and Fe(III)), whereas about 23% of Ln(III) was lost during the elimination process. In spite of this loss, the remaining Ln(III) in RE-chloride liquor is considered safe in viewpoint of radiation protection and free of the aggressive interfering metal ions, especially Th(IV) and Fe(III).

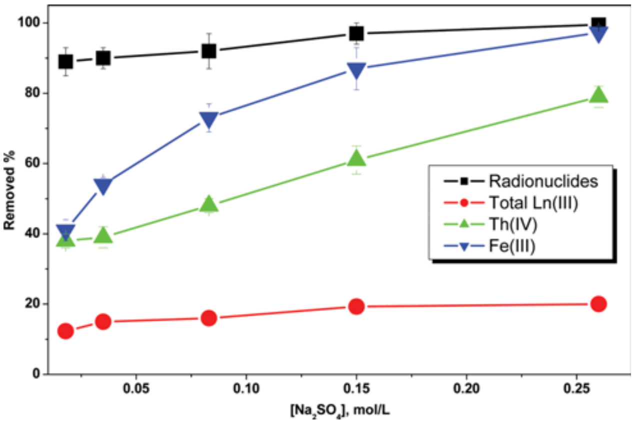

Fig. 7. Effect of Na_2SO_4 solutions on removal of radionuclides, Th(IV) and Fe(III) from rare earth chloride (RE-Cl_3) liquor.

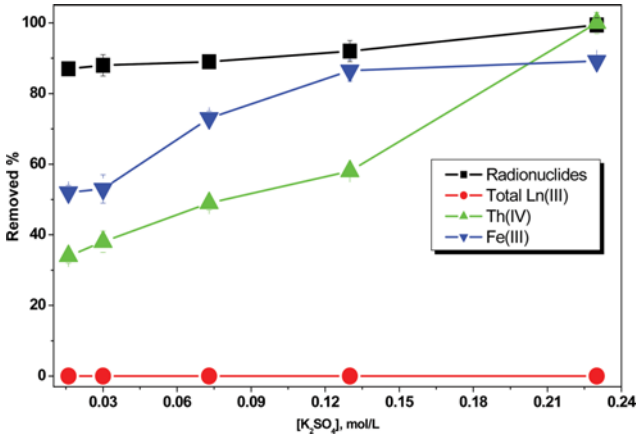

Fig. 9. Effect of K_2SO_4 solutions on removal of radionuclides, Th(IV) and Fe(III) from rare earth chloride (RE-Cl_3) liquor.

2-3-4. Elimination by Potassium Sulfate Solutions (K_2SO_4)

Influence of potassium sulfate concentration on elimination of the undesired species in the RE-chloride liquor was investigated within concentration range of 0.02-0.23 mol/L. The results obtained are displayed in Fig. 9. It was found that the removal % of radionuclides increased slowly, while the removal of Th(IV) and Fe(III) increased rapidly till 0.23 mol/L K_2SO_4. The maximum removed % reached to ~99% for both radionuclides and Th(IV), while it was ~90% for Fe(III). At the same time, there was no loss in the amount of the Ln(III) during the elimination process using K_2SO_4 solutions within the studied concentration range. By this way, most of the undesired species such as radionuclides, Th(IV) or Fe(III) were removed. Consequently, the elimination process of the undesired species (radionuclides, Th(IV) and Fe(III)) associated with Ln(III) in RE-chloride liquor is more efficient by 0.23 mol/L K_2SO_4 than that of sulfuric acid, sodium or ammonium sulfate.

2-3-5. Elimination by Potassium Chromate Solutions (K_2CrO_4)

For this purpose, potassium chromate solutions were examined as a precipitating agent to eliminate radionuclides of Ra-isotopes (^{228}Ra, ^{226}Ra, ^{223}Ra) as well as ^{210}Pb from Ln(III) chloride liquor. The results obtained are represented in Fig. 10. It was observed that the removal % of Ra-isotopes and ^{210}Pb as well as Fe(III) associated with Ln(III) in RE-chloride liquor were too high due to complete co-precipitated together within the studied concentration range of 0.25-0.85 mol/L of chromate solutions. In contrast, the removal % of Th(IV) and Ln(III) was decreased with the addition of chromate solutions. Removal of Ra-isotopes, ^{210}Pb, Th(IV) and Fe(III), and loss of Ln(III) was attributed to co-precipitation with the low soluble chromate species, such as barium chromate ($K_{SP}(BaCrO_4)$: 1.17×10^{-10}) and/or lead chromate ($K_{SP}(PbCrO_4)$: 3.0×10^{-13}) at 25 °C [31,32], Table 2. It is not recommended to use chromate solution for elimination of the undesirable species with Ln(III) in RE-chloride liquor, due to the high loss (65-83%) of Ln(III) during the elimination process.

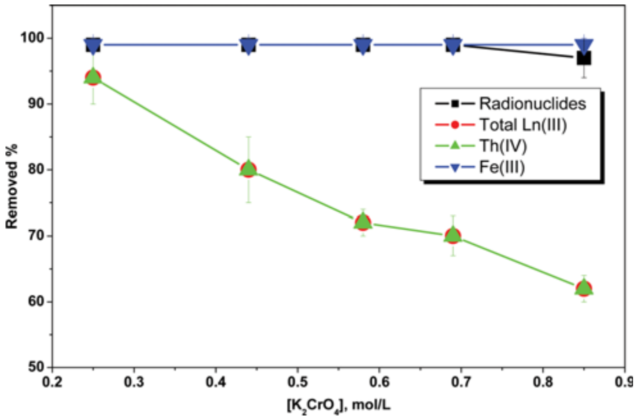

Fig. 10. Influence of K_2CrO_4 solutions on removal of radionuclides in the RE-chloride liquor.

