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Analysis of the effects of stirring condition of separation of thorium in the elution process of monazite partial solution by solvent impregnated resin method

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Abstract. Monazite is a natural mineral which contains abundant valuable element such as Radioactive Element and Rare Earth Element(REE). In this experiment, it is proven that solution of residual Thorium Sulfate from Monazite mineral process, can be seperated selectively by using extracting method of Solvent Impregnated Resin(SIR), with the elutant solution HNO_3. In the earlier process, Thorium solution is conditioned at PH 1 by using H_2SO_4. Then REE, Thorium and Uranium elements are seperated. This seperation is conducted by using adsorption method by Amberlite XAD-16 Resin, which has been impregnated by Tributhyl Phosphate extractant. It is continued with elution process, which is aimed to obtain Thorium solution of a higher level of concentration. This elution process is conducted by using HNO_3, with the elution variables of the lenght of mixing and amount concentration elutant. Based on this experiment, SIR extracting method is able to dissolve Thorium solution until 63,2%grade and a higher level of %grade about 92,40%. It can be concluded that this SIR method can extracted Thorium elements selectively, improve extracting process recovery, and determine optimum stripping condition in the 45^{th} minutes with elutant concentration of 1,0M HNO_3.

1. Introduction

Mineral Monazite contains valuable elements that can be further processed such as U, Th, and RE. In order to be processed, high purification of Thorium is required as in the use of nuclear fuel, as much as > 87.42%[1]. The extraction process is aimed on obtaining high concentration and pure elements. In the previous research, there has been a test of increasing the amount of Thorium extracts by using ion exchange resin method. However, Thorium cannot be separated with Uranium. The stripping method is a proper separation step between Thorium with another elements. Stripping Thorium can be selectively taken from Tributyl Phosphate (TBP) extraction using acid solution, whereas Uranium can be taken by using demineralized water[2]. The efficiency of stripping using TBP with 5M HNO3 solution condition was 96.1%[3]. TPB is a non-polar organic extractant with good sorption ability against Amberlite XAD-16 Resin[4]. So then stripping extraction is optimized by ion exchange mechanism by Amberlite XAD-16 Resin.

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2. Materials and Method

2.1 Feed Preparation

The Partial solution feed is prepared as a solution that is obtained from the previous process of Monazite in the form of partial solution of Th-U-RE. Partial solution is then extracted to get high recovery of thorium element using SIR method. The Thorium solution is conditioned on the acid condition of PH 1 by using H2SO4 solution. The feed is prepared as much as 3000ml, with a thorium content of 28480.0mg. Amount of thorium elements is obtained from the characterization of ICP-OES.

2.2 Resin Amberlite XAD-16 Preparation

In the SIR extraction method, it is necessary to prepare the resin as an absorbent element of Thorium in the feed. The resin in this method is Amberlite XAD-16 Resin. This resin is used in the Solid Phase Extraction, because of their physical and chemical features such as high surface areas, porosity, purity, and durability[5]. Resin preparation is done through the impregnation process of Tributyl Phosphate (TBP) extractant. Prior to the impregnation process, Amberlite resin is cleaned by using 2M HNO3, NaOH 2M and acetone. Then it is dried at a temperature of 50°C in the oven.

2.3 Elutant Preparation

A strong acid solute eluent is used for the elussion process. Elutant is a solvent for separating the thorium elements selectively from Amberlite resins. The elutant used in this experiment is HNO3 with various concentrations. The HNO3 solution concentration is obtained from dilution using concentration test on 0.5M, 1.0M, and 1.5M and aquades(0M).

