

Research of the thorium purification at monazite refinement processes

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Abstract. This paper is aimed to the research of the thorium purification processes at monazite refinement processes. We have investigated different solution containing thorium with different mix of rare-earth elements. It was found that the application of cation resin is well-recommended if we want to reach the highest yields of thorium purification process.

1. Introduction

One of the principle problems of nuclear energetics is the guarantee of safe handling with long-life components of nuclear fuel; those components produce a hard radioactivity in exhausted nuclear fuel after its decomposition. Application of thorium reduces the income of long-life actinides. There is a concept of new VVER-T reactor and the concept of high-temperature gas-cooled thorium reactor of low power with the realization of closed fuel cycle based on ^{232}Th as breeding material [1-5]. Monazite sand is one of the most important sources of thorium and it contains monazite, ilmenite and zircon. Monazite concentrate could be enriched on thorium using different techniques using various methods of physical enrichment. Also there are thorium deposits available which were obtained during the rare metals ores refinement. Such deposits could not be used for rare metals extraction because of high radioactivity and that is why they are stored special places [5-7]. Thorium exists in insoluble form in both cases, especially in phosphate form [1].

We made various investigations in the field of ion exchange separation of thorium and rare-earth metals in phosphate solutions and compared the effectiveness of anion resin and cation resin resins using for thorium and rare-earth metals separation. Those solutions were obtained by dissolving of monazite concentrate in phosphoric(V) acid.

2. Experimental

The initial monazite concentrate was pre-purified from zircon impurities using electromagnetic separation and from ilmenite impurities using electrostatic separation. Purified monazite concentrate was dissolved in phosphoric(V) acid solution at 400 °C within 2 hours with vigorous stirring. To prevent the thorium and rare-earth metals hydrolysis side process the 5M phosphoric(V) acid solution concentration was used. The qualitative and quantitative determination of thorium and rare-earth metals was performed using EDXRF spectrometry and ICP-AES spectrometry [2].

EDXRF analysis was performed using ThermoFischer Scientific ARL QUANT'X spectrometer using fundamental parameters methodic.

ICP-AES analysis was done using ThermoFischer Scientific iCAP 6300 DUO ICP-AES spectrometer.



It was found that thorium forms stable anion-based complex and does not sorb on cation-based resins. There is another situation with rare-earth metals set. Rare-earth metals except yttrium don't form anion-based complexes and well-sorb on cation-exchange resins. Yttrium forms various unstable complexes - anion-based and cation-based and could be extracted from the solutions using both types of resins.

3. Results and discussion

Results means that purification of thorium form rare-earth metals can be easily done by anion-exchange resins with the resulting extraction of thorium and using cation-exchange resins with the resulting extraction of the rare-earth metals set. We have investigated which variant is the most effective one at the static conditions with the 1-hour exposure time. Both resins were places in the phosphoric(V) acid solution of thorium and rare-earth metals. The results are shown at the table 1.

Table 1. Molar ratio of thorium ions and rare-earth metals ions on various anion resins.

Ions	Initial solution (molar %)	Anion resin after sorption (molar %)	Cation resin after sorption (molar %)
La	11.5	0.0	22.6
Ce	22.9	0.0	36.4
Nd	18.0	4.9	27.0
Y	26.5	27.5	13.4
Th	21.2	67.6	0.6

As we can see from the table 1 anion-exchange resin does not provide desirable purification from yttrium and contains considerable amount of neodymium. Cation-exchange resin sorbs well all rare-earth metals set and does not sorb thorium. It means that cation-exchange resins are the best ones for purification of thorium from the set of rare-earth metals [8].

There is significant separation of thorium and rare-earth metals on cation resin, but thorium is hold in the solution in this case and could be easily precipitated in the form of its peroxides and any other insoluble compound; ions of rare-earth metals are absorbed in the cation resin in this case [9].

As the result of ionic exchange in dynamic conditions the rare-earth metals sorption queue on cation resin was determined in comparison with its ionic radius. The precipitation queue is shown at the table 2. The unsaturated cation resin was analyzed using EDXRF spectrometry. The cation resin was flushed using 10 ml 5M phosphoric(V) acid solution [10-13].

Table 2. Molar ratios of thorium ions and rare-earth metals in various parts of anion resin from top to bottom.

Metal	Top	Middle	Bottom
	Metal molar ratio (mole parts)		
La	0.23	0.12	0.08
Ce	0.36	0.31	0.26
Nd	0.27	0.25	0.21
Y	0.14	0.32	0.45
Th	0.00	0.00	0.00

As we can see from the table 2 lanthanum has the highest sorption ability because of its largest ionic radius. Yttrium is worth absorbed and it moves directly to the column bottom. Thorium is not absorbed at all and easily flushed by phosphoric(V) acid solution. Thorium and rare-earth metals concentrations at the after-sorption solution are shown at figure 1 and figure 2.

