

Leaching of Asphaltite Ash With H₂SO₄ and Extraction of Mo, V, U in Solution

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Abstract

The aim of this study is to investigate the reaction of Mo, V, U and Ni while taking in to solution and recovering these elements from solution. The quantities of the above elements in solution were in 50-80 ppm. In the first stage, effect of parameters such as the ratio of ash/ H₂SO₄, temperature and time was investigated on the pressure leaching of the above elements. The best pressure leaching for 100 g asphaltite ash samples was achieved by 90 mL of 15 M H₂SO₄ for 100 min at 225⁰C in an autoclave. The yields of leaching were 99.5 % Mo, 100.0 % V, 100.0 % U, 100.0 % Ti and 99.9 % Ni. In the second stage, the pregnant solution was extracted with Alamine 336 to recover Mo, V, U, and also the effect of oxidants such as air, KMnO₄, H₂O₂ and MnO₂ were investigated. The best result was obtained with air. Extraction yields are 98 % Mo, 89 % V and 93 % U. For stripping 75 g/L Na₂CO₃ solution was used.

Keywords: Asphaltite ash; molybdenum; uranium; vanadium; nickel; extraction

Özet

Bu çalışmanın amacı, Mo, V, U' un çözeltiliye alınırken reaksiyonlarını incelemek ve çözeltiliden bu elementlerin kazanılmasını sağlamaktır. Bu elementlerin çözeltilideki miktarları 50-80 ppm dir. İlk aşamada, bu elementlerin basınç altında özütlenmesinde kül/ H₂SO₄ oranı, sıcaklık ve zaman parametrelerinin etkisi araştırılmıştır. En iyi özütleme, 100 g asfaltit kül örneklerinin 90 mL , 15 M H₂SO₄ ile 100 dk ve 225⁰C' de otoklav ortamında başarılmıştır. Özütleme verimleri, sırasıyla, %99,5 Mo, %100 V, %100 U, %100 Ti ve %99,9 Ni' dir.

2. aşamada, bu çözeltili Alamine 336 ile ekstrakte edilerek Mo, V, U' un organik faza alınması sağlandı ve ayrıca hava, KMnO₄, H₂O₂ ve MnO₂ gibi yükseltgenlerin etkisi araştırıldı. En iyi sonuç, hava ile elde edildi. Ekstraksiyon verimleri, %98 Mo, %89 V ve %93 U olarak belirlendi. Sıyırma işleminde, 75 g/L Na₂CO₃ çözeltilisi kullanıldı.

Anahtar Kelimeler: Asfaltit Külü, Molibden, Uranyum, Vanadyum, Ekstraksiyon

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Introduction

The investigation studies carried out to recover Mo, V, U, Ni and Ti from the ashes of Silopi (Turkey) asphaltites have earlier been reported. Mainly, various leaching investigations from solid were carried out, and of these, a leaching method was obtained and then applied to the solutions under optimal conditions.

Dilute H₂SO₄ was used for leaching, and leaching efficiency is about 90 % of Mo, V, U, and 60 % of Ni. The ratio of H₂SO₄ to ash is 2:1. If leaching is carried out by 14-15 M H₂SO₄ in atmospheric conditions, about 90 % of Mo, V and Ni passes into solution. The consumption of H₂SO₄ is the same (1,2).

Later, the solvent extraction method was carried out on these solutions. The extraction of Mo, U and V from aqueous solutions by using Alamine 336 (tri-n-octylamine) in kerosene was reported in earlier studies (3).

It has been shown that amines are potentially economical good extractant for some metals. Most of the studies in this field have been carried out to investigate the extraction mechanism and interaction of amines with aqueous phase (4-7).

Furthermore, the purpose of various studies of extraction of uranium (VI) is to explore industrial conditions for uranium extraction at ppm level concentration. The extraction of molybdenum, vanadium and uranium by amines, organophosphorus extractants and sulphoxides has also been reported (8-14).

The originality of this study is that we investigated the reactions that occurred during taking Mo, V, U, Ni and Ti from asphaltite ash into solution according to the oxidant used in the extraction conditions in order to improve the yield.

Experimental Procedure

Composition of the studied elements in the sample is, 0.33 Mo, 0.60 V, 0.45 Ni, 0.44 Ti, 9.47 Al, 2.96 Fe and 0.05 % U₃O₈.

Reagents and Apparatus

All chemicals used were of analytical reagent grade: Kerosene (Merck), n-nonanol (Fluka), Alamine 336 (Merck), H₂SO₄ (Merck).

