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THE SEPERATION OF MOLYBDENUM AND VANADIUM FROM TURKISH ASPHALTITE ASH BY ION EXCHANGE CHROMATOGRAPY

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ABSTRACT

The recovery of rare elements as by-products from the ash of coal or asphaltite has been important and the amount of them has been found suitable for economical recovering. The asphaltite in the southeast Anatolia region (Turkey) contains molybdenum, vanadium, nickel and uranium. In the present work, the ash sample obtaiend from Şırnak asphaltite was leached with sulphuric acid. This leachate contains 240 mg / L. Mo, 100 mg / L V, 71 mg / L Ni and 175 mg / L Fe. This leach solution was passed through a column of length 100 cm with an internal diameter of 1.5 cm. The metal ions were eluated with different H_2SO_4 solutions. 97 % of the total Mo as 72 % pure molybdenum and 25 % Mo as a mixture with vanadium were separated by elution with 0.01 N H_2SO_4 and 0.1 N H_2SO_4.

INTRODUCTION

The studies on ashes of coal or asphaltite have shown that many of these are potential and also utilizable resources with respect to their contents (Murtha, 1982; Robert, 1983; Stinespring, 1985; Eisenberg, 1986). Particularly the studies on the recovery of uranium which is the main cause of the radioactive pollution have been increased (Smith, 1977; Andersson, 1977). It has been shown that reasonable amounts of Mo, V, Ni, Ni and Al etc can be produced from appropriate coal ashes (Smith, 1977; Andersson, 1977; Whigham, 1965; Jack, 1979; Torma, 1983). There are many asphaltite deposits around the Southeast Anatolia of Turkey. However, these asphaltites tend to be of poor quality as fuels due to the relatively high ash and moisture contents. Some studies have shown that ashes of them contain valuable minerals such as Mo, Ni, V, U etc. in economical amounts (MTA, 1979; Tenler, 1979)

It is also possible to recover them by extraction or chemical precipitation methods from their leachates with sulphuric acid (Hamamcı, 1984; Atamer, 1979). There have been some difficulties during the separation molybdenum and vanadium from each other and another metal ions in the leachate of sulphuric acid (Korkisch, 1969). The aim of this work is to separate each of molybdenum and vanadium from the other ions in the acidic leach solution obtained from asphaltite ash, by ion exchange chromatography.

MATERIALS AND METHODS

100 kg asphaltite sample used in this work was taken from Avgamasya region in Southeast Anatolia with asphaltite reserve about 55 million tons. This asphaltic material containing 0.18 % Ni, 0.16 % Mo and 0.28 % V was characterized by the high ash content, up to 40 %. Asphaltite was burned and roasted at 950 °C for 3 hours. The ash obtained contains 0.33 % Ni, 0.30 % Mo and 0.57 V. It was ground to under 100 mesh. 200 g of this ash was terated with 500 ml of 1.0 M H_2SO_4, filtered and completed one liter with distilled water. This solution contains 1000 mg V, 240 mg Mo, 175 mg Fe and 71 mg Ni.

A column of length 100 cm with an internal diameter of 1.5 cm which was packed Dowex 50 WX8 (16-40 mesh) cation exchange resin was connected with LKB UltroRac-7000 fraction collector. A separating funnel with 500 ml size was settled at the top of this column. 100 ml of 0.01 N H_2SO_4 passed through the column for preventing the precipitation of metal ions in the leachate. The following studies were carried out by this column:

1. Elution with 3N H_2SO_4: 100 ml of the leachate was passed through the column with a rate of 0.2 ml / minute come out at the bottom. Then 200 ml of 0.01 N H_2SO_4 solution passed as the same manner and the effluents were evaporated to 100 ml (A1). After the charging and washing processes, 100 ml of 3N H_2SO_4 were passed as described above. Fractions of 33 ml were taken automatically different tubes from the bottom of the column by LKB Ultro-Rac-7000 fractioner. In each tube, the amounts of molybdenum, vanadium, nickel, iron, sodium, potassium and calcium were determined (Table 1). The column was washed with 0.01 N H_2SO_4 solution for a new process.

