BJRS

BRAZILIAN JOURNAL
OF
RADIATION SCIENCES
08-01 (2020) 01-12

SBPR
Sociedade Brasileira de Proteção Radiológica

Study of thorium and uranium isotopes activity concentration after percolation or agitation leaching, in mining lixiviation liquor samples

Reis Jr A. S., Monteiro R. P. G.

Comissão Nacional de Energia Nuclear - CNEN
Centro de Desenvolvimento da Tecnologia Nuclear - CDTN
Avenida Presidente Antônio Carlos – 6.627
CEP 31270-901 - Campus da UFMG - Pampulha
reisas@cdtn.br

ABSTRACT

This study refers to determination of thorium and uranium isotopes in mining lixiviation liquor samples. The analytical procedure involves sample preparation steps for rare earth elements, thorium and uranium separation, besides alpha spectrometry analysis of the isolated radionuclides. An isotopic tracer is used to determine the overall chemical yield and to ensure traceability to a standard sample from NIST. The paper presents and discusses that the chemical yield of thorium and uranium depends on the leaching method used, that is, column leaching or agitated leaching. We improved the method looking for reproducibility and isotopes isolation as required by alpha spectrometry and the method was effective in analysis of mining liquor.

Radiochemical separation, liquor samples, thorium and uranium determination, alpha spectrometry

.

ISSN: 2319-0612
Accepted: 2019-10-04

1. INTRODUCTION

Rare earth elements (REE) are found in various minerals. Depending on the mineralogy of the phases containing rare earth elements and the reactivity of the gangue phases, rare earth extraction, further processing / extraction and refining may involve acid or alkaline routes. The chemical treatment of these minerals can be carried out through the alkaline route by the addition of sodium hydroxide or via the acid pathway by digestion with sulfuric acid [1]. The acid method is usually the most used in the processing of the concentrates obtained in the chemical treatment due to the high cost of the alkali method in relation to this.

The rare earth leach liquor produced through digestion with sulphuric acid also contains other elements such as U, Th and Fe [2]. Radionuclides of both uranium and thorium decay series may be present associated with the rare earth deposits. It has been observed that the mining and processing of uranium and thorium bearing minerals alter the natural constituents of radionuclides and sometimes lead to enhanced radiation exposures [3; 4]. The presence of substantial uranium and/or thorium in the rare earth minerals causes considerable concern due to their radioactivity. Appropriate methods to separate them from rare earths for their proper management are therefore very important in order to avoid environmental pollution and the contamination of rare earth products [5].

We worked with a sample of a deposit whose typology is "Rare Earths associated with Ionic Clays", where rare earth elements are adsorbed on clays similar to the known deposits of southern China [6].

The main ore is of the saprolite type and the techniques used to dissolve the minerals are mainly percolation and agitation leaching. Agitation leaching makes it possible to avoid the sedimentation of the particles, but also promotes leaching kinetics, since the reactions are heterogeneous. In percolation leaching, the lixiviant percolates by gravity through the metalliferous mass which remains static. We studied the case in which the ore was arranged in column. The leaching was made using a 58 g / L sodium chloride solution acidified with sulfuric acid at pH between 1.5 and 2.

The pre-concentrated solution was treated in the hydrometallurgy stage, in which it purifies the liquor, concentrate and precipitates the REE [7].

Selective precipitation of thorium or selective dissolution of rare earths in chloride solutions is used to separate thorium from rare earths. Double salt precipitation of rare earths is widely adopted for some new process development. Solvent extraction is effective to separate uranium and thorium from rare earths. In this case, all amine compounds including primary, secondary and tertiary amines and quaternary amine salts have been widely investigated [8].

The present study was aimed at evaluating the activity concentration of radionuclides of the uranium and thorium series after percolation or agitation leaching in order to verify the natural activity concentration unbalance as a result from mining lixiviation of minerals rich in rare earths using radioanalytical techniques.

