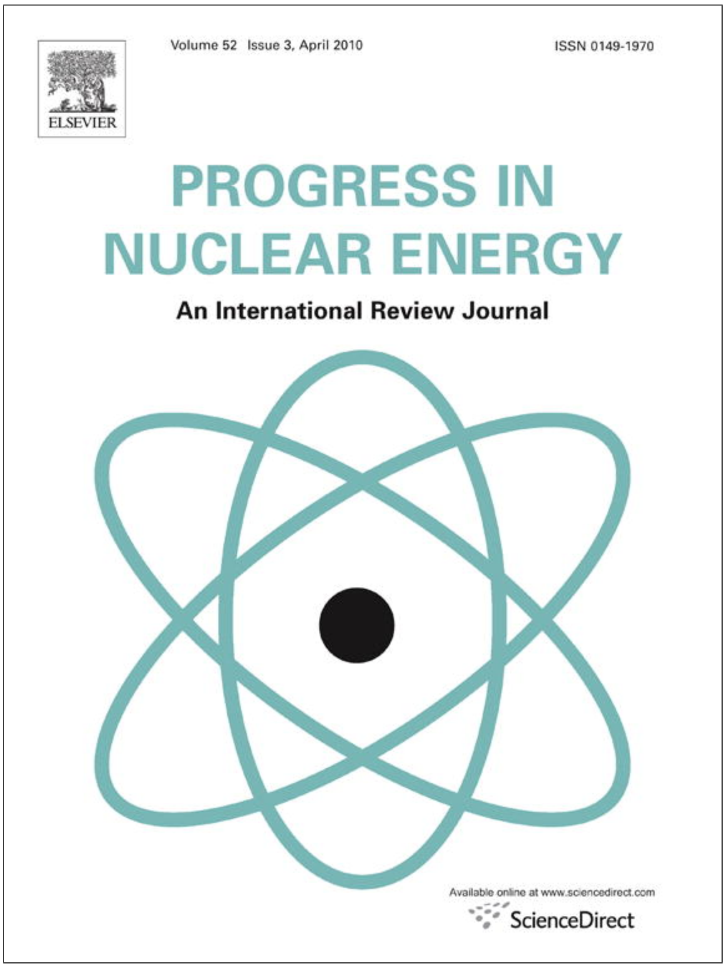

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Study on radiogenic lead recovery from residues in thorium facilities using ion exchange and electrochemical process

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ABSTRACT

Brazil has one of the biggest mineral thorium reserves, enabling the use of this material in its nuclear reactors. Consequently, this cycle of the fuel would need an initial purification stage of the natural thorium, generating residues from chemical treatment. This work provides operational parameters for the recovery of existing values in these residues, especially the radiogenic lead, that is a radioisotope of thorium decay chain, using ionic exchange technique associated to the electrochemical one. The treatment by ionic exchange in anionic resin and hydrochloric acid medium, provides about 33.4% of radiogenic lead. At the electrochemical process, lead was reduced to a metal in nitric acid medium, presenting a recovery of 98%. The electrochemical process presents an increase in the cost, nevertheless the technological importance of the radiogenic lead in the production of new elements, besides being a strategic material, justifies its use.

1. Introduction

The estimate of ThO_2 reserve in Brazil is about of 1,200,000 tons. Nowadays, some countries are interested in thorium, since it can be used in a nuclear breeder reactor with conceptual safety (Unak, 2000; Rubbia, 1995). In 1969 the Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN-SP), in Brazil, designed a project for the installation of a pilot plant for the purification of thorium compounds. The step was carried out using an extraction–scrubbing pulsed column. The thorium nitrate was extracted with TBP-Varsol after addition of sodium nitrate ($2.2\ mol\ L^{-1}$) solution and free nitric acid ($0.8\ mol\ L^{-1}$). The organic phase, rich in thorium nitrate, was scrubbed with a $2.2\ mol\ L^{-1}$ $NaNO_3$ and $0.8\ mol\ L^{-1}$ HNO_3 mixed solution. Finally, thorium nitrate was stripped from the organic phase with demineralized water. Then the organic phase was washed with sodium solution and re-equilibrated with nitric acid before initiating the new cycle.

The sludge was produced by precipitating raffinate containing thorium not extracted, all the rare earths and common impurities, with NaOH until final pH 9.0–9.5. It was separated by filtration and washed using $0.1\ mol\ L^{-1}$ NaOH solution (Bril and Kruhmholz, 1965a,b; Ikuta, 1976). This sludge, about 28 tons, is nowadays stocked into special poly(chloroethene) (PVC) drums, controlled by radiation protection norms, since it is radioactive due to the contribution of the ^{232}Th daughters. The average composition of this sludge and the results are presented in Table 1, indicating significant amounts of thorium, rare earths, iron, silica and minor constituents like lead from the decay of ^{232}Th. Its conditions were adjusted for this study.

