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FRACTIONAL PRECIPITATION AND SOLVENT EXTRACTION OF THORIUM

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ABSTRACT

The recovery of thorium from the H_2SO_4 and HNO_3 leach solutions by fractional precipitation and solvent extraction (SX) methods were studied for Turkish thorium ore of KTS-1. Precipitations were made by NH_4OH through controlled pH and Th precipitation efficiencies were determined. In solvent extraction studies, tri-butyl-phosphate (TBP) were used as solvent and factors affecting the thorium extraction were investigated.

ÖZET

KTS-1 Th cevherlerinin H_2SO_4 ve HNO_3 ile yapılan özütleme çözeltilerinden toryumu kazanmak için, kademeli çöktürme ve solvent ekstraksiyon çalışmaları yapılmıştır. Çöktürmeler, kontrollu pH da NH_4OH ile yapılmış ve toryum çökme verimleri bulunmuştur. Solvent ekstraksiyon çalışmalarında çözücü olarak tri bütil fosfat kullanılmış ve toryum ekstraksiyon verimini etkileyen koşullar araştırılmıştır.

INTRODUCTION

The aim of this study is recovery of thorium from leach solutions by SX and selective precipitation. Analysis of precipitates and SX samples for elemental composition will provide information about the degree of separation of each element by these methods. This is the first study to separate thorium from leach solutions by fractional precipitation in Turkey. Also, factors affecting the thorium extraction from H_2SO_4 leach solutions of Turkish thorium ore was investigated for the first time.

Th determinations were carried out by colorimetric

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method. The method is based on the separation of Th by solvent extraction and determination colorimetrically after back extraction /1/.

Present and future studies will provide information about the best methods to purify and recover thorium from Turkish thorium ores.

EXPERIMENTAL

1. Fractional Precipitation: H_2SO_4 leach solutions were prepared at 900 g. H_2SO_4/1000 g. ore ratio and solid/liquid ratio of 1/2 for 2 hours. The residue was washed with water and the solutions were combined. Precipitation studies were made with 250 ml portions of leach solution. Ammonium hydroxide was used as neutralizing agent. To control pH precisely, continuous stirring and pH measurement were made while adding 2N NH_4OH dropwise.

HNO_3 leach solutions were prepared at 1000 g. HNO_3/1000 g. ore ratio and solid/liquid ratio of 1/2 for 2 hours. The residue was washed with water and the solutions were combined. Precipitation was achieved with 2N NH_4OH as mentioned above.

The precipitates were filtered by Whatman-42 filter paper under vacuum, then dried at 110°C and weighed.

2. Solvent-Extraction Studies: In SX of H_2SO_4 leach solutions, first series of extractions with increasing TBP/leach solution (organic/aqua) ratios were made. Secondly, the effect of NO_3^- addition to Th SX efficiencies was investigated. Increasing amount of HNO_3 was added to leach solutions and extractions were made with the same amount of TBP.

In SX of HNO_3 leach solutions, the effects of Org./Aq. ratio, SX time, diluent type and solvent/diluent ratio on Th SX efficiencies were investigated. Org./Aq. ratio was changed from 10/100 to 100/100. At constant Org./Aq. ratios, a series of extractions at different SX periods from 4 to 20 minutes were made. Two types of diluent, namely benzene and kerosene, were used at different diluent/solvent ratios at constant TBP/Aqua ratio and SX period.

3. Determination of Thorium: Th determinations were made in aqueous phases by colorimetric method /1/. Thorium is separated from interfering substances by SX with tri-n-octylphosphine oxide (TOPO) dissolved in cyclohexane. Then, Th is back extracted from organic phase by 0.3 M H_2SO_4. Absorbances obtained

at 545 mμ from the red complex of Th and thorin (0-(2-Hydroxy-3, 6-disulfo-1- naphthylazo) benzenearsonic acid) is used to determine Th concentrations.

RESULTS AND DISCUSSION

In Table-1, recovery of thorium by precipitation as a function of pH is given for H_2SO_4 leach solution. Although precipitation started at pH = 1.7, the precipitate which could be filtered practically was obtained at pH = 2.5. Above this pH value, it is observed that all thorium was precipitated within the limits of error. Precipitation of Th would have probably been completed at a pH of 1.2, if the solution used for the experiments was more then 250 ml. in the laboratory conditions /2/.

Table-2 gives Th precipitation recovery for HNO_3 leach solutions. Precipitation was first observed at pH = 0.8, but practically filterable amount could be obtained at pH = 1.5 above which all Th was precipitated.

