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Separation of Mo, Cu, Zn and Pb from Concentrates of Fluorite Ore Containing Molybdenum

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This study deals with the separation of Mo, Cu, Zn and Pb from concentrates of a flotation process of Elazig region fluorite ore containing of molybdenum. The original ore contained (%) 1.08 Mo, 0.05 Cu, 1.12 Zn, 1.20 Pb and 12 F. The ore concentrate after flotation contained (%) 19.46 Mo, 0.87 Cu, 4.54 Zn and 2.65 Pb. The fluorite itself was separated and left in the residue during flotation process. A hydrometallurgical concentration process was used for the separation of Mo, Cu, Zn and Pb. In view of the existence of sulfide, the concentrate was roasted at 600ºC and the concentrations of dissolved ions were investigated. The result was not fruitful. In the following work, the concentrates were roasted at various temperatures and durations and the samples were later treated in a autoclave at 225ºC with 15 M H_2SO_4. Under suitable set of conditions Mo, Cu and Zn were dissolved and Pb was left behind in the form of $PbSO_4$. The molybdenum in the solution was separated from copper and zinc by an extraction process by using alamine 336 (trioctylamine). $(NH_4)_2S$ was used to separate molybdenum from the organic phase. Due to the presence of the other ions such as vanadium, tantalum and niobium, the separation of molybdenum could not be achieved with H_2S, but $(NH_4)_2S$ was utilized in the process.

Key Words: Molybdenum, Fluorite, Flotation, Extraction.

INTRODUCTION

Molybdenum is a unique transition element with a fundamental importance in plants and animals. It has also many useful industrial applications. This metal is known to have a toxic property in high concentrations[1,2]. Molybdenum is of strategic importance in industry such as health and medical industries[3] and has many other uses in wireless, heat batteries, in X-Ray tubes as anti catot, *etc*. For that reason, it is important to achieve the required purity of the element in the extraction process[4].

The method of solvent extraction is commonly used in separation of elements from solutions and in the use of rarer elements in technological applications[5]. The development of methods for a selective separation of low concentrations of rare elements is still a subject of research. The homogenous liquid-liquid extraction is a currently preferred method due to reduced time, lower costs of recovery and use of lesser amount of organic solvents in the process. On the other hand, amines are used as extracting agents in the extraction of molybdenum, vanadium, tantalum and niobium[6-9]. It has been pointed out that -Nonanol- provides a good prospect in the extraction process of Mo, V, Ta and Nb[5,10]. In such extraction systems, *n*-nonylalcohol is mostly used as a phase stabilizer. In another work related to extraction of Mo(VI) in a solution of $HClO_4$, Alamine 310 and Cyanex 301 were used as extractants. The concentration of the Mo(VI) in the liquid phase was determined with thiocyanate method in a spectrophotometer. The reaction mechanism was found to be as follows[11].

$$MoO_2(SCN)_{2(aq)} + 2SCN^-_{(aq)} + 2R_3NH^+_{(aq)} \rightarrow (R_3NH)_2MoO_2(SCN)_{4(aq)}$$

$$MoO_2^{2+}{}_{(aq)} + 2RH^-_{(aq)} \rightarrow MoO_2R_{2(aq)} + 2H^+_{(aq)}$$

In the same study, a better molybdenum extraction rate was achieved in a mixture of 5 % (volume) Cyanex 301 and of 5 % (volume) Alamine 310, where SCN^- ions are absent[11,12].

In an acidic (4 M HCl) medium, in the presence of niobium, the tantalum has been extracted with a rate of 98.9-99.7 % by using dibenzo-18-crown-6. The extraction rates were also investigated under various acid concentration and temperatures conditions[13]. In the industrial technology, commonly actonal, nonanol and methyl isobutyl ketones are used as extractants for tantalum and niobium extraction and purifications process. In the literature, the use of octanol and nonanol are preferred as extractants rather than methyl isobutyl ketone due to the flammability, explosiveness and solubility of the substance in the water[5.14]. Mayorov and Mikolaev[5] were successful in extracting tantalum and niobium with a rate of 99.6 % by using octyl alcohol in a fluorite solution and in the presence of other rare elements.

In another study, after some preliminary treatments, Mo, V, U, Ti and Ni were extracted from asphaltite in kerosene system using alamine 336. In this study, Mo and V were removed from the solution at a rate of 100 % and Ni^{2+} remained in the aqueous phase. It was found that V(IV) was also extracted with V(V)[15].