The objective of the present work is to separate and recover the lead-208 from the crude thorium-rare earth sludge. For this purpose anionic ion exchange and electrodeposition techniques were used. Because of the decay time of thorium-232 to lead-208, the isotope lead-208 has became higher than the natural lead in this sludge.

2. Materials and methods

The lab-scale batch reactor consisted of a 4000 mL capacity apparatus provided with agitator, thermometer and heated eletrically (Fig. 1). pH meter Micronal B 374. Electroanalyser Metrohm 757 VA computrace with electrode HMDE (hanging mercury drop electrode); energy dispersive X-ray fluorescence spectrometer (EDXRF), Shimadzu, Mod. EDX-700. Wavelength dispersive X-ray fluorescence spectrometer (WDXRF), Rigaku Denki, Mod. RIX 3000.

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Table 1
Chemical composition of typical sludge lot.

Constituent	%[a]	Constituent	%[b]
ThO_2	55.76 ± 1.15	P	3.42 ± 0.07
RE_2O_3[b]	13.76 ± 0.28	K	0.16 ± 0.01
Pb	0.42 ± 0.01	Ca	3.23 ± 0.07
Na	0.23 ± 0.01	Fe	1.01 ± 0.02
Mg	0.28 ± 0.01	Cu	0.11 ± 0.01
Al	0.65 ± 0.01	Zn	0.34 ± 0.01
Si	3.10 ± 0.06		

Analyzed by WDXRF.
[a] Dry mass.
[b] Rare earth's oxide.

Table 2
Chemical composition stock solution.

Constituent	$\% \times 10^{-3}$[a]	$\mu g\ mL^{-1}$[b]	Constituent	$\% \times 10^{-3}$[a]	$\mu g\ mL^{-1}$[b]
Th	460 ± 23.0		Mn	4.0 ± 0.2	
Fe	6 ± 0.3		Pb	55.0 ± 1.0	170.0 ± 0.8
Cr	4.0 ± 0.2		Ti	11.0 ± 0.6	
Ni	3.0 ± 0.2		Cl	9523 ± 476	
Zn	3.0 ± 0.2		H_2O	89,657 ±4480	

Vol. stock solution = 1000 mL.
[a] EDXRF analysis.
[b] Voltammetry analysis.

Stationary experiments of electrochemical process were carried out using an Autolab potentiostat/galvanostat model PGSTAT 30, equipped with a GPES Manager program for data acquisition.

The strong base anion resin, IRA-900 Cl 100–200 mesh, was used in the chloride form. A portion of the resin was suspended in demineralized water and allowed to settle the fines. A column of 14 mm internal diameter was packed with 7 mL of resin. The column has a feed reservoir of 300 mL capacity.

The sludge dissolution was carried out in a lab-scale stirred reactor using 50 g of sludge for each experiment and agitation speed of 500 rpm. The sludge was dissolved with hydrochloric acid solution, the digestion being performed at 85 °C during 1 h. Filtration was carried out at 25 °C into a 13 cm diameter Büchner funnel, at constant manometric depression. The suspension was transferred at once to the funnel and immediately the suction started. A medium porosity filter paper Whatman no. 41 was used as the filtration medium. The stock solution from which the lead was separated, comes from the treatment of this sludge with hydrochloric acid and diluted until concentration of total oxide of 10 g L^{-1}. The composition was obtained by EDXRF analysis, values presented in Table 2. Before each run the filtrate solution had its concentration in chloride adjusted to 1.75 mol L^{-1}. For each run, 100 mL of this solution was used varying flow rate from 0.3 to 2.0 mL min^{-1} cm^{-2}. After the loading operation, the resin was washed with 21 mL of HCl 1.75 mol L^{-1} to eliminate the occluded and interstitial ions.

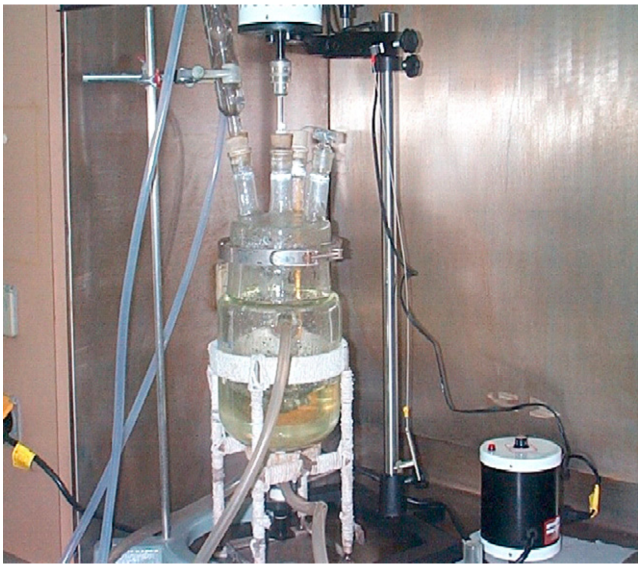

Fig. 1. The lab-scale batch stirred reactor.