The mixture of Alamine 336, n-nonanol and Kerosene (1:1:8) was used for the extraction. n-nonanol was added to Alamine solution to prevent the formation of the third phase.

The analyses of Mo, V, U, Ni and Ti were carried out by Jobin-Yvon JY 24 model ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectrophotometry). Extraction percentages were determined by comparison of the amounts of these elements present in aqueous solution before and after extraction treatments.

The pH measurement was also performed with a Nel pH 890 model pH meter.

Taking of Mo, V, U, Ni and Ti into solution

The first step of the works that have been done on recovery of Mo, V, U, Ni and Ti from Silopi asphaltite is the reaction of ash with H_2SO_4 . The ash and sulphuric acid were reacted at 175, 200, 225, 250, 275 and 300°C for different values of ash and H_2SO_4 (with solutions of H_2SO_4 13, 14 and 15 M). The experiment was conducted for 100 min in an autoclave. Experimental conditions and results are given in Figs 1 & 2.

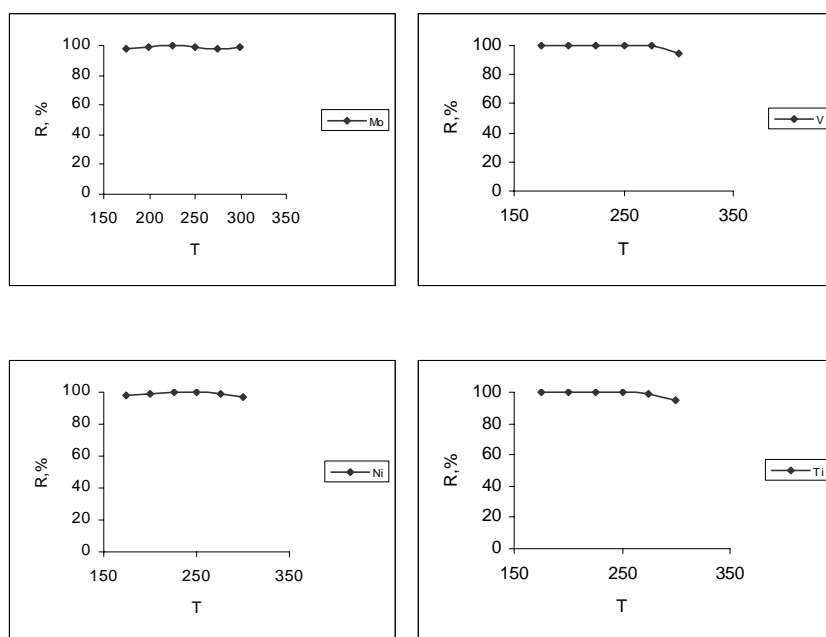


Fig. 1: Effect of temperature on the pressure leaching of Mo, V, Ni and Ti, respectively* (at 15 M H_2SO_4)
T: Temperature, **R:** Taking into solution, **M:** Molarity

* : Averages calculated for data obtained from three independent leaching experiments

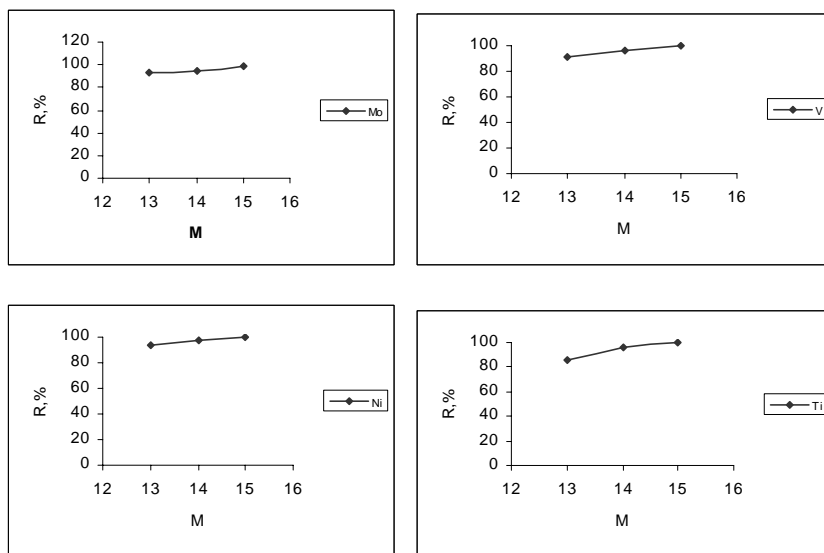


Fig. 2: Effect of concentration of H₂SO₄ on the pressure leaching of Mo, V, Ni and Ti, respectively* (at 225°C) **T:** Temperature, **R:** Taking into solution, **M:** Molarity

* : Averages calculated for data obtained from three independent leaching experiments

Under the same conditions, all of Uranium was leached into solution.

