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Recep Ziyadanoğulları[a]; Işıl Aydın[a]
[a] Department of Chemistry, Faculty of Science and Art, Dicle University, Diyarbakır, Turkey

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Recovery of Uranium, Nickel, Molybdenum, and Vanadium from Floated Asphaltite Ash

Recep Ziyadanoğulları* and Işıl Aydın

Department of Chemistry, Faculty of Science and Art, Dicle University, Diyarbakır, Turkey

ABSTRACT

In this study, asphaltite ash obtained from asphaltite was sulfurized under an autoclave condition, and then this sample was floated by two different xanthates. The amount of uranium, nickel, molybdenum, and vanadium in the asphaltite ash was concentrated approximately 12 times. Uranium, nickel, molybdenum, and vanadium in the concentrated samples were separated in the following stages: first the concentrate was leached with different concentrations of $(NH_4)_2CO_3$ to recover uranium and aluminium; in the second stage, the remaining sample was roasted with treated pyrite at 700°C and leached by water to obtain soluble nickel compounds; in the third stage, the remaining sample was leached with 15 M H_2SO_4 to solublise molybdenum, titanium, and iron compounds. A solid sample containing vanadium compounds was removed from a

*Correspondence: Recep Ziyadanoğulları, Department of Chemistry, Faculty of Science and Art, Dicle University, TR 21280, Diyarbakır, Turkey; E-mail: recepz@dicle.edu.tr.

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solution containing molybdenum, titanium, and iron compounds. This solution was extracted with alamine 336 to separate molybdenum from titanium and iron.

Key Words: Asphaltite ash; Molybdenum; Leaching; Nickel.

INTRODUCTION

Coal, as a sedimentary rock, is a complex mixture of organic and inorganic matter, containing intimately mixed solid, liquid, and gaseous phases that have allothigenic and authigenic origins. There are minerals and mineral groups in the coal samples. These are mainly silicates and oxyhydroxides, to a lesser extent sulphates and carbonates, and more rarely, sulphides and phosphates.[1] Also, coal rarely contains uranium, nickel, molybdenum, vanadium, titanium, iron, and aluminium compounds.[2] Hydrometallurgical, pyrometallurgical, and sometimes a combination of both processes are used to recover elements described above. The techniques followed for treating coal ash are direct leaching, roast-leaching, and autoclave leaching.

In direct leaching, H_2SO_4 is generally used as a leachant because of its relatively low cost and wide availability. Other applicable acids such as hydrochloric and nitric acid are more costly and cause more serious environmental pollution than sulphuric acid. Sulphuric acid leaching is used in many mills to dissolve uranium, nickel, molybdenum, vanadium, titanium, iron, and aluminium compounds from ores and concentrates. To obtain acceptable (i.e., 90–95%) uranium dissolution, the leaching of Elliot Lake ores consumes a large amount of acid (about 20 kg/t ore), requires relatively long leach duration (up to 96 hr), high temperature (around 75°C), and high residual sulphuric acid concentration (approximately 50 g/L free acid), because the predominant uranium mineral is brannerite, from which uranium is relatively difficult to leach. Limestone ore lime is needed to reduce the acid tenor prior to ion exchange.[3]

In autoclave leaching, leaching in carried out in an aqueous solution at a suitable temperature and pressure. The introduction of pressure leaching has enhanced the extent and rate of leaching of refractory ore. High recoveries are achieved in 2 hr using a temperature of 200°C and oxygen at 14 atm. pressure, whereas treatment for 16 hr in Pachuca tanks by the conventional method give at best only ~80% dissolution.[4]

In roast leaching, sample ore is heated for a suitable time and temperature in a furnace. The cooled calcine is then leached with leachant.

Various investigations show that recovery of uranium, nickel, molybdenum, and vanadium by using hydrometallurgical processes are not economical.[2]

Particularly in acid leaching, more than 90% of acid consumption is used for main components of original ash (lime stone, silica, and various metal oxides). Calcium, magnesium, iron, and aluminium ions in solution create different problems for recovering the elements mentioned above.