The solution was acidified with hydrochloric acid, to the range of 0.5–3.0 mol L^{-1} and then was percolated through the anionic resin in the flux rate range of 0.5–2.0 mL min^{-1} cm^{-2}. The resin had the function to retain and separate the lead in an anionic chloride complex form, as described in Eqs. (1) and (2) (Yatsimirskii and Vasilev, 1960).

$$Pb^{2+}_{(aq)} + 3Cl^{-}_{(aq)} \rightleftarrows PbCl^{-}_{3(aq)} \quad pk = 1.85 \tag{1}$$

$$R\text{-}Cl_{(s)} + PbCl^{-}_{3(aq)} \rightleftarrows R\text{-}PbCl_{3(s)} + Cl^{-}_{(aq)} \tag{2}$$

Finally the adsorbed lead ions were eluted from the resin with demineralized water (Kraus and Nelson, 1956), by rupture of lead chloride complex.

Lead was determined by an electroanalyzer 757 VA Computrace, Metrohm with HMDE. All the principal elements in the eluate solution were determined by energy dispersive X-ray fluorescence spectrometer (EDXRF).

Lead eletrodeposition was carried out in 77.9 mg Pb L^{-1} and 0.02 mol L^{-1} HNO_3 aqueous solution. The electrodeposition was performed in a conventional three-electrode electrochemical cell with an Ag/AgCl reference electrode, a cylindrical Ti working electrode of 68.16 cm^2 and a Pt auxiliary electrode of 2.0 cm^2. The lead reduction and oxidation process were investigated by cyclic voltammetry between 0.0 and 1.2 V (versus Ag/AgCl reference electrode) at a scan rate of 10 mV s^{-1}.

All reagents used were of analytical grade and the solutions were prepared using demineralized water.

3. Results and discussion

In the present study special attention was given for the recovery of lead. The lead species in chloride solution are mainly in the anionic complex form. The ion Pb^{2+} forms a stepwise series of

Table 3
Loading of lead as function of HCl (mol L^{-1}).

Effluent (mL)	3.00 mol L^{-1}		1.75 mol L^{-1}		0.50 mol L^{-1}	
	mg L^{-1} Pb	C/C_0	mg L^{-1} Pb	C/C_0	mg L^{-1} Pb	C/C_0
0	0	0.0	0	0.0	0	0.0
10	15	0.1	8	0.1	5	0.0
20	75	0.5	60	0.4	46	0.3
30	80	0.6	84	0.6	89	0.6
40	90	0.6	110	0.8	139	1.0
50	104	0.7	112	0.8	118	0.8
60	110	0.8	122	0.8	130	0.9
70	145	1.0	130	0.9	134	0.9
80	130	0.9	133	0.9	140	1.0
90	135	1.0	142	1.0	138	1.0
100	115	0.8	138	1.0	142	1.0

Resin vol. = 7.0 mL; intern. diameter = 14 mm; flow rate = 2.0 mL min^{-1} cm^{-2}, C/C_0 = conc. effluent/conc. initial.

Table 4
Loading of lead as function of flow rate ($mL\,min^{-1}\,cm^{-2}$).

Effluent (mL)	2.0 $mL\,min^{-1}\,cm^{-2}$		1.0 $mL\,min^{-1}\,cm^{-2}$		0.3 $mL\,min^{-1}\,cm^{-2}$	
	$mg\,L^{-1}$ Pb	C/C_0	$mg\,L^{-1}$ Pb	C/C_0	$mg\,L^{-1}$ Pb	C/C_0
0	0	0.0	0	0.0	0	0.0
10	15	0.1	6	0.0	2	0.0
20	75	0.5	65	0.5	50	0.4
30	80	0.6	102	0.7	125	0.9
40	90	0.6	110	0.8	140	1.0
50	104	0.7	123	0.9	153	1.1
60	110	0.8	130	0.9	155	1.1
70	145	1.0	135	1.0	152	1.1
80	130	0.9	140	1.0	150	1.1
90	135	1.0	145	1.0	148	1.0
100	115	0.8	138	1.0	152	1.1

Resin vol. = 7.0 mL; intern diameter = 14 mm; HCl = 1.75 mol L^{-1}, C/C_0 = conc. effluent/conc. initial.

complexes with chloride (Kraus and Nelson, 1956), specially the anionic ion complex $PbCl_3^-$. This negative ion complex can be used for the retention of Pb^{2+} ion low levels by anionic ion exchange. The reaction is usually represented by Eq. (2).