In radiochemistry, separation techniques are very common, for example, when a radionuclide is purified of other radioactive elements [9]. Techniques used for separation include co-precipitation, liquid-liquid extraction, ion exchange and extraction chromatography. In some cases, two or more of these techniques are combined. In this study, the radiochemical procedure consists of two steps performed by precipitation techniques and extraction chromatography using TRU chromatographic resin column.

The adaptation of the analytical procedure for the separation method was done from the development of separation methods previously used by us in other analyzes using alpha-spectrometry [10]. The alpha spectrometric analysis was applied to the determination of thorium and uranium isotopes and the analytical procedure involves thorium and uranium separation using selective etching with hydrofluoric acid and further radiochemical separation of these using TRU chromatographic resins (Eichrom Industries Inc USA) besides electroplating of the isolated radionuclides. In order to account for the inevitable loss of the sample during separation, a specific isotope called a tracer is added to the sample. A tracer represents the addition to an aliquot of a known quantity of a radioactive isotope that is different from that of the isotope of interest but expected to have the same behavior. Activity results for the samples are normally corrected assuming the tracer is homogeneously mixed.

2. MATERIALS AND METHODS

2.1. Reagents and Apparatus

Calibrated solutions were acquired from the Instituto de Radioproteção e Dosimetria (IRD), Rio de Janeiro, Brasil and the certified absolute activity level for each of them is: ^{230}Th 10.047 kBq, expanded uncertainty of 1,36% using a coverage factor of 2 (K=2) and ^{232}U 4.26 kBq, expanded uncertainty of 3.2% using a coverage factor of 2 (K=2).