2.4 Tributyl Phosphate

Tributyl Phosphate (TBP) is an extractant solution which has been proven to be able to extract Thorium element. The TBP is a non-polar organic solution that can bind with Amberlite resin well. The molecular size and polarity of TBP are known capable to produce adsorption capacity of Amberlite XAD-16 untill 900mg/g [4]. TBP is mixed with acetone to reduce the viscosity of the solution also the surface areas, pore volumes, and pore sizes of Amberlite resin[10]. It is therefore expected to be better adsorbed in the Amberlite resin

2.5 Adsorption Process

Thorium feed in this experiment is obtained through the adsorption step by Amberlite XAD-16 Resin. There are 30g impregnated Amberlite resin immersed in a 3000ml partial solution with a Thorium content of 28480.0mg. The impregnation process is performed on 3000ml Thorium feed and 30ml of TBP extractant. The process is terminated by drying the Amberlite resin in the oven at 50 °C. The adsorption process produces a new initial feed content in the SIR extraction method..

2.6 Elution Process

The result of impregnation on Amberlite resin is separated by HNO3 elution process. The elution process is carried out under conditions of HNO3 concentration as well as in different stirring times. Elution is performed at a concentration of 0.5M, 1.0M, 1.5M HNO3 with the stirring duration (5, 15, 30, 45, 50) minutes.

3. Result and Discussion

3.1 Mechanism of Amberlite XAD-16 Resin as an Ion Exchange Media

The elution process uses an Amberlite-XAD16 resin that has been impregnated by an organic solution of TBP. TBP in this case is known as an extracting solution in Thorium. It has a chemical structure between the TBP and the Amberlite XAD-16 resin as shown in figures 1 and 2.

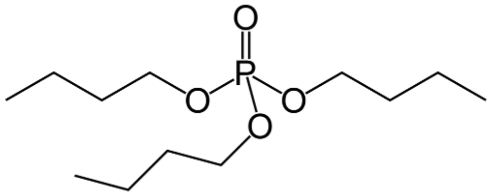

Figure 1. Tributyl Phosphate Structure

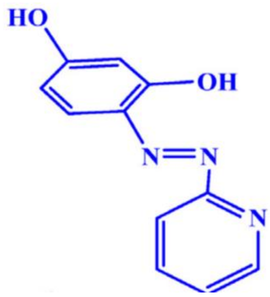

Figure 2. Amberlite XAD-16 Structure[9]

The impregnation process occurs complexly between ligand and Thorium. The ligands will be loaded by Amberlite XAD-16 Resin from TBP. The ligands present in the solid phase will react with Th4+, forming the neutral complex Th (nBPHA) 4, which is present in the XAD process [6]. Interaction can be seen in figure 3.

Figure 3. Interaction Between Solid phase and Thorium

So the equation is generated as in the model in the following equation, (S.Michaud. Modelling of Thorium Extraction by TBP)

Extraction equilibrium of Th(IV) by TBP with nitrate ion is:

$$Th_{aq}^{4+} + 4NO_{3aq}^{-} + nTBP_{org} \leftrightarrow (Th(NO_3)_4, nTBP)_{org} \quad (1)$$

Or it can be generated by TBP with Sulfate ion

$$Th_{aq}^{4+} + 4SO_{4\ aq}^{-} + nTBP_{org}^{-} \leftrightarrow (Th(SO_4)_4), nTBP)_{org} \quad (2)$$

From equationn 1 and 2 it can be simplified in the following equation:

$$Th^{4+} + n\,TBP_{org} \rightarrow Th(nTBP)_4$$

Solid phase extraction is one of the important pre-concentration-separation procedures for trace heavy metal ions, due to its simplicity and limited usage of organic solvents. Furthermore, it has many advantages, such as high enrichment factors, absence of emulsion, low cost due to low consumption of reagents, flexibility and being environmentally friendly [8].