So far, various investigations have been carried out for recovery of uranium, nickel, molybdenum, and vanadium from asphaltite ash, coal, and different concentrates.[5–13]

In this study, we aimed to investigate the ability of asphaltite ash to form concentrates via flotation, as well as economical separability of the elements mentioned above.

EXPERIMENTAL

Materials and Methods

Preparation of Asphaltite Ash

Asphaltite sample was provided from Silopi (Southeastern Anatolia Region in Turkey), ignited at atmospheric conditions, sieved to −100 mesh size, roasted at 900°C for 4 hr and again sieved to −100 mesh size, dried at 110°C, kept in bottles, and used later. The chemical analyses of asphaltite ash are given in Table 1.

Reagents

All the chemical used were of analytical grade.

Apparatus

A flame atomic absorption spectrometer (UNICAM 929 Model AAS) was used for determination of nickel and iron, and an atomic emission spectrophotometer (JOBIN YVON JY 24 Model ICP-AES) for uranium, molybdenum, aluminium, titanium, and vanadium concentrations in the solution. A D12 flotation apparatus, Heraus Model Furnace, and Nel 890 Model pH meter

Table 1. The chemical analysis of asphaltite ash.

Compounds	Mo	Ni	V	Ti	Al	Fe	U_3O_8
Composition (%)	0.33	0.45	0.60	0.44	9.47	2.96	0.05

Note: Averages calculated for data obtained from three independent experiments.

were used for flotation, roasting, and determination of pH of samples, respectively.

Sulfurization of Asphaltite Ash in Autoclave Conditions

First, 500.0 g of asphaltite ash obtained from asphaltite was sulfurized with H_2S (2.73 g of H_2S yielded 10.0 g modified pyrite $+8$ mL $H_2SO_4 + 20$ mL water) under an autoclave for 1 hr at 100°C. Thus, the elements were predominantly converted to sulfide and oxide compounds. Samples obtained from autoclave were floated with potassium amyl xanthate,[13] and the concentrated sample (CS) was subjected to different separation methods. The chemical analyses of this concentrate are given in Table 2.

RESULTS AND DISCUSSION

Separation of Nickel from CS

The CS and mixture of CS, treated with pyrite,[15] and sulphur were roasted at 650°C to be converted into nickel sulphate compounds. Roasted samples were cooled and then leached with water. The results are given in Table 3.

As shown in Table 3, it was determined that nickel passed into solution by high yield only in the mixture of sulfurized asphaltite ash and treated pyrite. Then, different ratios of sulfurized asphaltite ash and treated pyrite were roasted at 650°C for various times. The above processes were repeated, and the results are given in Table 3.

As shown in Table 4, it was determined that the highest yield (99.5%) was obtained from a mixture of 2 g of sulfurized asphaltite ash and 0.53 g of treated pyrite roasted at 650°C for 5 hr. The experiments were carried out three times, and similar results were obtained.

As shown in Tables 3 and 4, small amounts of Mo, U, V, Fe, and Al passed into solution under conditions in which all the nickel was extracted. Therefore, it was concluded that concentrate could be extracted to recover uranium.

Table 2. The chemical analyses of SFC.

Compounds	Mo	Ni	V	Ti	Al	Fe	U_3O_8
Composition (%)	3.73	5.42	6.90	5.21	9.74	31.95	0.62

Note: Averages calculated for data obtained from three independent experiments.

Table 3. Effect of roasting time on the sulfurized asphaltite ash.