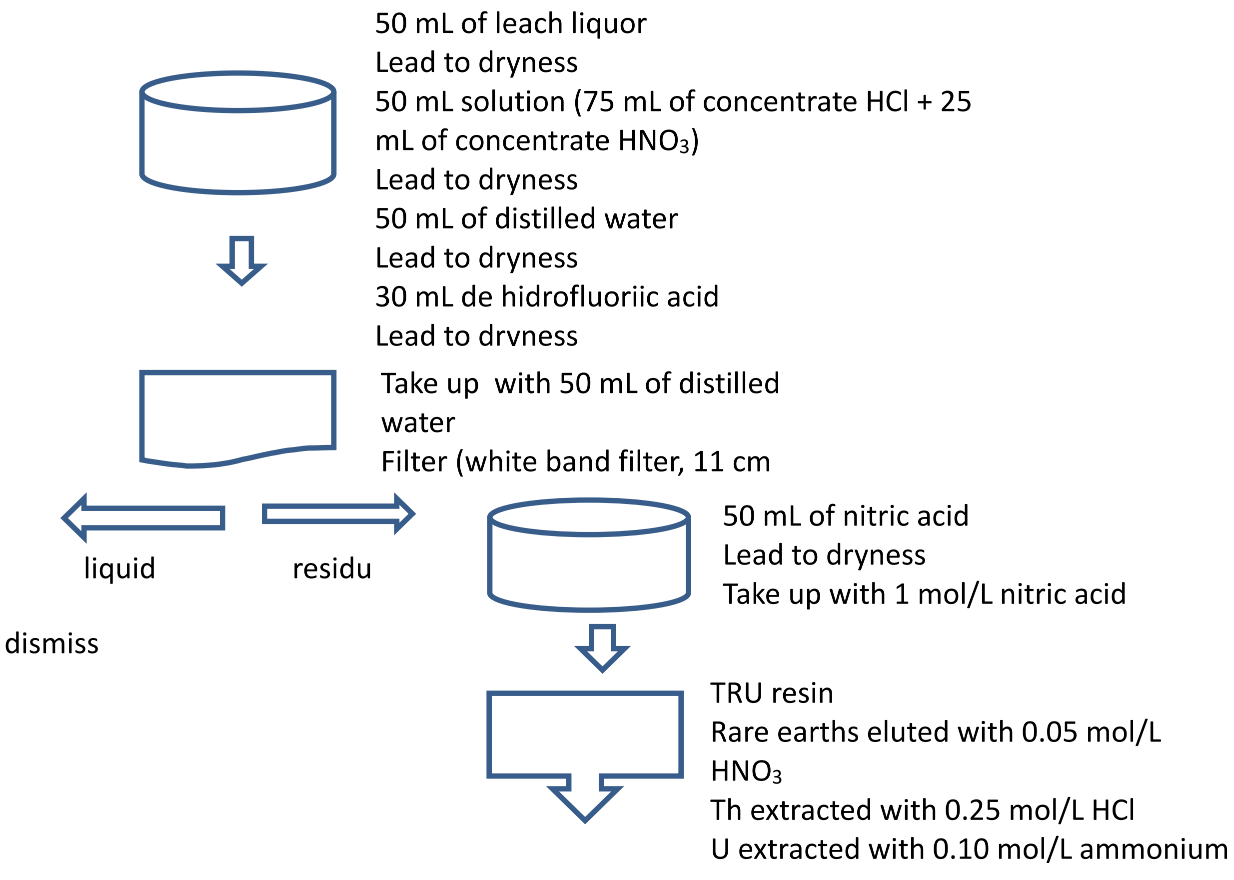
2.2. Methodology

Experiments were done to find out which tracer could be used. 50 ml aliquots of each solution without the tracer were prepared which were treated in the same way as the aliquots to be analyzed. In the spectrum obtained without the adiction of any tracer the ^{230}Th was bellow detection limit for the method. So the ^{230}Th was chosed to be the tracer for thorium. ^{232}U was chosed to be the tracer for the uranium determination. The contribution to ^{228}Th given by the decay of ^{232}U can be determined by considering the secular equilibrium at ^{232}U decay. By gamma spectrometry it was found that the system was in equilibrium by determining the activities of ^{212}Bi and ^{212}Pb. Therefore, for the ^{228}Th activity determined in the sample analyzes, the activity of 3.98 Bq / L should be discounted due to the contribution of ^{228}Th given by the decay of ^{232}U tracer. The tracers were added, 0.1965 Bq of ^{232}U and 0.156 Bq of ^{230}Th, to 50 mL aliquot of the leach liquor sample before the chemical treatment was started.

A 50 mL aliquot of the liquid samples (leach liquor) was initially heated to dryness at 200 ° C. The solid obtained was then treated with 50 mL of cold water (75 mL of concentrate hydrochloric acid + 25 mL of concentrate nitric acid) and taken to dryness. The solid obtained was taken up in 50 mL of hydrofluoric acid (60%) and taken to dryness. This solid was dissolved in deionized water and filtered. The solid collected by the filter was dissolved in 30 mL of concentrated nitric acid to obtain the nitrate of the retained elements: rare earths, thorium and uranium. It was taken to dryness and the solid obtained was dissolved in 10 ml of 1 mol/L HNO3 solution.

The solution obtained was eluted on a TRU chromatographic resin column (Eichrom Industries Inc. USA). The rare earths were separated by eluting them with 0.05 mol/L HNO3. The thorium was eluted with 30 mL of aq. 0.25 mol/L HCl and uranium with 0.1 mol/L of ammonium oxalate solution. Flowchart for obtaining Th and U separately is presented in Fig 1.

Figure 1: *Flowchart for obtaining thorium and uranium, separately, from a leach liquor solution*



50 mL of leach liquor
Lead to dryness
50 mL solution (75 mL of concentrate HCl + 25 mL of concentrate HNO_3)
Lead to dryness
50 mL of distilled water
Lead to dryness
30 mL de hidrofluoriic acid
Lead to drvness

Take up with 50 mL of distilled water
Filter (white band filter, 11 cm

50 mL of nitric acid
Lead to dryness
Take up with 1 mol/L nitric acid

TRU resin
Rare earths eluted with 0.05 mol/L HNO_3
Th extracted with 0.25 mol/L HCl
U extracted with 0.10 mol/L ammonium

2.3. Determination of Uranium and Thorium

The alpha-spectrometry measurements were carried out with Canberra PIPS (passivated ion implanted planar silicon) detectors and the spectrometer used was a Canberra Model S509 Genie 2000 Alpha Analyst. The alpha-energy calibration, the measurement of counting efficiency of the detector and the procedure to electrodeposition and determination of U and Th by alpha spectrometry were the same as that described in a previously paper [10].