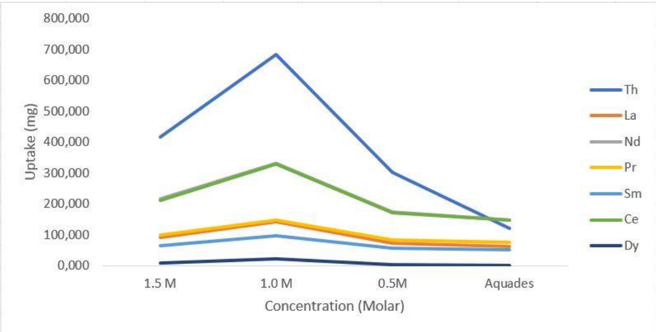

Figure 4. Influence of HNO_3 Concentration

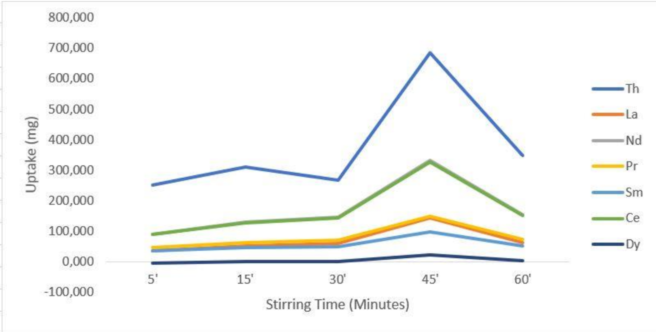

Figure 5. Influence of Stirring Time

3.2 Analysis Effect of solution concentration *(PH Condition)*

By comparison of elution test results between the Rare Earth Elements (REE) element and the Thorium element, as shown in figure 4. there is an increase in elution concentration at Th4+ with a peak of 1.0N HNO3 solvent concentration of 684mg. While in the next concentration after the peak, the elution concentration decreases. So in this process equilibrium point at a concentration of 1.0M is obtained and this process is sufficiently conducted until the concentration of 0.5M - 1.0M HNO3. The elution process may also be applicable to the REE that may be adsorbed by the impregnated resin.

Having the same tendency as Th4 + elution, there is an increase with a peak at a concentration of 1.0M HNO3 with the highest concentration of REE on Neodymium and Cerium elements, but not as many elution results in Thorium, Neodymium produces only 331,25mg and Cerium 327,65mg. In conclusion, of the total mass impregnated by the resin, 1.0M HNO3 solvent has succeeded in eluting each element with the ratio between Thorium and Neodymium of 2,06mg : 1mg. Each 1mg Neodymium will produce 2,06mg element Thorium at the optimum concentration condition.

At higher acidity, the process can be attributed to the competitive adsorption between proton from HNO3 and Th4+. Also at higher concentrations, the reaction of thorium nitrate complex is not perfect. So, it could be resulting the decreased of Th4+ adsorption as HNO3 is increased [7,10, 11]. The increase of adsorption capacity can be attributed to the salting-out effect of HNO3[11]. As it is been studied that elutant HNO3 can act as an absorption or desorption [5]. Based on temporary conclusion that, HNO3 will act contradictively until it is peak concentration as shown in figure 4.

3.3 Analysis *Effect* of Stirring Time

As in figure 5, the fixed variable HNO_3 concentration in the elution process in this experiment is 1.0M. The resulting elution concentration increase at Th^{4+} with a concentration of 684mg is obtained at the peak of stirring time of about 45 minutes. While longer than that, the elution concentration will decrease drastically.

Having the same tendency of elution process on REE has increased with a peak at 45 minutes stirring time. The highest concentration is obtained on the elements of Neodymium as much as 331,25mg and Cerium as much as 327,65mg.

As in figure 5, it is found that the peak is the saturation time of the elution process. Considering HNO3 could act as both adsorption or desorption, It is concluded that the elution process is sufficient for the duration of stirring not more than 30-45 minutes or the elution process will result contrary.

4. Conclusion

An optimum Elution process of Thorium element is obtained as much as 684mg with the stirring condition on 45 minutes at 1.0M HNO3 solvent concentration. The SIR method of the thorium extraction process has selective properties. This process results in 92,432 %recovery, which is equivalent to 684mg of Thorium that is eluted from 740mg of Thorium feed which is contained in the impregnated resin. The lowest elution result is obtained on 5 minutes stirring time at 0M conditions (aquades) with the result of 9.101 %recovery, which is equivalent to 67,350mg. The separation under the optimum conditions of the elution process yielded good results with a very high selectivity of Th4+ element. However, consider the turning point of the solution condition in which the solution will work in reverse. So that the separation process by HNO3 is better done at specific condition.

Acknowledgment

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