All of these studies were carried out to take Mo, V, U, Ni and Ti into solution medium. As it can be seen from the figures, the best results were obtained by the reaction between 90 mL of 15 M H₂SO₄ with 100 g of ash at 225°C.

Separation of metal ions by liquid-liquid extraction

After taking these elements to solution, the liquid-liquid extraction method was applied to samples. A series of experiments were carried out with Alamine 336. Two-step extraction method was used. The aqueous solution used in extraction works was prepared by the roasting of the ash of Silopi asphaltites with 15 M H₂SO₄ for 100 min at 225°C. Extraction treatments were carried out in a glass apparatus of 100 mL volume. All tests were performed at constant temperature (25°C), time (5 minute) and stirring speed (1500 rpm). In addition, a certain amount of n-nonanol was added to both of the above solutions so that they could be 10% in solution to prevent the third phase. Fifteen mL of aqueous phase, which contained a certain amount of Mo, V, U, Ni and Ti, was shaken with 15 mL of organic phase. Furthermore, for stripping 75 g/L Na₂CO₃ solution was used.

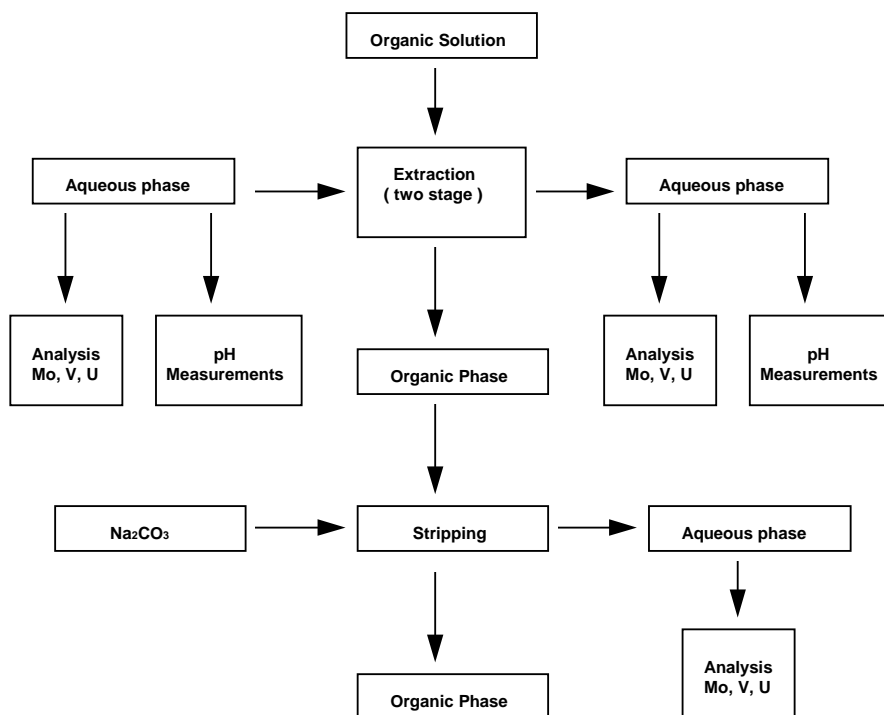


Fig. 3: The flow sheet of the separation process.

All of the elements present in solution were extracted by Alamine 336 with kerosene. Also, as an oxidant 0.1 M KMnO_4 was added into solution, and air was passed through it. The same procedure was repeated by using MnO_2 instead of KMnO_4 . Two step extractions were applied to this solution. Results are given in Table 11 and Table 12.

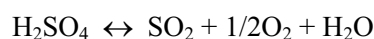
Results and Discussion

This study was carried out to recover U, Mo, V, Ni and Ti from Silopi asphaltite by reacting ash with H_2SO_4 . The parameters such as the ratio of ash/ H_2SO_4 , temperature and time were investigated.

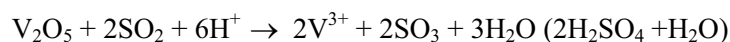
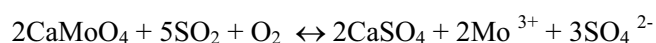
The best leaching for asphaltite ash was determined by using 15 M H_2SO_4 for 100 min at 225°C for 100 g sample in autoclave. From the sample, which was reacted with 15 M H_2SO_4 at 225°C during 100 minutes, 99.5 % Mo, 100.0 % V, 100.0 % U, 100.0

% Ti and 99.96 % Ni were taken into solution. This result is obtained when solid/H₂SO₄ ratio is 1g/0.9 mL .