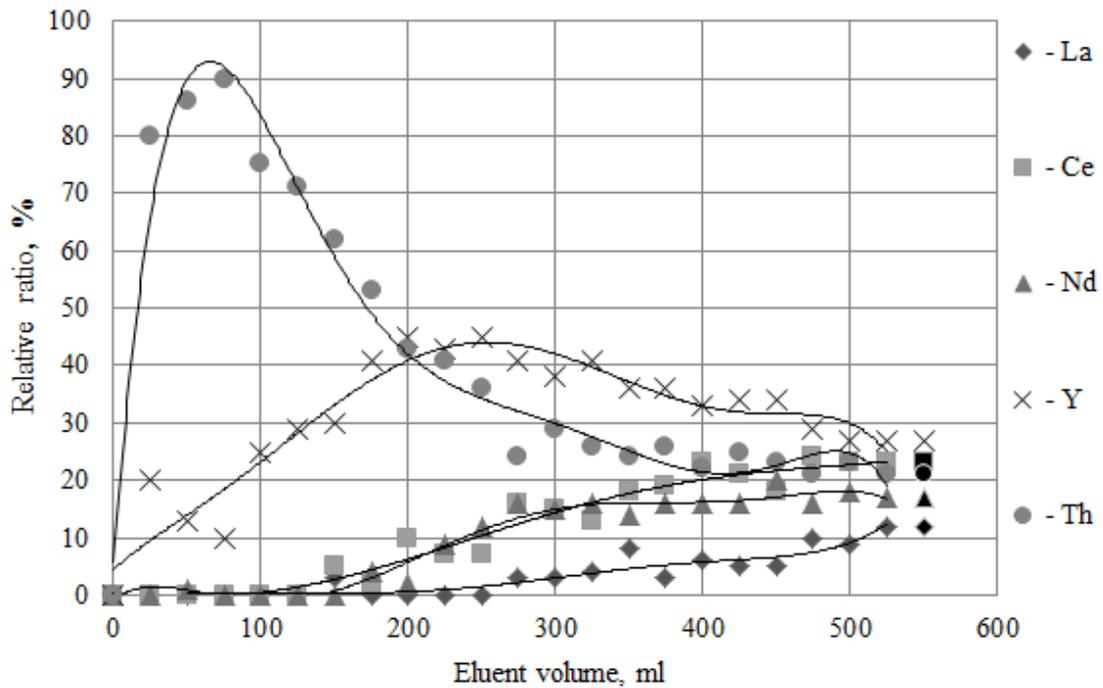


Figure 1. Thorium and rare-earth metals concentrations at the after-sorption solution.

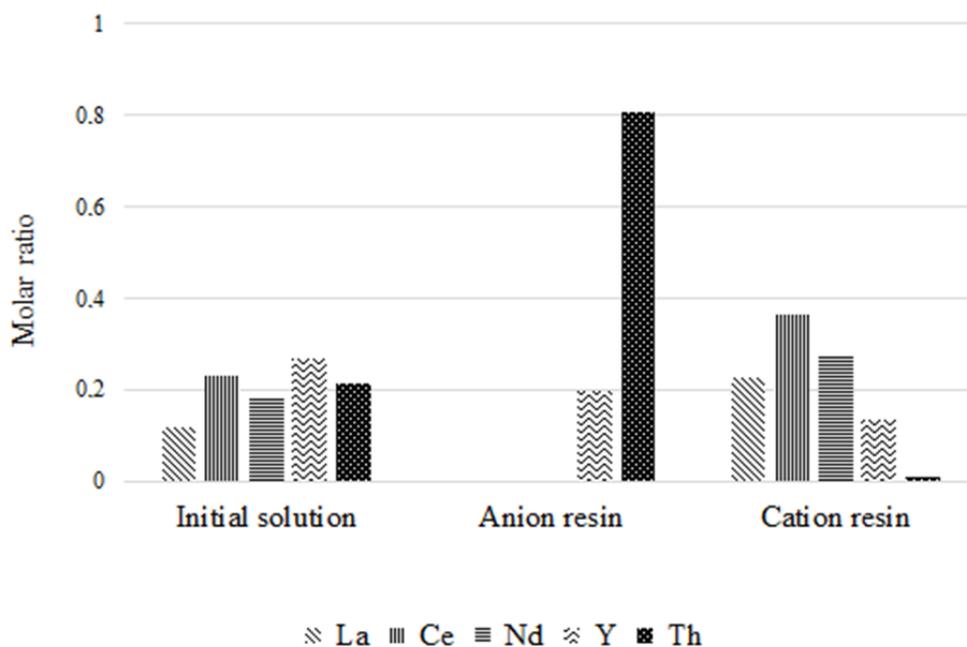


Figure 2. Thorium and rare-earth metals concentrations at the after-sorption solution.

As we can see from the figure 1 and figure 2 the relative concentration of thorium is decreased while eluent is moving through the column. It can be explained by cation resin saturation by rare-earth metals ions and further ion slippage to eluate. In order to get the purest thorium, it was necessary to carry out the ionic exchange process with the large excess of cation resin. In this case all rare-earth metals ions will be absorbed on cation resin and thorium will be hold in the solution. Thorium could be precipitated in the form of its peroxide and with further heating we can easily get thorium(IV) oxide. The metallic thorium could be obtained using simple metal thermic procedures [14-15].

Rare-earth metals can be extracted from resin using strong mineral and organic acids, and also using various complexation compounds like EDTA. Then the concentration of rare-earth metals occurs [16-17].

4. Conclusion

Thorium can be obtained from the monazite concentrate and moved to phosphate solution. In this case rare-earth metal also moved to the solution. Anyway thorium purification procedure is necessary in case of its usage in modern energetics.

We have researched the separation of soluble thorium and rare-earth metals phosphate compounds by ionic exchange method. It was shown that thorium ions are mostly absorbed on anion resin with the slight sorption of yttrium ions. It means that it is not necessary of anion resins use for the soluble thorium phosphates separation.

Ions of rare-earth metals are well-absorbed on cation resin and thorium phosphates are hold in the solution. This method provides more effective separation of elements. Thorium can be precipitated in the form of peroxide for further refinement. Rare-earth metals can be extracted using strong mineral or organic acids.

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