The samples were analyzed immediately after the electrodeposition and the count time in the spectrometer was 48 hours. All activities of the radionuclides presented were calculated taking into account the added tracer activity. Detection limits are low, alpha spectrometry achieves a detection limit of 1.0 mBq / L. All samples were made in triplicate, and the results were presented with the standard deviation obtained for the measurements.

3. RESULTS AND DISCUSSION

The alpha spectra obtained in the sample analyses are shown in the Fig 2, spectrum for the thorium, and Fig 3, spectrum for the uranium. As can be observed in the spectra, the radiochemical procedure was successful in the separation of thorium and uranium radionuclides. Although ^{235}U is present in the sample, indicated by the presence of your daughter ^{227}Th in the Fig.2, we should not consider its possible interference with ^{234}U peak in the Fig.3, due the close energy for both, considering that ^{238}U has 99.28% relative abundance by weight and 48.8% relative abundance by activity, ^{235}U has 0, 72% and 2.4% and ^{234}U has 0.0057% and 48.8%, respectively.

Figure 2: *Alpha spectrum showing the characteristic peaks for the isotopes in the ^{232}Th series for the agitated leaching sample, using ^{230}Th as a tracer*

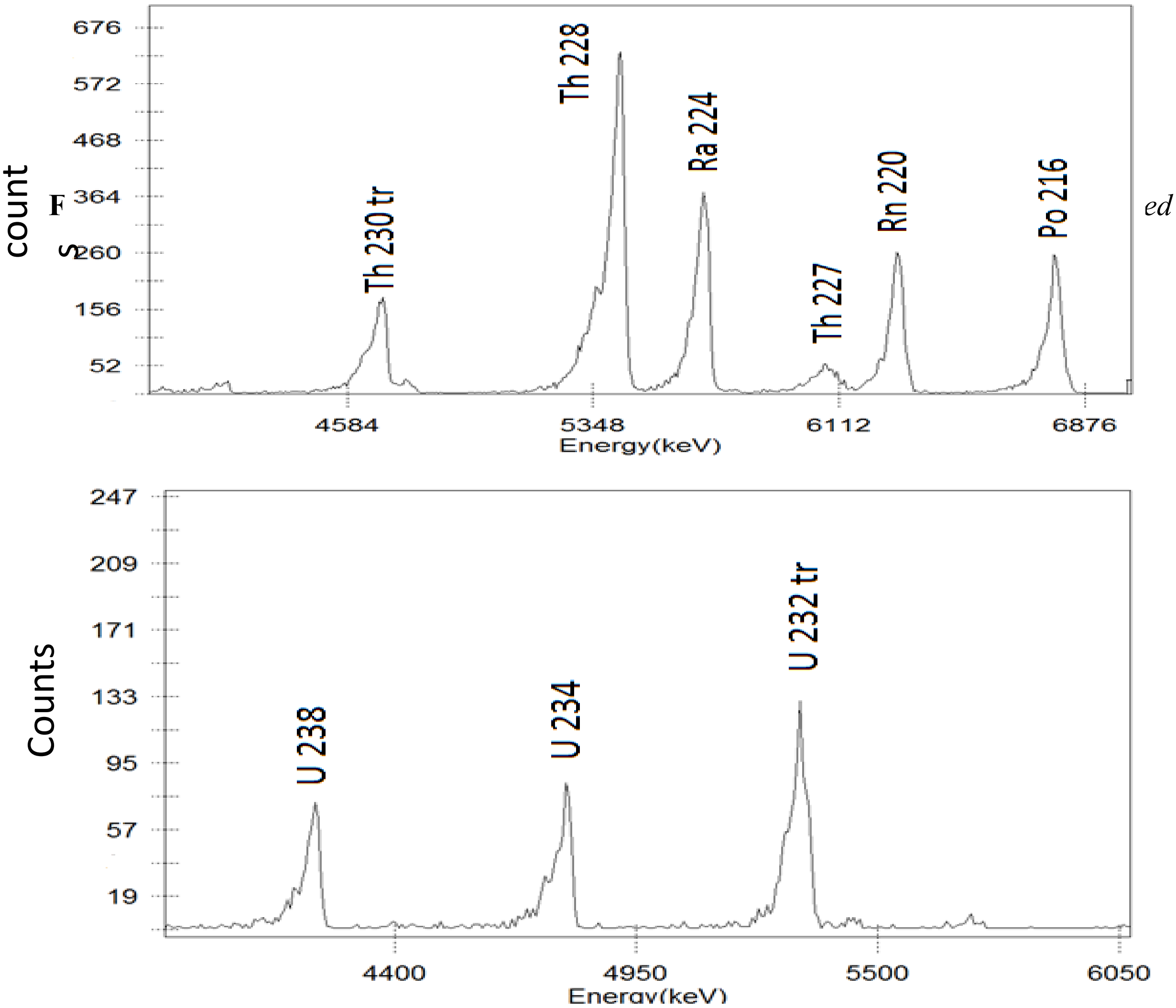