The reactions that occur as a result of reaction of ash with H₂SO₄ in autoclave medium are as follows (1).



or

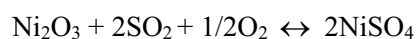
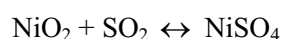


or

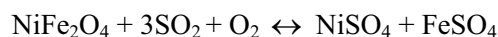


The following reactions were considered if nickel in ash was present as NiO₂, Ni₂O₃ and NiFe₂O₄ respectively.

NiFe₂O₄ respectively.



Nickel and iron are probably present in the asphaltite ash as NiFe₂O₄ (NiO.Fe₂O₃) inverse spinel structure. Therefore, it is thought that the following reaction may occur.



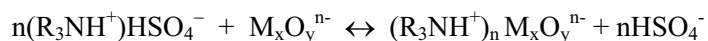
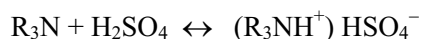
Due to lack of efficiency of dissolution, about 10-12 % of these elements were not dissolved. This result is obtained when solid/H₂SO₄ ratio is 1/2 .

By using mixture of ash and H_2SO_4 in autoclave medium, the following results were observed for Mo, V, U, Ni and Ti, which passed into solution.

- (i) All of Mo and V passed into solution as Mo^{+3} and V^{+3} respectively.
- (ii) All of U passed into solution as U^{+4} .
- (iii) All of Ni passed into solution as Ni^{+2} .
- (iv) All of Ti passed into solution as $TiO^{+2}(v)$ After an effective dissolution procedure, all of Mo, V, U and Ni were taken into solution. Also, the differences that occurred in extraction work emerged as a result of this structural change.

A solvent extraction procedure is given below :

$M_xO_y^{n-}$ (aq) : Metal ion in aqueous solution



(R:C₈H₁₇ for Alamine 336)

It was observed that Mo and V did not pass into organic phase by direct extraction with Alamine 336. This shows that molybdenum and vanadium passed into aqueous solution due to lower oxidation state in leaching process.

Extraction process was progressed by adding oxidants such as Air, $KMnO_4$, H_2O_2 and MnO_2 . Extraction processes were carried out at 25, 40, 50, 60°C temperature, and pH values were 1.17, 1.25, 1.70 respectively.

Table 1: The results of two -Stage extraction and Strippings with 10% Alamine336 at 25°C *

| Elements | First Concentration (ppm) | 1 st extraction | 2 nd extraction | 1 st stripping | 2 nd stripping |
|----------|---------------------------|-----------------------------|-----------------------------|----------------------------|----------------------------|
| | | remove to organic phase (%) | remove to organic phase (%) | remove to liquid phase (%) | remove to liquid phase (%) |
| Mo | 64.94 | 1.35 | 4.11 | - | - |
| V | 83.80 | 4.42 | 6.25 | 96.6 | 96.0 |
| U | 8.29 | 4.82 | 10.13 | - | 94.6 |

Table 2: The results of two -Stage extraction and Strippings with 10 % Alamine336 at 40°C *

| Elements | First Concentration (ppm) | 1 st extraction | 2 nd extraction | 1 st stripping | 2 nd stripping |
|----------|---------------------------|-----------------------------|-----------------------------|----------------------------|----------------------------|
| | | remove to organic phase (%) | remove to organic phase (%) | remove to liquid phase (%) | remove to liquid phase (%) |
| Mo | 64.94 | 1.60 | 9.19 | - | 98.82 |
| V | 83.80 | 5.19 | 6.80 | 98.1 | - |
| U | 8.29 | 13.8 | 14.95 | 97.3 | 96.80 |

Table 3: The results of two -Stage extraction and Strippings with 10% Alamine 336 at 50°C *

| Elements | First Concentration (ppm) | 1 st extraction | 2 nd extraction | 1 st stripping | 2 nd stripping |
|----------|---------------------------|-----------------------------|-----------------------------|----------------------------|----------------------------|
| | | remove to organic phase (%) | remove to organic phase (%) | remove to liquid phase (%) | remove to liquid phase (%) |
| Mo | 64.94 | 22.36 | 26.84 | 99.8 | 98.6 |
| V | 83.80 | 26.24 | 28.17 | 90.4 | 95.76 |
| U | 8.29 | 26.05 | 25.0 | 99.0 | 95.6 |

