

Possibilities of utilizing organic-poor metalliferous black shales (argillite)

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Abstract. *The present paper is focused on the possibilities of recovering rare metals molybdenum (Mo), uranium (U) and vanadium (V) from organic-poor metalliferous black shales on an example of Estonian argillite. For this purpose two flowsheets for processing argillite have been proposed: one is based on the separation of organic matter (OM) together with allied rare metals, and the other on the combustion of argillite in the presence of salts without prior separation of OM. For the recovery of rare metals from leaching solutions the anion exchange method was used. The influence of different parameters, such as metals concentrations and pH of leaching solutions, on the sorption process was studied.*

Keywords: *argillite, molybdenum, uranium, vanadium, anion exchange, leaching solution.*

1. Introduction

In North Estonia Ordovician graptolitic argillites extend along the shore from west to east, forming a dark-brown layer of 1–7 m decreasing eastward. Argillites overlie shelly phosphorites and underlie glauconitic sandstones. The hypothetical geological reserves of argillite in Rakvere phosphorite field are estimated at 3×10^9 t, while those of Toolse amount to 141×10^6 t [1, 2]. Argillites are characterised by an average organic matter (OM) content of 12–16% and a relatively high content of rare metals such as molybdenum (Mo), uranium (U) and vanadium (V). A comparative study of the contents of Mo, U and V in argillites from different deposits was carried out by Lippmaa et al. [3]. Due to their low organic content, argillites are not suitable for direct use as solid fuel or for production of oil. In addition, in the process of phosphorite mining they may represent a potential environmental hazard. During the open-cast mining of phosphorite at Maardu quarry, North Estonia argillite was disposed of in dumps. The unused argillite caused the leaching of heavy metals into the natural water. In the dumps the oxidation and decomposition of pyrite took place, causing their self-ignition, which in turn promoted the leaching process. For that reason the Institute of Chemistry of Estonian Academy of Sciences, during the period 1960–1980, carried out complex research on the

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possibilities of utilizing argillite remained by phosphorite mining. A process of multistage leaching using fluidized-bed ashing and subsequent treatment of ash with concentrated sulphuric acid was developed by Maremäe et al. [4]. The percolation leaching method was investigated in terms of the possibilities of argillite processing for recovery of metals and reducing processing costs [5]. However, the disadvantages of the sulphuric acid leaching process are a high consumption of concentrated sulphuric acid and a large amount of acidic wastes generated. The method of water leaching of mildly preroasted argillite using chemical additives was suggested earlier, but there was a problem with organic matter utilization [3]. The present study aims to find other possibilities of utilizing low-grade black shales argillites. One option would be to separate organic matter and rare metals allied with it, thus significantly decreasing the amount of material to be processed, as well as reducing the costs of further processing [6]. An alternative would be the leaching of metals from ground argillite after its combustion by salt roasting, which enables using weaker reagents in the leaching process and thereby reducing the costs. The possibilities of applying the ion exchange method for the selective recovery of Mo, U and V by using model solutions were studied. On the basis of the data obtained, a scheme for the recovery of metals is presented.

2. Experimental setup

In this work, the results of neutron activation analysis of metal contents in argillite from the deposits of Maardu in North Estonia and Toolse in Northeast Estonia obtained earlier by Pelekis et al. [7, 8] were used. The samples under study were analysed for uranium content by using X-ray fluorescence spectroscopy, while atomic absorption spectroscopy was applied to determine the contents of molybdenum and vanadium. In the ion exchange process, titration was used for determination of the contents of U and V, and colorimetry was employed to determine the Mo content. The results of metal content analysis show molybdenum, uranium and vanadium to be the most important metals in argillite, due to their relatively high concentrations, as well as good commercial potential, and significant environmental impact by phosphorite mining. Therefore the recovery of these metals from argillite is the primary focus of the current study.

3. Correlations between rare metal contents in argillites

The flowsheets for splitting argillites into different fractions with the aim to obtain organic matter and pyrite concentrates have been presented previously [9, 10]. On the basis of the distribution of rare metals in the different fractions of argillites, the coefficients of linear correlation between the contents of

metals and minerals were calculated and the correlation matrixes for Maardu and Toolse argillites were presented [11]. The data show a strong positive correlation to exist between the contents of Mo and U and that of OM, the respective coefficients being 0.9 and 0.8. At the same time, the content of V does not have such a good relationship with that of OM (the correlation coefficient for Toolse argillite is 0.7), while the correlation between the contents of V and illite is positive (the correlation coefficient is 0.51). The contents of all three rare metals are negatively correlated with that of pyrite, the respective correlation coefficients being -0.46 , -0.6 and -0.59 , and of quartz, the correlation coefficients are -0.41 , -0.32 and -0.41 , respectively. It must be pointed out that Toolse and Maardu argillites differ significantly in mineral composition [12]. The content of pyrite in Toolse argillite is higher, and pyrite and quartz are mainly present as macrocrystals and concretions. In Maardu argillite fine-grained pyrite is strongly impregnated with quartz and clay minerals. Hence, in the beneficiation process, pyrite may be separated from Toolse argillite at relatively high recovery (about 80%), while its recovery from Maardu argillite is not as high. However, unlike Maardu argillite, OM in Toolse argillite is more strongly associated with the mineral part, which requires a more thorough fine grinding for its complete disaggregation. These specificities must be taken into account during the recovery of OM-associated rare metals from argillites. The rare metal contents in Toolse argillite are many times these in Maardu argillite.