Roasting time (hr)	Sample	Extraction yield (%)						
		Ni	Al	Mo	V	U	Ti	Fe
2	2.0 g CS	10.1	8.2	11.5	5.3	13.6	9.9	9.2
3	2.0 g CS	12.5	7.2	14.0	13.8	16.4	11.9	9.0
4	2.0 g CS	30.7	5.1	36.0	32.2	42.9	36.8	21.2
5	2.0 g CS	61.9	3.8	64.1	58.8	72.7	53.8	28.4
5	2.0 g CS + 0.5 g TP	95.1	2.5	3.6	2.2	6.0	4.3	3.1
6	2.0 g CS	53.3	3.7	50.5	53.3	62.5	48.7	25.0
6	2.0 g CS + 0.20 g S	55.4	3.5	54.4	56.0	64.7	50.9	25.8

Note: CS, concentrated sample; TP, treated pyrite, S, elemental sulfur. Averages calculated for data obtained from three independent extraction experiments.

Separation of Uranium

To separate uranium from sulfurized and floated concentrates (SFC), the analyses of which are given in Table 2, SFCs were leached with different concentrations of $(NH_4)_2CO_3$ for 5 min at room temperature. Extraction yields of the elements are given in Table 5.

Table 5 shows that all the uranium and aluminium and only 1–11% of molybdenum were extracted, while 89–99% of molybdenum and all the iron, titanium, and vanadium remained in the precipitate. Duplicate samples were extracted for each concentration of $(NH_4)_2CO_3$.

Into a solution containing uranium, aluminium, and molybdenum and extracted with 1.6 M $(NH_4)_2CO_3$, 12.5 mL of 4 M NH_4Cl was added to precipitate aluminium as $Al(OH)_3$. Then the solid/liquid ratio was investigated; the effect of the solid/liquid ratio on leaching efficiency is shown in Table 6. The leaching efficiency increases with decreasing solid/liquid ratio over the entire range tested.

As shown in Table 6, while all the uranium and aluminium were extracted with 1.5 g solid concentrate/10 mL of 1.6 M $(NH_4)_2CO_3$, the other elements remained in the precipitate. An amount of 20 mL of 4 M NH_4Cl was added to the solution obtained from the extraction. To precipitate aluminium as $Al(OH)_3$, while aluminium remained in the precipitate, uranium passed into solution as $UO_2(CO_3)_3^{4-}$ ions. After separating uranium and aluminium from solid concentrate, separation of nickel from the remaining sample (SNI: uranium and aluminium removed sample) was studied.

Table 4. Effect of roasting (650°C) time on mixture of the concentrated sulfurized asphaltite ash and treated pyrite.

Roasting time (hr)	Extraction yield (%)						
	Ni	Mo	U	V	Ti	Fe	Al
2.00 g CS + 0.50 g TP							
3	85.48	7.35	9.57	5.92	8.17	6.82	3.51
4	91.96	5.21	8.12	4.43	6.33	5.02	2.97
5	96.57	4.02	5.99	2.48	4.48	3.17	2.11
6	89.28	3.61	5.53	2.12	4.05	2.85	1.69
2.00 g CS + 0.53 g TP							
3	88.45	3.98	3.63	1.71	3.14	2.21	0.97
4	92.68	2.17	1.87	0.93	0.93	1.03	0.51
5	99.15	0.12	0.91	0.08	0.01	0.01	0.02
6	91.35	0.15	0.99	0.06	0.07	0.03	0.01
2.00 g CS + 0.55 g TP							
3	75.76	3.65	2.51	1.07	2.82	1.71	0.31
4	77.95	1.96	1.33	0.67	0.72	0.04	0.15
5	82.60	0.10	0.77	0.05	0.01	—	—
6	75.99	0.17	0.81	0.20	0.05	—	—

Note: Averages calculated for data obtained from three independent extraction experiments.

Separation of Nickel from Uranium and Aluminium Removed Sample

The following processes were carried out for elements such as Mo, Ti, Fe, Al, U, Ni, and V, which did not predominantly pass into solution. To that end, 0.5, 1.0, 1.5, 2.0, and 2.5 g of concentrate were leached with 10 mL of 1.6 M $(NH_4)_2CO_3$ to remove U and Al. The remaining solid was roasted with 0.13, 0.26, 0.4, 0.53, and 0.66 g of treated pyrite at 650°C for 5 hr. The roasted samples were leached by water to obtain soluble nickel compounds. It was determined that all the nickel passed into solution as nickel sulphates and the other elements (molybdenum, iron, titanium, and vanadium) remained in the precipitate.