Table 4: The results of two -Stage extraction and Strippings with 10 % Alamine 336 at 60°C *

| Elements | 1 st extraction | 2 nd extraction | 1 st stripping | 2 nd stripping |
|----------|-----------------------------|-----------------------------|----------------------------|----------------------------|
| | remove to organic phase (%) | remove to organic phase (%) | remove to liquid phase (%) | remove to liquid phase (%) |
| Mo | 4.08 | 6.93 | 97.70 | 91.56 |
| V | 4.86 | 5.94 | 94.90 | 98.60 |
| U | 14.20 | 14.1 | 92.30 | 96.56 |

Table 5: The results of two -Stage extraction and Strippings with 10 % Alamine 336 at 70° *

| Elements | First Concentration (ppm) | 1 st extraction | 2 nd extraction | 1 st stripping | 2 nd stripping |
|----------|---------------------------|-----------------------------|-----------------------------|----------------------------|----------------------------|
| | | remove to organic phase (%) | remove to organic phase (%) | remove to liquid phase (%) | remove to liquid phase (%) |
| Mo | 64.94 | 1.60 | 1.26 | - | - |
| V | 83.80 | - | 1.96 | - | 96.3 |
| U | 8.29 | 8.80 | - | 98.2 | - |

Table 6: The results of two -Stage extraction and Strippings from aqueous solution (pH=1.17) using Alamine 336 in air medium with different time at 50°C *

| Elements | First Concentration (ppm) | 10 min air | | 20 min air | | 30 min air | | 40 min air | | 50 min air | | 60 min air | |
|----------|---------------------------|-----------------------------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|
| | | remove to organic phase (%) | | remove to organic phase (%) | | remove to organic phase (%) | | remove to organic phase (%) | | remove to organic phase (%) | | remove to organic phase (%) | |
| | | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext |
| Mo | 64.94 | 76.36 | 75.44 | 73.85 | 70.42 | 71.11 | 82.13 | 70.16 | 74.33 | 70.95 | 74.12 | 67.70 | 68.13 |
| V | 83.80 | 56.83 | 53.48 | 56.98 | 64.13 | 56.02 | 69.71 | 55.29 | 68.79 | 54.54 | 58.61 | 52.62 | 52.90 |
| U | 8.29 | 73.21 | 70.49 | 71.13 | 68.27 | 71.28 | 80.49 | 70.54 | 81.02 | 71.81 | 79.11 | 71.52 | 72.61 |

| Elements | 10 min air | | 20 min air | | 30 min air | | 40 min air | | 50 min air | | 60 min air | |
|----------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| | Stripping (%) | | Stripping (%) | | Stripping (%) | | Stripping (%) | | Stripping (%) | | Stripping (%) | |
| | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp |
| Mo | 98.10 | 99.95 | 91.40 | 98.30 | 94.10 | 98.50 | 95.70 | 97.91 | 94.69 | 97.80 | 97.20 | 99.80 |
| V | 67.50 | 77.70 | 74.30 | 84.21 | 79.10 | 90.60 | 78.86 | 81.10 | 86.20 | 92.60 | 86.58 | 92.76 |
| U | 97.40 | 97.31 | 99.03 | 94.50 | 99.10 | 98.90 | 97.01 | 97.90 | 98.10 | 96.70 | 99.80 | 99.10 |

Table 7: The results of two -Stage extraction and Strippings from aqueous solution (pH=1.17) using Alamine 336 in air medium with different time at 25°C *

| Elements | First Concentration (ppm) | 10 min air | | 20 min air | | 30 min air | | 40 min air | | 50 min air | | 60 min air | |
|----------|---------------------------|-----------------------------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|
| | | remove to organic phase (%) | | remove to organic phase (%) | | remove to organic phase (%) | | remove to organic phase (%) | | remove to organic phase (%) | | remove to organic phase (%) | |
| | | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext |
| Mo | 66.73 | 97.90 | 96.25 | 97.72 | 97.05 | 99.82 | 98.13 | 97.67 | 95.61 | 97.74 | 96.62 | 96.82 | 97.13 |
| V | 82.21 | 88.78 | 89.12 | 90.35 | 88.23 | 89.75 | 86.42 | 89.02 | 88.25 | 90.87 | 88.71 | 92.18 | 90.51 |
| U | 8.93 | 92.64 | 90.05 | 91.93 | 89.28 | 84.61 | 82.16 | 87.33 | 85.51 | 87.61 | 84.13 | 88.43 | 82.59 |

| Elements | 10 min air | | 20 min air | | 30 min air | | 40 min air | | 50 min air | | 60 min air | |
|----------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| | Stripping (%) | | Stripping (%) | | Stripping (%) | | Stripping (%) | | Stripping (%) | | Stripping (%) | |
| | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp |
| Mo | - | - | 95.40 | 85.40 | 95.01 | 90.10 | 90.10 | 89.90 | 94.50 | 92.60 | 98.70 | 95.20 |
| V | 81.10 | 88.87 | 96.60 | 85.20 | 92.30 | 95.60 | 95.30 | 98.80 | 92.20 | 95.60 | 96.51 | 99.70 |
| U | 93.60 | 96.70 | - | - | - | - | - | - | - | - | - | - |