Table 1: For column leaching and agitated leaching the results of activity in Bq/L for thorium and uranium isotopes are inserted in Tab.1

Isotopes	**Activity concentration**	
	Column leaching	Agitated leaching
Thorium 232	nd	1.49 ± 0.02
Thorium 227	2.40 ± 0.39	1.70 ± 0.20
Thorium 228	17.12 ± 1.67	6.12 ± 2.90
Uranium 238	0.43 ± 0.04	1.79 ± 0.09
Uranium 234	0.60 ± 0.09	2.00 ± 0.20
Uranium 235	nd	nd

nd = bellow detection limit of the method

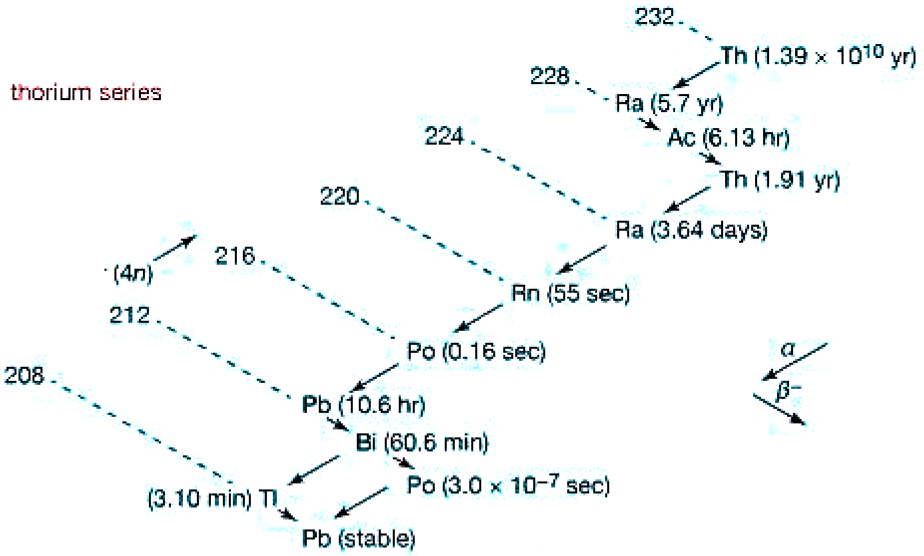
Results obtained in the analysis for quantitative determination of thorium and uranium isotopes using the experimental procedure for separation and isolation of the Th and U isotopes by precipitation with hydrofluoric acid and using the TRU resin in column chromatography are presented in Table 1, for column leaching and for agitated leaching. The experiments were performed involving data points with three replicates and the results are presented with standard deviations. We can compare the results obtained for both processes which allow us to do an analysis of the separation of thorium and uranium in such form to make an evaluation of that during the rare earth processing. By the obtained results we can observe discrepancy in activities for each isotope between the two methods used and this can be due to the different chemical yields obtained when different methods were used in leaching (column or agitation).