In another study, Mo, V and Ni were extracted in an acidic solution by using solvents such as LIX64N, alamine 336 and aliquat 336. At a pH of 1-2 vanadium and at a pH range of 1-10 molybdenum has been extracted with a 95 % recovery rate. At pH 2 with aliquat 336, only vanadium as V(V) has been extracted, while Ni has remained in the aqueous phase[16].

This study deals with the issues related to extraction of Mo from fluorite ore containing molybdenum obtained from Elazig region. In the process, the behaviour of Ta, V and Nb that were present with molybdenum in the solution phase, have also been investigated.

EXPERIMENTAL

The original ore was firstly pulverized to 100 mesh. A sample taken was placed in an autoclave and sulfurized in ($H_2S + H_2O$) steam environment. Samples obtained from this treatment were subjected to flotation process collectively and then selectively to produce concentrates.

The concentrate samples, taken after treatment under suitable sulfurization and optimum flotation process condition, were found to contain (%) 19.46 Mo, 0.87 Cu, 4.54 Zn and 2.65 Pb. The subsequent work in this study was carried out on this sample. The analysis of Mo, Cu, Zn and Pb were conducted, by using Unicom 929 Atomic Absorption Spectrometer. In the concentrates, the presence of some limestone, silica, compounds of some rare elements (V, Nb and Ta), metal sulphides and pyrite have been determined.

In the study, Merck chemicals were used. The 1.3 L steel autoclave employed in the study was suitable to operate under 250 atmosphere pressure and temperature of 350ºC.

The separation experiments were carried out with the knowledge that the majority of the compounds in the concentrates were in the form of sulphides and oxides. Because the copper was in the form of copper sulphide; in the first step, the samples were subjected to baking process. According to the results found from this experiment, we tried to find appropriate method for this process.

RESULTS AND DISCUSSION

Concentrates from collective flotation process: The results of the flotation carried out under optimum set of conditions are given in Table-1.

Selective flotation of the collective flotation's concentrates: In the flotation process, the most suitable pH was 7.5 and in this pH; 7 kg sulfurized ore flotation concentrate was accumulated (denoted as*). The sample was later subjected to a selective flotation and the results of this work are seen in Table-2. As indicated in Table-2, the best results were obtained at a pH of 13. At this pH, the concentrate contained (%) 19.46 Mo, 2.65 Pb, 0.87 Cu and 4.54 Zn. A sample of this concentrate was subjected to a hydrometallurgical process.

As indicated in Table-2, at a pH of 13, large proportion of molybdenum and copper was floated while lead and zinc remained suppressed[17].

Separation of copper from the concentrate: Dissolve the copper and zinc and leave the rest in the solid phase, the sample was subjected to roasting process. The roasting process was carried out at 600ºC on mixtures of various proportions of pyrite and concentrates. The roasting process was conducted under various temperature and durations as defined[18]. The results are shown in Table-3.

TABLE-1
RESULTS OF THE COLLECTIVE FLOTATION OF THE SAMPLES OBTAINED UNDER OPTIMUM SULFURIZATION CONDITIONS (pH=7.5)

$CuSO_4$ (mg)	Na_2SiO_3 (mL)	Time (min)	Froth flotation (g)	Tailing (g)	Recovery (%)				Concentrate (%)				Unfloated (%)			
					Mo	Pb	Cu	Zn	Mo	Pb	Cu	Zn	Mo	Pb	Cu	Zn
5.0	0.5	1.30	29.85	70.29	100	87.0	94.0	66.0	3.61	3.48	0.15	2.46	-	0.23	0.004	0.55
15.0	1.0	2.10	19.75	79.66	95.0	80.0	84.0	78.0	5.18	4.85	0.21	4.41	0.07	0.31	0.010	0.31
20.0	1.5	2.20	19.56	79.91	91.0	66.0	55.0	67.0	5.01	4.03	0.14	3.82	0.13	0.52	0.028	0.52
20.0	1.0	2.30	19.94	79.43	96.0	67.0	76.0	69.0	5.18	4.02	0.19	3.86	0.05	0.50	0.015	0.44
20.0	0.5	2.20	22.74	78.27	89.0	73.0	72.0	65.0	4.21	3.84	0.15	3.20	0.15	0.42	0.018	0.51
25.0	1.0	1.50	24.90	74.64	96.3	92.0	95.6	89.0	4.16	4.42	0.19	4.00	0.05	0.13	0.003	0.17
30.0*	1.0	1.40	23.47	75.92	97.3	93.0	98.0	95.2	4.46	4.74	0.21	4.53	0.04	0.11	0.001	0.07
35.0	1.0	1.30	23.85	75.49	96.3	86.0	100	66.2	4.35	4.31	0.21	3.10	0.05	0.22	-	0.50