Experiments were repeated two times, and the same results were obtained. It is shown that results of experiments can be repeated. The ratio of concentrate/treated pyrite was kept constant in the experiments. The remaining precipitate contained molybdenum, iron, titanium, and vanadium (SMO).

Table 5. Effect of $(NH_4)_2CO_3$ concentration on extraction yields of the elements (0.5 g sample + 10 mL $(NH_4)_2CO_3$).

$(NH_4)_2CO_3$ (M)	Extraction yield (%)					
	U	Al	Mo	Fe	Ti	V
0.5	98.0	100.0	10.7	—	—	—
0.8	98.2	100.0	11.5	—	—	—
1.0	100.0	100.0	5.3	—	—	—
1.6	100.0	100.0	1.3	—	—	—
2.0	100.0	100.0	1.2	—	—	—

Note: Averages calculated for data obtained from three independent extraction experiments.

Separation of Molybdenum and Vanadium

Molybdenum, iron, titanium, and vanadium in the precipitate (SMO) are considered to be converted into their oxides, and thus, samples were leached with different concentrations of H_2SO_4 according to the following reactions:

$$MoO_{3\,(s)} + H_2SO_{4\,(aq)} \rightleftarrows MoO^{2+}_{2\,(aq)} + SO^{2-}_{4\,(aq)} + H_2O \quad (1)$$

$$V_2O_{5\,(s)} + 2H_2SO_{4\,(aq)} \rightleftarrows 2VO^{+}_{2\,(aq)} + 2HSO^{-}_{4\,(aq)} + H_2O \quad (2)$$

$$TiO_{2\,(s)} + H_2SO_{4\,(aq)} \rightleftarrows TiO^{2+}_{(aq)} + SO^{2-}_{4\,(aq)} + H_2O \quad (3)$$

$$Fe_2O_{3\,(s)} + 3H_2SO_{4\,(aq)} \rightleftarrows 2Fe^{3+}_{(aq)} + 3SO^{2-}_{4\,(aq)} + 3H_2O \quad (4)$$

Experimental results are given in Table 7.

Table 6. Effect of the solid/liquid ratio on leaching efficiency (liquid is 10 mL of 1.6 M $(NH_4)_2CO_3$).

Solid (g)	Extraction yield (%)					
	U	Al	Mo	Fe	Ti	V
0.50	100.0	100.0	1.3	—	—	—
1.00	100.0	100.0	0.5	—	—	—
1.50	100.0	100.0	—	—	—	—
2.00	99.4	97.3	—	—	—	—
2.50	98.9	96.4	—	—	—	—
3.00	98.2	95.9	—	—	—	—

Note: Averages calculated for data obtained from three independent extraction experiments.

Table 7. Effect of H_2SO_4 concentration on the leaching of SMO (amount of sample: 1.0 g; leaching time: 1 hr; leaching temperature: 50°C).

H_2SO_4 concentration (M)	Extraction yield (%)			
	Mo	V	Ti	Fe
0.4	68.8	—	—	3.0
0.8	68.5	—	—	3.0
1.1	68.6	—	—	3.1
1.5	68.7	—	—	3.1
2.1	68.9	—	—	3.2

Note: Averages calculated for data obtained from three independent extraction experiments.

None of the titanium and vanadium, and about 97% iron in the precipitate was extracted, while about 69% of molybdenum was extracted. The same sample (SMO) was leached with different concentrations of NaOH solution according to the following reactions:

$$MoO_{3\,(s)} + 2OH^-_{(aq)} \rightleftarrows MoO^{2-}_{4\,(aq)} + H_2O \quad (5)$$

$$V_2O_{5\,(s)} + 2OH^-_{(aq)} \rightleftarrows 2VO^-_{3\,(aq)} + H_2O \quad (6)$$

The effect of NaOH concentration on the leaching of SMO is given in Table 8.