Table 8: The results of two -Stage extraction and Strippings from aqueous solution (pH=1.25) using Alamine 336 in air medium with different time at 25°C *

| Elements | First Concentration (ppm) | 10 min air | | 20 min air | | 30 min air | | 40 min air | | 50 min air | | 60 min air | |
|----------|---------------------------|-----------------------------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|
| | | remove to organic phase (%) | | remove to organic phase (%) | | remove to organic phase (%) | | remove to organic phase (%) | | remove to organic phase (%) | | remove to organic phase (%) | |
| | | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext |
| Mo | 67.25 | 82.92 | 82.13 | 84.32 | 83.52 | 85.53 | 83.44 | 89.21 | 87.29 | 87.62 | 85.13 | 85.69 | 85.12 |
| V | 81.59 | 85.61 | 83.59 | 86.42 | 85.59 | 87.23 | 85.42 | 88.97 | 86.69 | 85.35 | 83.23 | 85.15 | 84.51 |
| U | 9.51 | 90.23 | 88.56 | 92.77 | 90.27 | 92.04 | 90.55 | 97.94 | 95.43 | 96.36 | 95.58 | 93.57 | 91.18 |

| Elements | 10 min air | | 20 min air | | 30 min air | | 40 min air | | 50 min air | | 60 min air | |
|----------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| | Stripping (%) | | Stripping (%) | | Stripping (%) | | Stripping (%) | | Stripping (%) | | Stripping (%) | |
| | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp |
| Mo | 99.50 | 99.60 | 97.80 | 99.50 | 98.90 | 97.30 | 93.80 | 98.71 | 96.60 | 96.20 | 96.40 | 96.10 |
| V | 76.20 | 85.10 | 93.20 | 93.40 | 90.21 | 92.04 | 86.03 | 90.90 | 93.50 | 92.40 | 82.30 | 84.60 |
| U | 99.01 | 99.10 | 97.90 | 99.30 | 99.01 | 98.80 | - | 98.20 | - | 97.50 | 98.70 | 98.60 |

Then, the extraction was fulfilled by taking two 15 mL of solution adding 1 mL 0.38 M KMnO₄ and 1 mL, 30 % H₂O₂ and experimental results are given in Table 10.

In addition, extraction was performed by adding various amounts of 0.38 M KMnO₄, passing into to air at different time;the results are given in Table 11.

Table 9: The results of two -Stage extraction and Strippings from aqueous solution (pH=1.70) using Alamine 336 in air medium with different time at 25°C *

| Elements | First Concentration (ppm) | 10 min air remove to organic phase (%) | | 20 min air remove to organic phase (%) | | 30 min air remove to organic phase (%) | | 40 min air remove to organic phase (%) | | 50 min air remove to organic phase (%) | | 60 min air remove to organic phase (%) | |
|----------|---------------------------|--|---------------------|--|---------------------|--|---------------------|--|---------------------|--|---------------------|--|---------------------|
| | | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext |
| | | Mo | 66.71 | 74.60 | 72.19 | 76.22 | 74.11 | 79.10 | 76.17 | 79.81 | 77.26 | 72.22 | 70.45 |
| V | 80.82 | 68.66 | 65.47 | 60.29 | 59.61 | 66.20 | 64.72 | 69.93 | 67.49 | 68.96 | 66.13 | 67.12 | 65.17 |
| U | 8.72 | 55.81 | 55.12 | 64.25 | 62.27 | 67.24 | 63.55 | 73.10 | 71.63 | 76.83 | 75.41 | 72.10 | 70.16 |

| Elements | 10 min air Stripping (%) | | 20 min air Stripping (%) | | 30 min air Stripping (%) | | 40 min air Stripping (%) | | 50 min air Stripping (%) | | 60 min air Stripping (%) | |
|----------|--------------------------|---------------------|--------------------------|---------------------|--------------------------|---------------------|--------------------------|---------------------|--------------------------|---------------------|--------------------------|---------------------|
| | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp |
| | Mo | 92.20 | 93.20 | 96.60 | 99.30 | 96.30 | 93.90 | 95.30 | 94.20 | 96.10 | 94.60 | 94.50 |
| V | 84.10 | 76.48 | 74.01 | 67.20 | 90.01 | 90.40 | 74.50 | 83.40 | 86.80 | 79.40 | 87.10 | 86.90 |
| U | 97.70 | 97.80 | 99.10 | 96.70 | 96.10 | 96.40 | 96.50 | 97.40 | 99.02 | 96.70 | 96.50 | 99.01 |