If the Th series isotopes and the U series isotopes are present in the solution to be eluted, the Th spectrum, Fig. 2, should contain the isotopes ^{226}Ra, ^{222}Rn and ^{218}Po, alpha emitters, belonging to the ^{238}U series, since ^{224}Ra, ^{220}Rn and ^{216}Po are the same elements, respectively, and are present in the spectrum. The absence of these in the spectrum could suggest that the children of ^{238}U is not present in the solution to be eluted or may indicate that the daughter isotopes of ^{232}Th are growing after separation by column being a decay product after elution and / or after electrodeposition.

In the case of uranium activity concentration determination, a result that should be expected to happen is that the ratio between the activities for the reason ($A_{u\text{-}238}/A_{u\text{-}234}$) that in natural minerals, in secular equilibrium, is approximately 1. The results for CDTN are in according with this approximation, (0.71 ± 0,19) for column leaching and (0.90 ± 0.11) for agitated leaching, being that the results are in good agreement with each other within the experimental uncertainty.

One must also consider the method used in leaching (column or agitation) since the results for activity are different in the determination by the two methods. For example, ^{232}Th does not appear in column leaching and appears in agitated leaching. When we analyze the results obtained in the case of ^{228}Th and ^{227}Th the activities are much higher in column leaching than that in agitated leaching, on the other hand the activities for ^{238}U and ^{234}U are much larger in the case of agitated leaching than those for column leaching.

***Figure 4:** Decay scheme of ^{232}Thorium family*



As it can be seen from the Fig 4 showing the decay scheme for ^{232}Th family practically all the daughter ^{232}Th alpha emitters appear in the spectrum, Fig 2. The half-life of the father is much greater than those of the children, which would guarantee the prerequisite to the balance in the activities. In some chemical step of both processes the ^{232}Th was removed leaving its decay products.

The application of alpha spectrometric analysis technique for radiochemistry purpose of detection and quantitative determination of thorium and uranium in lixiviation liquor makes it possible to establish the following result, in view of the analysis done previously. This can be determined by comparing the values for activity concentration for the same isotopes in Table 1. When compared the two leaching process the recovery to the Th and U can be summarized as follow: in the column leaching the ^{232}Th series isotopes activity concentration, is twice as high as in agitation leaching and the uranium isotopes activity concentration for column leaching is about a quarter of that for agitated leaching.

Therefore, we can consider that the recovery of the isotopes of thorium and uranium by the column leaching in rare earth minerals was preferentially made for thorium recovery while the agitated leaching was selective for uranium recovery. The uranyl-carbonate bond is exceptionally strong. Various ligands are arranged in the following decreasing strength of their bond with uranium such as CO_3^{-2},$\geq F^-$,$>C_2O_4^{-2}$,$>SO_4^{-2}$ [11]. Whether acid or alkaline leaching is used, uranium must be oxidized to the hexavalent state [U(VI)] before it can be dissolved. In acid leaching, the uranium oxidation reaction requires the presence of ferric ion, regardless of the reagent used as oxidant, since it appears that the ferric ion actually oxidizes the uranium while the oxidant reagent oxidizes ferrous ion to ferric ion. Uranium forms a very strong complex with these ligands which is soluble in the excess ligand in agitated leaching. The different behavior for column leaching and agitated leaching can be explained by the different solubility behavior of Th and U in these ligands solution, once, differently of the uranium, thorium solubility increases in the excess ligand solution due to complex $[Th(SO_4)_2]^0$ formation at $pH \leq 5$ values and at low temperatures [12].