For the loading of lead, the uptake of the anionic lead complex is very relevant. The results in Table 3 shows the uptake of lead from stock solution as a function of the HCl concentration. In this work it is recommended an acidity of 0.5–3.0 mol L^{-1} HCl. The lead separation was performed in 1.75 mol L^{-1} HCl. At the HCl molarity lower than 0.5 mol L^{-1} there is no retention of lead, because the complex $PbCl_3^-$ is broken. At the molarity higher than 3.0 mol L^{-1} the adsorption of $PbCl_3^-$ ion complex decreases with the increasing of the chloride concentration (Kraus and Nelson, 1956).

The loading flow rate is also important. Several runs for the uptake of lead complex with flow rate in 0.3–2.0 mL min^{-1} cm^{-2} range and 1.75 mol L^{-1} HCl were carried out. The results of the uptake of lead from a stock solution, as a function of the flow rates (see Table 4) suggest that at flow rate higher than 2.0 mL min^{-1} cm^{-2} there is a leakage of the lead and at flow rate lower than 0.3 mL min^{-1} cm^{-2} has a tendency to reversibility.

The elution of the lead after washing the resin was carried out using demineralized water. The stability of lead complex was broken (Kraus and Nelson, 1956). The solution contains 33.4% of lead (see Table 5).

After ion exchange, with the objective of an additional purification of the Pb solution, an electrochemical process, to reduce Pb^{2+} to metallic Pb was carried out. A cyclic voltammetry was performed to evaluate the reduction potential, in the interval between 0.0 and 1.2 V (Fig. 2). A mild anodic peak can be seen at about 0.55 V, suggesting the presence of some impurity, but the corresponding reduction peak was not observed. The Pb reduction peak was at 0.43 V. The eletrodeposition of Pb was carried in stirring cell (400 rpm), applying 30.75 ± 1.65 V and 1.67 ± 0.08 A during 1 h, using a source of direct current. A dark deposit was seen in the working electrode.

Table 5
Composition of Pb solution after elution.

Constituent	$\% \times 10^{-3}$ [a]	$\mu g\,mL^{-1}$ [b]	Constituent	$\% \times 10^{-3}$ [a]	$\mu g\,mL^{-1}$ [b]
Pb	17.0 ± 0.9	218.0 ± 0.8	Mn	3.0 ± 0.2	
Zn	5.0 ± 0.2		Cl	4023.0 ± 201.2	
Cr	4.0 ± 0.2		H_2O	95945.0 ± 4797.3	
Th	3.0 ± 0.2				

Vol. solution after elution = 250 mL.

[a] EDXRF analysis.

[b] Voltametric analysis.

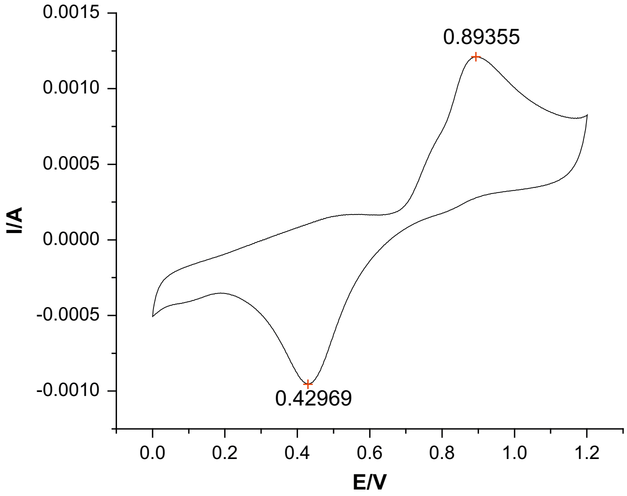

Fig. 2. Voltagram of Pb solution.

4. Conclusions

In this paper a feasible technological procedure was proposed for separation and recovery of "heavy" lead, ^{208}Pb (88.34% abundance and thermal neutron capture cross-section 14.6 ± 0.7 mb), from a thorium purification pilot plant sludge, by retaining a lead-chloro complex in an anionic resin. The quantitative retention of the lead into resin was not verified because of the chloride concentration of the solution that makes difficult the mechanism of lead diffusion. The "heavy" Pb obtained in this process is an important raw material to be considered in nuclear technology because of the different isotope abundance in ^{208}Pb that justify its recovery.

Nowadays, the isotope ^{208}Pb has a considered interested by increased uses in the synthesis of new elements (Karol et al., 2001) and as a tracer in several applications (Vergara, 2001).

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