Note: 1.0 mL solution contains 5 × 10^{-3} g Na_2SiO_3.
Conditions under which the best results were obtained for Mo, Cu, Pb and Zn recovery.

TABLE-2
VALUES OBTAINED BY FLOTATION OF RESULFURIZED COLLECTIVE CONCENTRATE

Time (min)	pH	Froth flotation (g)	Tailing (g)	Recovery (%)				Concentrate (%)				Unfloated (%)			
				Mo	Pb	Cu	Zn	Mo	Pb	Cu	Zn	Mo	Pb	Cu	Zn
3.0	12.00	74.06	25.88	97.6	94.0	97.0	83.0	5.87	6.01	0.27	5.06	0.41	1.10	0.024	2.98
2.5	12.50	36.05	64.68	96.0	64.0	88.0	44.0	11.87	8.40	0.51	5.51	0.28	2.64	0.038	3.92
2.30	13.00	22.45	77.69	98.0	12.6	94.0	22.5	19.46	2.65	0.87	4.54	0.11	5.33	0.016	4.52

TABLE-3
VALUES OF MATERIAL DISSOLVED FROM ROASTED OF THE CONCENTRATE AND PYRITE MIXTURES AT 600ºC

Roasting period (h)	Pyrite quantity (g)	Concentrate quantity (g)	Passed into Solution (%)			
			Mo	Cu	Zn	Pb
5	0.2	10.16	42.60	69.90	68.00	35.10
5	0.4	10.07	40.20	39.28	65.00	28.20
5	0.6	10.05	48.12	79.00	79.40	20.02

In this study, the aim was to dissolve the copper and zinc while leaving other elements (Mo, Pb) in the solid phase. It was observed that some low quantities of molybdenum and lead were also dissolved. The follow up investigations were mainly concentrated on the separation of molybdenum, copper and zinc from lead in the solution.

Dissolving the molybdenum, copper and zinc from the concentrate: In this work, the concentrate was roasted at temperatures of 600 and 650ºC for varying durations. Later, the roasted samples were treated in an autoclave at 225ºC for 1 h with varying quantities of 15 M H_2SO_4. The samples from resulting material were treated with water and the amount of dissolved molybdenum, copper, zinc and lead was determined. The results are presented in Table-4.

As indicated in Table-4, 100 g sample after roasting at 600ºC and treatment with 5 M H_2SO_4 at 225ºC in an autoclave, the amount of Mo, Cu and Zn dissolved was found to be less than that obtained from a sample that was roasted at 650ºC and treated in an autoclave with the same amount of 15 M H_2SO_4 for the same duration (1 h). The dissolved amount of Mo, Cu and Zn are at maximum level from a 100 g sample roasted at 650ºC and followed by a treatment in an autoclave with 32.50 mL 15 M H_2SO_4 and water. The Pb remains as precipitates in the form of $PbSO_4$. When the solution topped up to a volume 500 mL, pH was found to be 1.15. The analysis showed that the solution contained 19.46 g/500 mL molybdenum, 0.87 g/500 mL copper and 4.57 g/500 mL zinc.

Separation of molybdenum from solution: The separation of molybdenum from the solution containing copper and zinc was carried out using liquid-liquid extraction process. Alamine 336 (three-*n*-octylamine) was used as extracting agent. All extraction experiments were carried out as two level extractions and under previously determined conditions[15].

In all extraction experiments, the temperature, duration and the mixing speed were kept constant. In the process 100 mL capacity glass extractor was used. The temperature was provided by a Grand W14 thermostatically controlled heater and the mixing was done, using Jamtal Kunkel RW12 Model mechanical mixer.