4. CONCLUSION

The determination of Th and U in leach liquor samples was done using an adapted separation method. The results for Th and U isotopes activity concentration in column leaching and agitated leaching for the same sample presented significant differences, which can be attributed to application of methods different of obtaining the liquor that result in different chemical yields.

The results for the activities concentrations determined by us were justified and it was possible to establish that the differences between agitated leaching and column leaching may be due to the selectivity of retention and removal of the Th and U isotopes from the ore.

It is evident in this study that the chemical processes used in the two extraction processes beside to break the secular equilibrium of Th and U radioactive series can be an important indicator associated with contamination by by-products in industrial process that concentrate dangerous radionuclides. That is, during the process to obtain the product, wastes and by-products containing enhanced natural radioactivity - the TENORM material - are generated.

ACKNOWLEDGMENT

The authors are very grateful to the *Instituto de Radioproteção e Dosimetria* for its radiotracer standards supply and to the *Centro de Desenvolvimento de Tecnologia Nuclear* – (CDTN) for the research support.

REFERENCES

[1] Haque N, Hughes H, Lim S, Vernon, C. Rare Earth Elements: Overview of Mining, Mineralogy, Uses, Sustainability and Environmental Impact. **Resources,** v. .3: p. 614-635, 2014.

[2] Abreu R, Moraes A.C. Purification of rare earth elements from monazite sulphuric acid leach liquor and the production of high-purity Ceric Oxide. **Minerals Engineering, v.** 23,:p. 536-540, 2010.

[3] United Nations Scientific Committee on the Effects of Atomic Radiation **Sources and Effects of Ionizing Radiation**. **UNSCEAR**, Report to the General Assembly with Scientific Annexes, Vol. I Sources, United Nations, New York, 2000.

[4] Lipsztein J.L, Dias da Cunha K.M, Azeredo A.M.G.F, Lamego F Exposure of workers in mineral processing industries in Brazil. **Journal of Environmental Radioactivity, v.** 54(1):, p 189-99, 2001.

[5] Soldenhoft K Challenge in rare earth processing. **In: ALTA 2013 Uranium-REE conference**. May 25-june 1, Perth, Western Australia,2013.

[6] Mineração **Serra Verde** , O Projeto de Terras Raras. http://www.mineracaoserraverde.com.br/projeto/ .Last accessed: 16 September 2017

[7] Chong S, Hawker W, Vaughan J. Processing of Niquel Ores and Concentrates Selective reductive leaching of oxidized cobalt containing residue. **Minerals Engineering, v.** 54, p: 82-87, 2013.

[8] Zolotov YuA Separation in analytical chemistry and radiochemistry: similarities and differences**. Journal of Analytical Chemistry, v.** 60(11):, p 999 , 2005.

[9] Zhu Z, Pranolo Y, Cheng C.Y Separation of uranium and thorium from rare earths for rare earth production – A Review. **Minerals Engineering, v.** 77, p: 185-196, 2015.

[10] Reis A.S jr, Temba E.S.C, Kastner G.F, Monteiro R.P.G Combined Procedure Using Radiochemical Separation of Plutonium, Americium and Uranium Radionuclides for Alpha-Spectrometry. **Journal of Radioanalytical and Nuclear Chemistry,** v. 287(2), p**:** 567, 2011.

[11] P. Govindan A, Palamalai K.S, Vijayan M, Raja S, Parthasarathy S.V. Mohan R.V, Subba Rao Purification of ^{233}U from thorium and iron in the reprocessing of irradiated thorim oxide rods. **Journal of Radioanalytical and Nuclear Chemistry,** v. 246(2), p 441-444, 2000.

[12] Langmuir D, Herman J.S The mobility of thorium in natural waters at low temperatures. **Geochimica et Cosmochimica Acta, v.**, 44, p 1753-1766, 1980.