2. Elution with 0.1 N H_2SO_4: 100 ml of the leachate was passed through the column as in the first procedure. The effluent taken from the bottom of the column and the fraction of washing solution provided by passing 200 ml of 0.01 N H_2SO_4 from the column were mixed and then evaporated to 100 ml (A2). After these processes, 1000 ml of 0.1 N H_2SO_4 were passed through the column as 0.2 ml / minute come out and fraction

Table 1. Elution of some ions with 3 N H_2SO_4 solution on Dowex 50 WX8 cation exchange resin

Volume (ml)	Mo ppm	V ppm	Ni ppm	Fe ppm	Na ppm	K ppm	Ca ppm
A1	41	0	0	0	0	0	0
33	16	0	0	0	0	0	0
66	93	0	0	1	2	0	0
99	59	23	0	3	10	0	0
132	50	99	0	7	40	0	0
165	84	285	2	34	76	4	0
198	119	363	5	67	90	25	0
231	111	396	10	81	100	50	1
264	95	426	13	76	> 100	85	2
297	6a	426	14	72	> 100	> 100	3
330	33	411	15	67	> 100	> 100	4
363	11	378	13	61	> 100	> 100	5
396	5	300	12	58	> 100	> 100	5
429	3	204	12	52	92	> 100	5
462	2	66	11	41	60	> 100	4
494	0	30	11	15	36	> 100	3
528	0	24	11	12	10	> 100	3
561	0	0	11	5	4	100	2
594	0	6	11	3	0	80	1
627	0	3	9	2	43	43	0
660	0	0	8	2	0	24	0
693	0	0	6	2	0	13	0
726	0	0	4	1	0	5	0
659	0	0	3	0	0	4	0
792	0	0	3	0	0	3	0
825	0	0	3	0	0	1	0
858	0	0	3	0	0	0	0

33 ml were taken automatically into tubes. For completion of elution of metal ions 350 ml of 1 N H_2SO_4 passed through the column and fractions were taken into tubes as the same way. Then the column was washed with 350 ml of 4 N H_2SO_4 and eluate collected as a single fraction. In all fractions the amounts of molybdenum and vanadium were determined. The results are shown in Table-2. The column was washed with 0.01 N H_2SO_4 for a new process.

3. Elution with 1 N H_2SO_4: 90 ml of the leachate was passed through the column as the same way and the metal ions held by the resin were eluated by 2000 ml of 1 N H_2SO_4 and fractions of 33 ml were taken into tubes (Figure-1). The effluents were taken into tubes from bottom of the column analyzed for their Mo, V, Ni, Fe, Na, K and Ca contents. The determinations of Mo, V, Nu and Fe in the samples were made by Varian Techtron Model 1200 Atomic Absorption Spectrophotometer. Na, K and Ca were determined by Bruno-Lange M6a Flame Photometer.

Table 2. Elution of molybdenum and vanadium with three different H_2SO_4 solutions on Dowex 50 W×8 resin

Volume ml	Molybdenum		Vanadium	
	ppm	mg	ppm	mg
Elution with 0.1 N H_2SO_4				
A2	118	11.8	0	0
33	52	1.7	0	0
99	33	1.1	0	0
132	21	0.7	0	0
165	14	0.5	13	0.4
198	14	0.5	18	0.6
231	11	0.4	20	0.7
264	10	0.3	24	0.8
297	8	0.3	29	1.0
330	4	0.1	22	0.7
363	4	0.1	22	0.7
396	4	0.1	22	0.7
429	6	0.2	24	0.8
462	10	0.3	29	1.0
495	11	0.4	33	1.1
528	11	0.4	24	1.0
561	11	0.4	26	0.9
594	11	0.4	24	0.8
627	10	0.3	24	0.8
660	10	0.3	20	0.3
693	10	0.3	15	0.5
726	8	0.3	14	0.5
759	4	0.1	11	0.4
297	2	0	11	0.4
825	1	0	2	0.1
891	0	0	0	0
924	0	0	0	0
957	0	0	0	0
990	0	0	0	0
Elution with 1 N H_2SO_4				
33	0	0	0	0
66	0	0	0	0
99	0	0	20	0.7
132	0	0	24	0.8
165	0	0	22	0.7
198	0	0	24	0.8
231	0	0	24	0.8
264	0	0	24	0.8
267	0	0	26	0.9
330	0	0	29	1.0
Elution with 4N H_2SO_4				
350	2	0.7	227	87.2

RESULTS AND DISCUSSION

As can be seen in Table-1, during charging of the leachate that obtained from the ash of Şırnak asphaltite on the column packed with Dowex 50 WX8 cation exchange resin, some amount of molybdenum was eluated from the bottom of the column while other metal ions were held completely. When these metal ions were eluated by 3 N H_2SO_4 solution molybdenum came out first. However, as a result of using concentrated H_2SO_4 solution these elements were not separated from each other. The results of this study showed that, for separation of these elements, more dilute sulphuric acid must be used. Consequently, 0.1 N H_2SO_4 solution was used in the second elution process (Table 2).