TABLE-4
VALUES OF DISSOLVED IONS FOLLOWING H_2SO_4 TREATED CONCENTRATES IN THE AUTOCLAVE (100 g CONCENTRATE)

Temperature (ºC)	Roasting duration (h)	H_2SO_4 volume (mL)	Passed into solution (%)				Remained in the solid phase (%)			
			Mo	Pb	Cu	Zn	Mo	Pb	Cu	Zn
600	3	20.0	19.7	40.0	10.0	52.0	80.3	60.0	90.0	48.0
600	3	30.0	25.5	30.5	26.7	86.5	74.5	69.5	73.3	13.5
600	3	40.0	8.6	36.2	17.5	72.0	91.4	63.8	82.5	28.0
600	5	30.0	22.0	38.8	30.8	88.0	78.0	61.2	69.2	12.0
600	5	40.0	12.4	40.2	19.0	74.6	87.6	59.8	71.0	25.4
650	3	20.0	82.4	5.6	80.2	78.0	17.6	94.4	19.8	22.0
650	3	30.0	84.0	4.8	81.0	80.0	16.0	95.2	19.0	20.0
650	5	15.0	51.0	-	49.0	53.6	49.0	100.0	51.0	46.4
650	5	17.5	72.0	-	77.7	55.4	28.0	100.0	22.3	44.6
650	5	20.0	90.0	-	84.5	100.0	10.0	100.0	15.5	-
650	5	25.0	93.3	-	89.0	100.0	6.7	100.0	11.0	-
650	5	30.0	99.8	-	98.8	100.0	0.2	100.0	1.2	-
650	5	32.5	100.0	-	99.4	100.0	-	100.0	0.6	-
650	5	35.0	97.7	-	99.1	100.0	2.3	100.0	0.9	-

The organic reactive chemicals used in the extraction process were prepared and used as follows; the organic phase by volume consisted of 10 % Alamine 336, 80 % Kerosene and 10 % *n*-Nonanole.

The extraction carried out under the following conditions:

Organic phase :	20 mL
Water containing phase :	30 mL
Temperature of extraction :	25ºC
Duration of extraction :	5 min
Mixing speed :	1500 rpm

The result of the experiment showed that, with alamine 336, molybdenum was largely moved to the organic phase, while cations such as copper, zinc and iron did not. The result of the experiments is seen in Table-5.

The following result was obtained under pH 1.15 with the Alamine 336 extraction carried out in the aqueous solution. As shown in Table-5, Cu, Zn and Fe do not move to organic phase but molybdenum moves with a high rate. In the process, molybdenum in the aqueous phase is in the form of molybdate (in anionic form).

TABLE-5
VALUES OBTAINED FROM ALAMINE 336
EXTRACTION EXPERIMENTS

Elements	One level Extraction		Two level Extraction		Total of material passed into organic phase (from the one and two level extractions) (%)
	Remaining in aqueous phase (%)	Passed into organic phase (%)	Remaining in aqueous phase (%)	Passed into organic phase (%)	
Mo	5.0	95.0	26.0	74.0	98.6
Cu	100.0	-	100.0	-	-
Zn	100.0	-	100.0	-	-

When the elusion is carried out in a H_2S solution, the organic phase appears to have a blue colour. When the reason for the colouration was investigated, it was found that the organic phase, in addition to molybdenum, contained Nb, Ta and V. Keeping this in mind, standard solutions of molybdenum, tantalum, niobium and vanadium were prepared by using pure substances. Experiments carried out with these standard solutions showed that, when the ions individually or in a mixture of two in an organic phase were subjected to elution with H_2S solution, no blue colouration was developed. However, if the extraction was carried out where Mo, V and Ta are present and H_2S passed through the solution, the organic phase became blue in colour. Even after a few days, these ions did not pass into aqueous phase. After the analysis of the concentrate obtained from the selective flotation gave the values of Ta, Nb and V as 0.16, 2.43 and 1.49 %, respectively.

The concentrates were obtained from the selective flotation process then roasted under previously determined optimum conditions; 100 g sample of that was treated in an autoclave with 32.5 mL of 15 M H_2SO_4 at 225ºC and with water. The dissolved amount of Mo, V, Ta and Nb as a result of the process was determined and the values obtained are presented in Table-6.