For both H_2SO_4 and HNO_3 leach solutions, the amounts of precipitates increase with increasing pH values, indicating precipitation of other elements. Further analysis of the precipitates will show the effect of pH on fractional precipitation of other elements, especially the rare earths.from leach solutions.

In solvent extraction experiments TBP was selected as solvent /3/. In Fig.1 the effect of Org./Aq. ratio to thorium recovery for H_2SO_4 leach solutions are given. Although the Org./Aq. ratio was increased up to 250/100, Th recovery remained as low as 0.8 %. So, detrimental effect of sulfate ion on thorium recovery was observed. To overcome this effect, NO_3^- (HNO_3) was added to leach solution. As seen from Fig.2, Th recovery increases with increasing NO_3^- concentration.

Therefore, to extract Th from H_2SO_4 leach solutions to organic phase, it is required to overcome the detrimental effect of $SO_4^=$. One method is the addition of NO_3^- to the feed. Another one is to separate Th from $SO_4^=$ by fractional precipitation and to extract it after the dissolution of the precipitate by HNO_3.

In Fig.3, the effect of Org./Aq. ratio to Th recovery for HNO_3 leach solutions is given. At Org./Aq. ratio of 25/100, maximum recovery was observed as 69.6 %. Above this ratio recovery was almost constant within the limits of error.

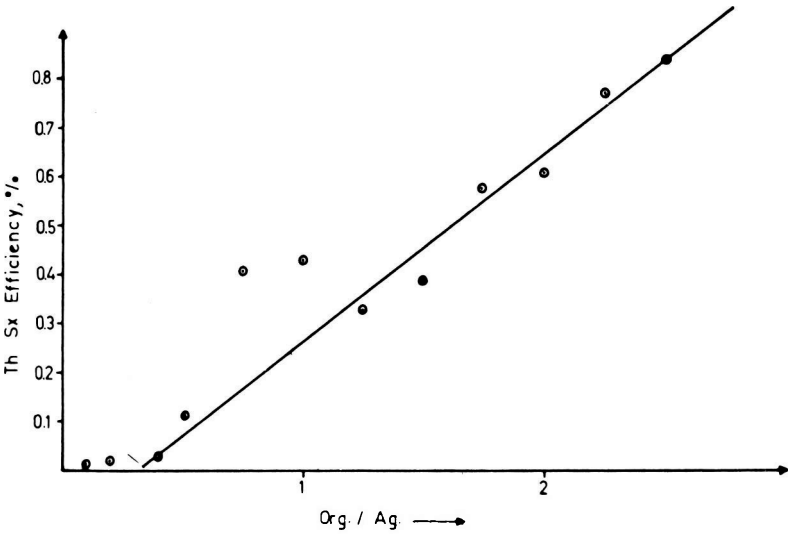


Fig.1. Effect of Org./Aq. Ratio on Th SX Efficiency for H_2SO_4 Leach Solution.

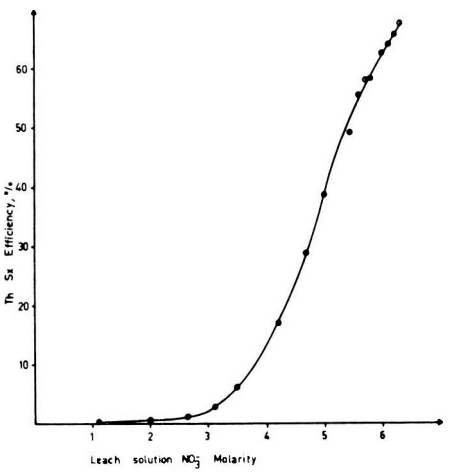


Fig.2. Effect of NO_3^- Molarity on Th SX Efficiency for H_2SO_4 Leach Solution.

The effect of SX period on Th recovery was given in Fig.4. As it is seen from the Fig., 8 min. is a sufficient period to obtain maximum efficiency.

In Fig.5, the effect of diluent type and diluent/ solvent ratio on Th SX efficiency was given. As the amount of diluent increases, Th SX efficiency decreases. This was the expected result for the solutions which contain less than 10 g/l of Th, which was the case /2/.