Table 10 : The results of two -Stage extraction and Strippings of aqueous solution with 0.38 M KMnO₄ at 50°C *

| Elements | First Concentration (ppm) | Extraction with KMnO ₄ | | | | Extraction with H ₂ O ₂ | | | |
|----------|---------------------------|-----------------------------------|---------------------|---------------------|---------------------|---|---------------------|---------------------|---------------------|
| | | remove to organic phase (%) | | Stripping (%) | | remove to organic phase (%) | | Stripping (%) | |
| | | 1 st ext | 2 nd ext | 1 st stp | 2 nd stp | 1 st ext | 2 nd ext | 1 st stp | 2 nd stp |
| Mo | 66.73 | 68.26 | 62.45 | 89.10 | 97.40 | 71.74 | 70.13 | 99.10 | 97.70 |
| V | 82.21 | 54.54 | 49.81 | 93.71 | 93.90 | 57.52 | 55.61 | 94.10 | 93.90 |
| U | 8.93 | 70.88 | 63.12 | 99.62 | 97.90 | 72.67 | 69.43 | 98.42 | 98.60 |

Table 10: The results of two-Stage extraction and Strippings of aqueous solution with 0.38 M KMnO₄ at 50°C

| Elements | Remove to organic phase (%) | | | | | | | |
|----------|--|---------------------|--|---------------------|---|---------------------|---|---------------------|
| | 15 mL solution +2 mL KMnO ₄ | | 15mL solution +5 mL KMnO ₄ +10 min. Air | | 15 mL solution +5 mL KMnO ₄ +20 min. air | | 15 mL solution +5 mL KMnO ₄ +30 min. air | |
| | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext |
| Mo | 3.80 | 3.25 | 5.67 | 5.21 | 5.47 | 5.32 | 7.43 | 7.02 |
| V | 47.40 | 46.30 | 52.40 | 50.13 | 50.91 | 49.57 | 50.90 | 49.97 |
| U | 35.01 | 34.20 | 63.00 | 60.49 | 41.20 | 40.28 | 35.83 | 33.21 |

| Elements | Stripping (%) | | | | | | | |
|----------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp |
| Mo | 99.90 | 98.60 | 99.70 | 97.70 | 99.80 | 98.40 | 99.70 | 96.90 |
| V | 78.30 | 84.00 | 80.40 | 82.03 | 91.10 | 90.30 | 91.20 | 90.10 |
| U | 92.30 | 93.80 | 91.20 | 97.90 | 99.80 | 98.10 | 98.80 | 96.60 |

Table 11: The results of two -Stage extraction and Strippings in solution which has been effected with 0.38 M KMnO₄ in air medium*

| Elements | Remove to organic phase (%) | | | | | | | |
|----------|---|---------------------|--|---------------------|---|---------------------|---|---------------------|
| | 15 mL solution +2 mL KMnO ₄ | | 15mL solution +5 mL KMnO ₄ +10 min. Air | | 15 mL solution +5 mL KMnO ₄ +20 min. air | | 15 mL solution +5 mL KMnO ₄ +30 min. air | |
| | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext |
| Mo | 3.80 | 3.25 | 5.67 | 5.21 | 5.47 | 5.32 | 7.43 | 7.02 |
| V | 47.40 | 46.30 | 52.40 | 50.13 | 50.91 | 49.57 | 50.90 | 49.97 |
| U | 35.01 | 34.20 | 63.00 | 60.49 | 41.20 | 40.28 | 35.83 | 33.21 |

| Elements | Stripping (%) | | | | | | | |
|----------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| | 1 st stp | | 2 nd stp | | 1 st stp | | 2 nd stp | |
| | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp |
| Mo | 99.90 | 98.60 | 99.70 | 97.70 | 99.80 | 98.40 | 99.70 | 96.90 |
| V | 78.30 | 84.00 | 80.40 | 82.03 | 91.10 | 90.30 | 91.20 | 90.10 |
| U | 92.30 | 93.80 | 91.20 | 97.90 | 99.80 | 98.10 | 98.80 | 96.60 |

Finally, extraction was performed by adding various amounts of MnO₂ and results are given in Table 12.