TABLE-6
VALUES OF THE IONS DISSOLVED FROM 100 g ROASTED
CONCENTRATE TREATED IN AN AUTOCLAVE WITH H_2SO_4

Temperature (ºC)	Roasting duration (h)	H_2SO_4 volume (mL)	Passed into solution (%)				Remained in the solid phase (%)			
			Mo	V	Ta	Nb	Mo	V	Ta	Nb
650	5	32.5	100	96.0	97.7	96.2	-	4.0	2.3	3.8

When the solution topped up to a volume of 500 mL, the pH reading was 1.15 and the solution contained 19.46 g/L molybdenum, 1.43 g/500 mL vanadium, 0.155 g/500 mL tantalum and 2.33 g/500 mL niobium. This solution was subjected to the extraction process carried out under previously determined conditions and the results are given in Table-7.

TABLE-7
VALUES OBTAINED FROM THE EXTRACTION CARRIED OUT WITH ALAMINE 336

Elements	One level extraction		Two level extraction		Total of material passed into organic phase (from the one and two level extractions) (%)
	Remaining in aqueous phase (%)	Passed into organic phase (%)	Remaining in aqueous phase (%)	Passed into organic phase (%)	
Mo	4.5	94.5	26.0	74.0	98.6
V	24.0	76.0	17.7	82.3	96.0
Ta	20.4	79.6	16.0	84.0	96.0
Nb	19.0	81.0	25.0	75.0	95.0

A blue colouration is developed after elution of the organic phase with H_2S solution where tantalum and molybdenum are present may indicate that partially reduced vanadium or molybdenum, or both of them forms complexes with tantalum distinctively. These complexes do not transform to sulfide compounds when treated with H_2S. This was thought to show the stable nature of the complexes. Following that, for elution, drops of $(NH_4)_2S$ solution were added to the organic phase until the development of brown coloured precipitation ends. Then, the organic phase was separated from the aqueous phase; 15 mL $(NH_4)_2S$ added to the organic phase and mixed for 45 min until the separation of the phases is complete. For the third and last time 15 mL $(NH_4)_2S$ solution was added to the organic phase and the process was repeated. The amount of Mo, V, Ta and Nb in the separated aqueous phase was determined. The results are shown in Table-8.

TABLE-8
VALUES OF Mo, V, Ta AND Nb OBTAINED FROM THE ANALYSIS OF AQUEOUS PHASE

Elements	Passed into aqueous solution at the first elution (%)	Passed into aqueous solution at the second elution (%)	Passed into aqueous solution at the third elution (%)	Total elution (%)
Mo	26.9	49.1	24.4	98.5
V	39.0	44.8	13.7	97.5
Ta	24.7	63.4	8.6	96.8
Nb	28.9	57.5	9.3	95.8

Because this process was tried for the first time here, following the elusion with $(NH_4)_2S$, the remaining organic phase was used again in the extraction process to investigate changes in recovery rates.

After the elution of the organic phase with $(NH_4)_2S$, the phase was once more washed with 0.1 M H_2SO_4 and used in the extraction. The process was repeated four times. After the first elution process, it was determined that 98.1 % of molybdenum was concentrated in the organic phase. Using the same process in the second extraction of the molybdenum the rate was seen to be 97.5 %, in the third extraction this was 97.2 % and in the fourth time the rate of molybdenum in the organic phase was determined to be 97.1 %. The changes at the level of recovery rate appear to be negligible and it seems possible that, after each elution process, the organic phase can be washed with 0.1 M H_2SO_4 solution and following elution of (Mo, Ta, Nb and V) ions, the organic phase can be used again in the extraction process.

To determine how effective the elution process is, at the first step, $(NH_4)_2CO_3$ solution and in the second step, $(NH_4)_2S$ solution was used. The resulting concentrations are shown in Table-9.

TABLE-9
RESULT OF THE ELUSION EXPERIMENTS CARRIED OUT USING $(NH_4)_2CO_3$ AND $(NH_4)_2S$

Elements	Result of elusion with $(NH_4)_2CO_3$ (%)		Result of elusion with $(NH_4)_2S$ (%)	Total (%)
	Precipitate	Solution	Solution	
Mo	49.4	28.0	19.4	96.8
V	67.7	13.3	17.0	98.0
Ta	48.5	33.6	12.6	94.7
Nb	73.6	21.8	2.0	97.4

Table-9 indicates that after the elution with $(NH_4)_2CO_3$ (25 g/L) solution, while part of Mo, V, Ta and Nb precipitates the other part remains in the solution. This process continued until the precipitate disappeared. To achieve that, 50 mL of $(NH_4)_2CO_3$ solution was used. In the second elution process carried out by using $(NH_4)_2S$, it was observed that some part of the ions in the organic phase moved to $(NH_4)_2S$ solution.