Experimental results in Tables 7 and 8 show that vanadium could not be extracted in the acidic medium, but a small amount (about 18%) was extracted

Table 8. Effect of NaOH concentration on the leaching of SMO (amount of sample: 1.0 g; leaching time: 1 hr; leaching temperature: 50°C).

NaOH concentration (M)	Extraction yield (%)			
	Mo	V	Ti	Fe
0.1	2.4	18.1	—	—
0.2	2.5	18.2	—	—
0.3	2.5	18.3	—	—
0.4	2.5	18.3	—	—
0.5	2.5	18.3	—	—

Note: Averages calculated for data obtained from three independent extraction experiments.

in basic medium. Approximately 69% and 2% of molybdenum were extracted in the acidic and basic medium, respectively.

Since the expected yields were not achieved, the sample (SMO) was reacted with 15 M of different volumes of H_2SO_4 in an autoclave at 225°C for 1 hr according to the total stoichiometric amount of molybdenum, iron, titanium, and vanadium in the sample [Eqs. (1–4)]. Experimental results are given in Table 9.

It was determined that all the molybdenum, iron, and titanium in the sample were extracted with 3.2 mL of 15 M H_2SO_4, while vanadium remained in the precipitate (SV).

The remaining solid sample (SV) containing vanadium was analyzed, and the results show that the precipitate is a mixture of V_2O_5 $1/2$ H_2O and VO_2HSO_4, which contains 4% SO_4^{2-} ions. It is thought that VO_2HSO_4 passed by adsorption into V_2O_5 $1/2$ H_2O.

After vanadium was separated, the remaining solution containing molybdenum, iron, and titanium was extracted with alamine 336. Before extraction, one drop of 0.1 M $KMnO_4$ solution was dropped into an acidic solution containing molybdenum, iron, and titanium, and it was seen that the color of $KMnO_4$ did not change, suggesting that molybdenum, iron, and titanium in the solution were present as MoO_4^{2-}, TiO^{2+}, and Fe^{3+} ions, respectively.

To remove molybdenum from the solution containing 91.1, 837, and 95.8 ppm of molybdenum, iron, and titanium, the solution was extracted with alamine 336 at optimum conditions described.[14] Two-step extraction processes were carried out, and the results are shown in Table 10. M_{aq} and M_o in Table 10 indicate percentages of metals remaining in aqueous and passing into organic phases, respectively.

As seen in Table 10, while 87% of molybdenum was extracted in the organic phase, all the iron and titanium remained in the aqueous phase. Thus, 99% of molybdenum was extracted in the organic phase by two-step extraction. To strip molybdenum from the organic phase, H_2S gases were used. A mixture

Table 9. Effect of H_2SO_4 volume on extraction of Mo, V, Ti, and Fe.

H_2SO_4 volume (mL)	Sample (g)	Extraction yield (%)			
		Mo	V	Ti	Fe
4.5	5.00	100.0	3.9	100.0	100.0
3.2	5.00	100.0	—	100.0	100.0

Note: Averages calculated for data obtained from three independent extraction experiments.

Table 10. Removal of molybdenum from solution by two-step extraction processes.

	One-step extraction		Two-step extraction		
Metals	M_{aq} (%)	M_o (%)	M_{aq} (%)	M_o (%)	M_o (%)
Mo	12.8	87.2	0.12	87.3	99.1
Ti	100.0	—	100.0	—	—
Fe	100.0	—	100.0	—	—

Note: Averages calculated for data obtained from three independent extraction experiments. Organic phase: mixture of 80% kerosene, 10% alamine 336, and 10% nonanol; ratio of aqueous phase/organic phase: 1 : 1, extraction time: 5 min; extraction temperature: 25°C and equilibrium pH: 1.17 alamine 336: Tri-*n*-octylamine.