It can be summarized that the optimized conditions in viewpoints suitability of the reagents and carriers used for elimination of undesired species associated with Ln(III) in the $RECl_3$ liquor, Table 3. It was observed that elimination of rare earth liquor succeeded to eliminate >95% of the undesirable species (e.g., radionuclides of Ra-isotopes and Pb, Th(IV), Fe(III)), using solutions of potassium sulfate or sulfuric acid solution in presence of Ba/Pb-carrier (1 : 1). Furthermore, all Ln(III) remained completely (~100%) soluble in the liquor without loss.

In contrast, 20-83% of Ln(III) was lost when the $RECl_3$ liquor was treated by sodium or ammonium sulfate, or potassium chromate solutions. In case of 2.6 M H_2SO_4 solutions, ~95% of radionuclides and Th(IV) is removed, while Ln(III) still interfered with Fe(III). The loss of Ln(III) in $RECl_3$ liquor was 20-83% when the liquor treated by sodium or ammonium sulfate solutions, or potassium chromate. Accordingly, the removal efficiency of Ra-isotopes, ^{210}Pb, Th(IV) and/or Fe(III) from $RECl_3$ liquor can be ordered as: K_2SO_4 (0.23 M)>H_2SO_4 (2.6 M). By these options, $RECl_3$ liquor is considered as nearly free of radionuclides without serious radiological effects for the workers in monazite processing. For instance, total activity concentration of total radionuclides (^{228}Ra, ^{226}Ra, ^{223}Ra, ^{210}Pb) found in $RECl_3$ liquor was ~16,200 Bq/L. This level was decreased to ~160 Bq/L (i.e., <370 Bq/L) after treatment by solution of K_2SO_4 or H_2SO_4. In addition, groups or individual Ln(III) can be processed, chemically without the interference of Fe(III) and Th(IV). Regarding previous studies in literature, it was found that 85% of ^{226}Ra and ^{210}Pb was removed from the rare earth chloride liquor produced from processing of Australian monazite [7,9]. Whereas, ~97% of thorium was eliminated from sulfate leach solution obtained from Malaysian monazite [13]. Finally, in the present work, the removal of radionuclides reached ~100% by potassium

Table 3. Summary for the optimized conditions required to obtain Ln(III) free of radionuclides, Th(IV) and Fe(III)[*]

Reagent used	Carrier type	Eliminated % of:			
		Loss % of Ln(III)	Undesired species		
			R[*]	Th(IV)	Fe(III)
Sulphuric acid (2.60 M)	25 mg Pb	0.0	47±2	96±4	0.0
Sulphuric acid (2.60 M)	25 mg Ba	0.0	93±4	97±3	0.0
Sulphuric acid (2.60 M)	25 : 25 mg (Ba : Pb)	0.0	93±2	98±2	0.0
Sod. sulphate (0.26 M)	25 : 25 mg (Ba : Pb)	20±1	99±1	79±3	97±2
Amm. sulphate (1.7 M)	25 : 25 mg (Ba : Pb)	23±2	94±3	93±4	95±2
Pot. sulphate (0.23 M)	25 : 25 mg (Ba : Pb)	0.0	99±1	99±1	87±2
Pot. chromate (0.25 M)	25 : 25 mg (Ba : Pb)	83±3	99±1	94±3	99±1

[*] Radionuclides of three radium-isotopes (^{228}Ra, ^{226}Ra, ^{223}Ra) and long-lived lead isotope (^{210}Pb)

sulfate or sulfuric acid solutions, while the removal % of Th(IV) and Fe(III) reached to 94-99% and 0.0-99%, respectively (Table 3). Thus, elimination of the enhanced undesirable species (e.g., Ra-isotopes, ^{210}Pb, Th(IV) and Fe(III)) is more efficient and significant compared to those achieved by elsewhere [7,9,13]. Consequently, the present results are promising for production of rare earth elements (REEs) from Egyptian monazite.

CONCLUSION

Removal of the undesired species in $RECl_3$ liquor was investigated and optimized. In summary, i) more than 95% of radionuclides (^{228}Ra, ^{226}Ra, ^{223}Ra, ^{210}Pb), Th(IV) and/or Fe(III) by K_2SO_4> H_2SO_4 in presence of Ba/Pb-carrier (1 : 1), ii) activity concentration of the enhanced radionuclides was decreased to the recommended safe limits (<370 Bq/kg or Bq/L), and iii) use solutions of sodium or ammonium sulfate, or potassium chromate caused loss in Ln(III) reached to 20-83%. It is recommended that 0.23 M K_2SO_4 or 2.6 M H_2SO_4 is efficient for minimization of the possible radiological hazards before the chemical processing (extraction, separation and purification) of $RECl_3$ liquor. In addition, Th(IV) or Fe(III) interfering with Ln(III) was also eliminated to large extent.

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