Table 12: The results of two -Stage extraction and Strippings in solution which has been effected with MnO₂ in air medium *

| Elements | Remove to organic phase (%) | | | | | | | |
|----------|---|---------------------|--|---------------------|---|---------------------|---|---------------------|
| | 15 mL solution +solid MnO ₂ | | 15mL solution +solid MnO ₂ +10 min. Air | | 15 mL solution +solid MnO ₂ +20 min. air | | 15 mL solution +solid MnO ₂ +30 min. air | |
| | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext | 1 st ext | 2 nd ext |
| Mo | 6.20 | 5.93 | 3.52 | 3.05 | 6.45 | 6.02 | 6.48 | 5.92 |
| V | 67.80 | 66.23 | 55.28 | 53.20 | 64.20 | 62.29 | 66.50 | 65.21 |
| U | 69.80 | 67.12 | 65.95 | 64.82 | 60.70 | 59.03 | 59.6 | 57.16 |

| Elements | Stripping (%) | | | | | | | |
|----------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| | 1 st stp | | 2 nd stp | | 1 st stp | | 2 nd stp | |
| | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp | 1 st stp | 2 nd stp |
| Mo | 98.20 | 99.10 | 99.20 | 99.40 | 99.90 | 99.10 | 99.20 | 98.90 |
| V | 94.40 | 86.30 | 95.00 | 94.30 | 92.16 | 91.50 | 93.70 | 94.10 |
| U | 90.01 | 92.70 | 90.10 | 90.80 | 92.60 | 93.80 | 94.50 | 97.30 |

* : Averages calculated for data obtained from three independent extraction experiments

By taking Tables 6, 7, 8 and 9 into consideration, maximum extraction yield was carried out with condition in Table 7. It seems that oxygen is the best oxidant. Because Mo, V and U was oxidation with oxygene. Thus, M_xO_yⁿ⁻ anions happen to polymeric structure.

In all these analyses, Fe, Al, Ti and Ni were not shown in the tables since they could not be extracted. When the tables above are examined, it is seen that extraction yields

of Mo, V and U passing into solution as a result of autoclave process, are rather low. This proves that ions of these elements are reduced under autoclave conditions and when taken into solution at oxidation steps that do not pass into organic phase. In very few of extraction experiments, as a result of autoclave process as regards the passing of these elements into organic phase, these elements are seen to be at oxidation step where they can pass into organic phase. This is shown in Table 1-5.

Through the solution obtained after autoclave process, air was passed at different times, and the extraction yield is seen to increase remarkably as illustrated in Table 6. In case of performing oxidation procedures with KMnO₄ and MnO₂, it was found that extraction yields were low. It would be convenient to perform extraction procedure by passing air through solution in view of both easiness of the experiment and high extraction yield. For this, it seems sufficient to pass air for 10 min through solution whose pH has been brought to 1,17. The first extraction yields obtained under these circumstances were determined to be about 98 for Mo, 89 for V and 93 % for U.

Conclusions

Hydrometallurgical processing consists usually of leaching followed by treatment of resulting pregnant aqueous solution by chemical or electrochemical means to obtain the separation, purification and recovery of the metals.

Recovery of Mo, U, V, Ni and Ti from asphaltite ash by H₂SO₄ leaching displays differences according to application method. For example, the leaching yield of elements are about 90 % for Mo, V, U, and 60 % of Ni can be leached by diluted H₂SO₄. The ratio of H₂SO₄/ash is 2/1. If leaching is carried out by 14-15 M H₂SO₄ in atmospheric conditions about 90 % of Mo, V and Ni pass into solution. Consumption of H₂SO₄ is the same. In the pressure leaching, all of these elements were leached by H₂SO₄ in autoclave conditions. The ratio of H₂SO₄/ash is 1.

In the pregnant solutions of direct leaching with H₂SO₄, extraction can be performed with Alamine 336 by high yields, but it can not be fulfilled by pressure leaching because some of the elements in asphaltite ash reduced by SO₂ formed in reactions resulting. As a result, Mo (VI), V(V) and U(VI) reduce to Mo³⁺, V³⁺ and U⁴⁺. These reduced ions can not be extracted with Alamine 336. If these ions are oxidized with air, extraction can be achieved. After extraction of these elements, an acidic solution remains. Gradually, more concentrate solutions of Ni and Ti are obtained by using this solution in leaching of the sample after autoclave. Ni and Ti can be separated from this solution with different methods.

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