(1 : 1) of the organic phase containing molybdenum and the aqueous phase containing 0.1 M H_2SO_4 was blown with H_2S gases to precipitate molybdenum as MoS_3 and to accumulate it in the aqueous phase. Reusability of the remaining organic phase was examined, and it was determined that the yield of extraction of molybdenum decreased at a rate of 71% during the fifth extraction. To prevent a further decrease in the yield, the organic phase was blown with H_2S gases and then washed with 0.1 M H_2SO_4. After sulfur compounds in the organic phase were removed, the organic phase was reused and the yield of extraction increased 87% of molybdenum as previously described in one-step extraction.

Extraction may occur as the following reaction:

$$[(R)_3 - NH]^+HS^-_{(o)} + HSO^-_{4\,(aq)} \rightleftarrows [(R)_3 - NH]^+HSO^-_{4\,(o)} + HS^-_{(aq)} \quad (7)$$

Equilibrium may be shifted to the right side depending on the H_2SO_4 concentration.

CONCLUSION

From the present study, it can be concluded that uranium, nickel, molybdenum, and vanadium in asphaltite ash can be removed. The important features and results of the methodology are:

1. Flotation of original ash was not successfully achieved. For this purpose, original ash was sulfurized to change its structure and surface.

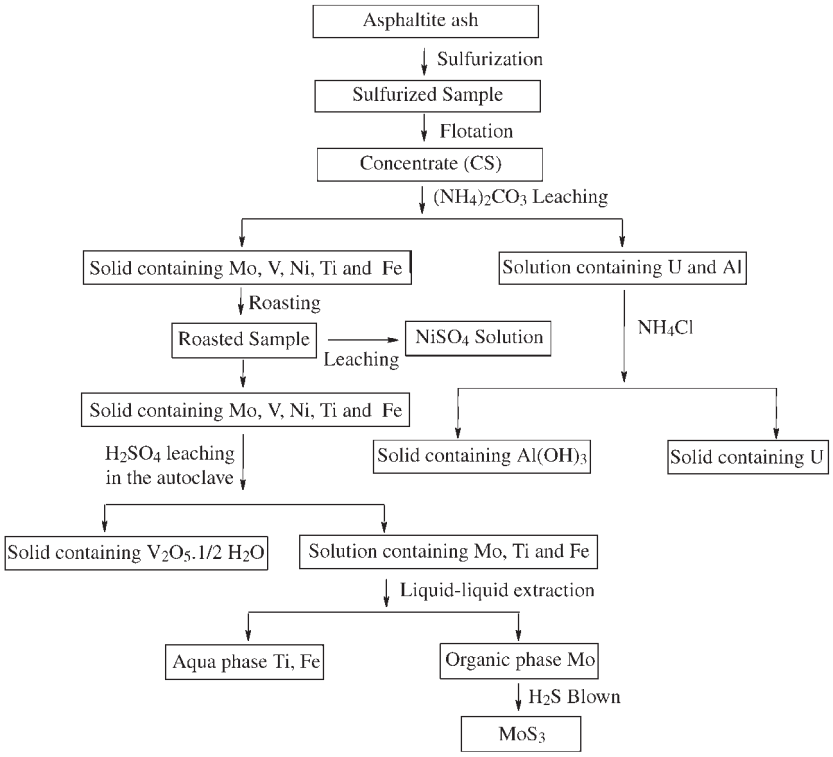

Figure 1. Flowsheet for recovering U, Mo, Ni, and V from asphaltite ash.

2. The results of flotation show that sulfurization of asphaltite ash is a very effective method. The amount of uranium, nickel, molybdenum, and vanadium in the asphaltite ash was concentrated approximately 12 times.
3. To recover uranium, nickel, molybdenum, vanadium, titanium, aluminium, and iron from SFC, the processes described in Fig. 1 should be followed.

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