TABLE-1. Effect of pH on fractional precipitation of thorium for H_2SO_4 leach solutions

Ore : 1 kg.
900 g. H_2SO_4/1000 g. Ore S/L : 1/2
Washing : 1.0 l. H_2O
Th : 607 mg/l
Leach Solution : 250 ml
Neutralizing Agent : 2N NH_4OH

pH	weight of precipitate, g	Th recovery, %
2.5	0.971	99.6
2.9	1.772	100.0
3.4	2.542	99.7
4.0	3.094	99.9
4.5	3.618	100.0
5.0	3.514	100.0
5.4	3.810	100.0
6.1	4.063	100.0
7.1	4.311	100.0
7.7	4.273	100.0

TABLE-2. Effect of pH on fractional precipitation of thorium for HNO_3 leach solutions

Ore : 750 g.
1000 g. HNO_3/1000 g. Ore S/L : 1/2
Washing : 1.5 l H_2O
Th : 426 mg/l
Leach solution : 500 ml.
Neutralizing Agent : 2N NH_4OH

pH	weight of precipitate, g	Th recovery, %
1.5	1.436	99.56
3.0	2.109	99.44
4.0	2.556	99.71
5.0	3.187	99.68
7.0	4.670	99.77
8.4	7.963	100.00

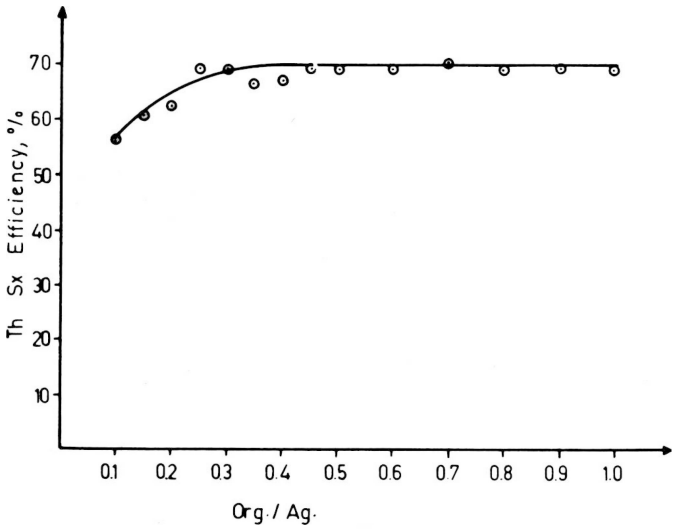


Fig.3. Effect of Org./Aq. Ratio on Th SX Efficiency for HNO_3 Leach Solution.

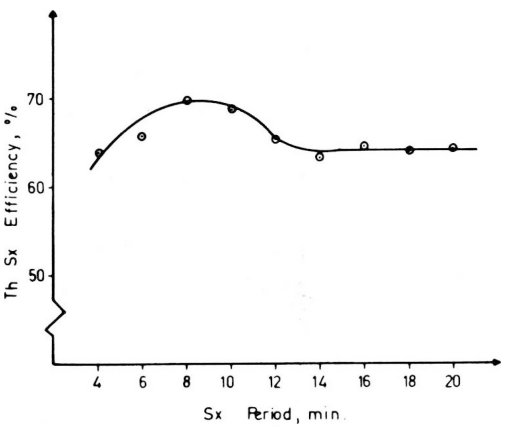


Fig.4. Effect of SX Period on Th SX Efficiency for HNO_3 Leach Solution.

The precipitates and SX samples were analyzed only for thorium, therefore the behaviour of the other elements during precipitation and extraction was not yet determined. On the other hand, to determine the optimum process conditions, it is necessary to know concentration and influence of each element present in ore, leach and extraction solutions. This is necessary for both recovery and purification of thorium and all the other elements as by products. Further study will take all these criteria into account during each step of the process.

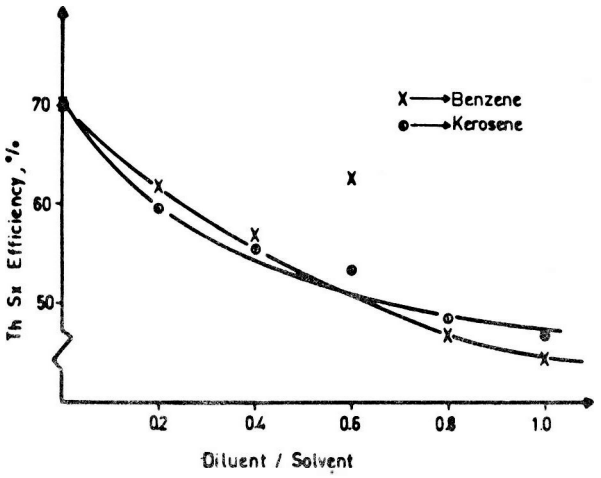


Fig. 5. Effect of Diluent type and amount on Th SX efficiency for HNO_3 leach solution

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