Before beginning to the elution with 0.1 N H_2SO_4 solution, the charged column was washed with 0.01 N H_2SO_4 and thus 50 % molybdenum could be separated from other metal ions (A2). During the elution with

0.1 N H_2SO_4 solution first 132 ml contain molybdenum only (Table-2) Thus 72 % molybdenum was separated completely from vanadium and other metal ions. The passing of molybdenum is lasted up to 825 ml. Thus, 97 % Mo in Şırnak asphaltite ash of which 72 % pure, 25 % mixed with vanadium could be separated by elution with 0.1 N H_2SO_4 solution. Molybdenum was not found in the following elution with 1 N H_2SO_4. But there was 2 ppm of Mo in the washing solution of 4 N H_2SO_4 The results showed that molybdenum could be recovered as by-product from ash of Şırnak asphaltite by elution with dilute sulphuric acid solutions. This data also shows that molybdenum in the leachate has different oxide forms (including anion state). Passing of vanadium begins at 165 ml and ends at 860 ml in elution with 0.1 N H_2SO_4. Because of the effluents of 1 N H_2SO_4 and 4 N H_2SO_4 contain vanadium, there must be different oxide states of vanadium except anion form.

As shown in Figure-1, if the loaded column was directly eluted by 1 N H_2SO_4 solution without any washing process with dilute sulphuric acid, only molybdenum came out from the bottom of column up to 400 ml. Thus pure solution of molybdenum can be obtained. Lasting of molyb denum peak tail up to 860 ml support that our previous studies and shows that molybdenum has another form that held strongly by cation exc-

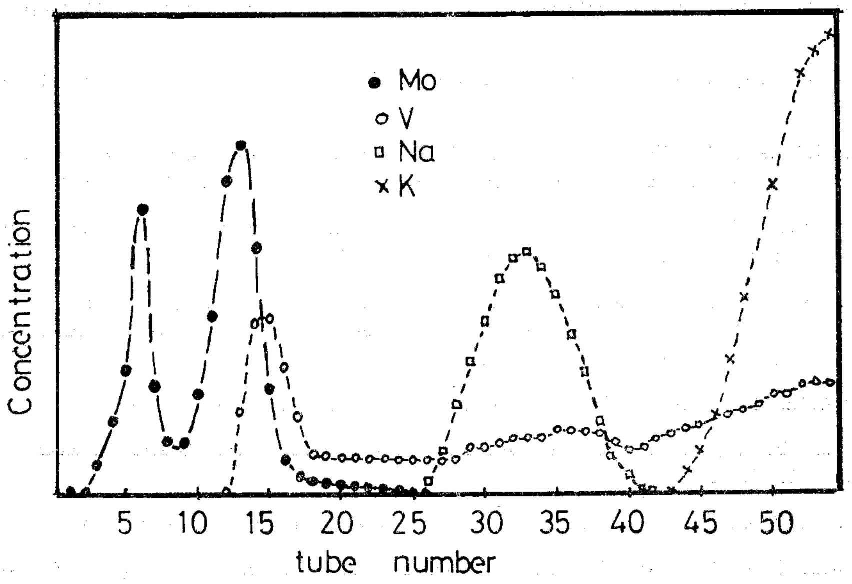

Figure 1. Elution of some metal ions with 1 n H_2SO_4 solution on Dowex 50 W=8 cation exchange resin

hange resin. Passing of vanadium begins with 430 ml and after a maximum value at 500 ml, goes on till the end. This behavior sustains the data in the second procedure. Sodium begins to pass between 860 ml and 1350 ml, potassium begins to pass at 1450 ml and goes on till the end. Nonexistence of nickel and iron ions in any tube shows that they are not eluted. Thus vanadium can be recovered as separated from these ions.

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