Following the extraction of molybdenum, tantalum, niobium and vanadium from the solution, the remaining copper and zinc containing solution, after autoclave process was used to remove molybdenum from the solid phase into solution. As a result of this process, copper and zinc concentration increased to a high level in the aqueous solution. This high concentration of copper enabled the element to electrolytically be removed. As a result of the electrolyses, zinc remained in the solution. The electrolyses were conducted at 45-50ºC with 2.80 V current, using Pt electrodes.

Conclusion

In present study, the sample used was fluorite ore containing molybdenum involving some Ta, Nb and V. Although the primary target of the study is the extraction of molybdenum, following the identification of the existence of the elements Ta, Nb and V the behaviour of these elements were also investigated. For this firstly, the molybdenum was dissolved from the concentrate into a solution phase followed by the removal of molybdenum from the solution phase by using suitable methods. To get molybdenum into the solution it was found that it is necessary to bake the concentrate for 5 h at temperature of 650ºC. The cooled sample was later treated with H_2SO_4 in and autoclave at 225ºC for 1 h. For a 100 g sample if 32.50 mL 0.15 M H_2SO_4 was used and found that all of the Mo and 96.0 % of V, 97.7 % of Ta and 96.2 % of Nb passed into the liquid phase. Since the pH of the solution obtained in this way was 1.15, the solution at this pH was used in the extraction with alamine 336. The molybdenum was removed by moving it to the organic phase. In the process, tantalum, niobium and vanadium were also passed to organic phase with molybdenum. When tantalum and vanadium were present with molybdenum, it was found that it was better to use $(NH_4)_2CO_3$ and then $(NH_4)_2S$ solutions in the elution process.

REFERENCES

1. J. Carlos de Andrade, C.J. Cuelbas and S.P. Eiras, *Talanta*, **47**, 719 (1998).
2. G. Bagur, M. Sanchez-Vinas and D. Gasquez, *Anal. Chim. Acta*, **309**, 157 (1995).
3. J.C. Bailar, H.J. Emeleus Jr., R. Nyhlom and A.F. Trotman-Dichenson, Comprehensive Inorganic Chemistry, Pergaman Press Ltd., USA, Vol. 3 (1973).
4. K. Saberyan, M.G. Maragheh, P. Ashtari and S.K. Alamdari, *Miner. Eng.*, **16**, 391 (2003).
5. V.G. Mayorov and A.I. Nikolaev, *Hydrometallurgy*, **66**, 77 (2002).
6. C.K. Vun, *Hydrometallurgy*, **12**, 285 (1984).
7. R.A. De Carvalho Cruedes and M.N.M. Sampaio, *Hydrometallurgy*, **26**, 137 (1991).
8. S.I. Stepanov, Chemistry of Solvent Extraction of Rare Metals by Quaternary Ammonium Salts, ISEC'96, Melbourne, 19-23 March, Vol. 1, p. 553 (1996) .
9. N.I. Gerhardt, A.A. Plant, V.A. Petrova and R.K. Tagirov, *Hydrometallurgy*, **60**, 1 (2001).
10. J. He, Z. Zhang and Z. Xu, Hydrometallurgical Extraction of Tantalum an Niobium in China Tantalum-Niobium International Study Center, Bulletin N93, pp. 1-6 (1998).
11. P. Behera and V. Chakravortly, *Indian J. Chem.*, **32A**, 823 (1993).
12. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, (ELBS) Longsman, London), edn. 3, p. 903 (1971).
13. Y.K. Agrawal, *Talanta*, **58**, 875 (2002).
14. A.G. Babkin, V.G. Mayorov and A.I. Nikolaev, *Science*, 223 (1988).
15. T. Cosar and R. Ziyadanogullari, *Turk J. Chem.*, **22**, 379 (1998).
16. H. Atamer, D. Derman and G. Özdil, Recovery of Mo, V, Ni and U from Southeast Anatolian Asphaltites, MTAE Technology Department, Ankara, Turkey (1981).
17. A. Akgün, Y. Teoin and R. Ziyadanogullari, *J. Miner. Mater. Charact.*, **5**, 103 (2006).
18. R. Ziyadanogullari, *Sep. Sci. Technol.*, **27**, 389 (1992).

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