The association of rare metals with organic matter in black shales has been demonstrated by several authors. The strong correlation of the contents of Mo (0.79) and V (0.71) with that of organic carbon in the Middle Cambrian alumina shale in Sweden has been reported by Armands [13]. Leventhal and Hosterman [14] show a good correlation to exist between the contents of organic carbon and uranium, as well as between those of organic carbon and molybdenum in U.S. Devonian black shales.

On the basis of the available data about the association of rare metals with OM, Palvadre and Ahelik [6] developed a flowsheet for argillite processing that involved the separation of OM.

4. The recovery of rare metals into different fractions by the separation of organic matter from argillite

Processes for beneficiation of Maardu and Toolse argillites relative to organic matter have been described earlier [6]. In this paper, a detailed flowsheet, which involves combined hydrocycloning and flotation, for the process of separation of OM from Toolse argillite, with yields of fractions, is shown in Figure 1. The results of recovery of rare metals into different fractions of OM are presented in Table 1. The table reveals that in the hydrocycloning processes, an approximately 70% recovery of rare metals into light fractions at the 55%

product yield from the feed material was obtained. Light fractions of both hydrocycloning processes were directed to the flotation process. As seen from Table 1, in the beneficiation process of Toolse argillite the recovery of rare metals into the froth products of flotation F-1-1 and F-2-2 was 72–75% at the product yield of approximately 50% from the feed material, while the recovery of OM in this case was 87.9%. In the further cleaning flotation, the concentrations of rare metals increased, but their recovery into froth products and the product yield from the feed material decreased. For example, the total recovery of rare metals into cleaner flotation concentrates F-1-2 and F-2-2 was approximately 60–65% at the 40% product yield from the feed material, the OM recovery being 80%. The rare metals recovery into total final concentrates C-1 and F-2-2 was approximately 30% at the 15.5% product yield. Thus the process of flotation must be optimized for a compromise between metals recovery and product yield. The recovery of metals can be improved by directing the tailings back to the flotation process. The mineral tails from both flotation processes and the products of pyrite flotation were removed as wastes. The total yield of wastes from the processing of Toolse argillite was approximately 40% and the recovery of rare metals into wastes was 22–25% [6].

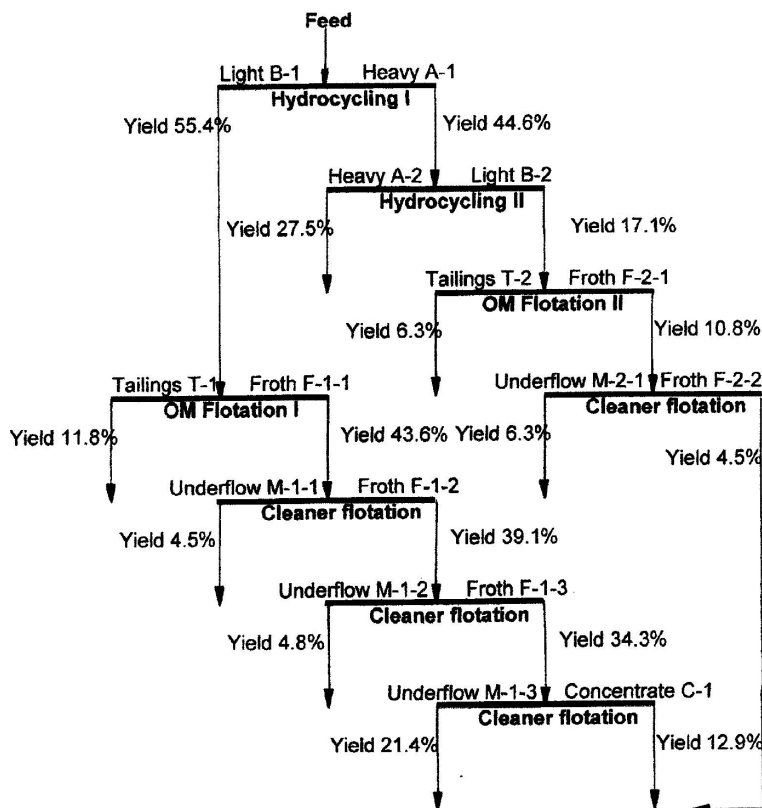


Fig. 1. A detailed flowsheet for the process of separation of organic matter from Toolse argillite, with yields of fractions.

Table 1. The recovery of molybdenum, uranium and vanadium into fractions by OM separation.

Fraction	Yield, %	OM		Mo		U		V	
		Assay, %	Recovery, %	Assay, g/t	Recovery, %	Assay, g/t	Recovery, %	Assay, g/t	Recovery, %
Feed	100.0	17.3	100.0	453	100.0	162	100.0	1105	100.0
Hydrocycling I									
Light B-1	55.4	24.1	76.9	545	66.7	212	72.5	1436	72.0
Heavy A-1	44.6	9.0	23.1	339	33.3	100	27.5	693	28.0
Hydrocycling II									
Light B-2	7.1	16.4	16.2	600	22.6	179	18.9	1253	19.4
Heavy A-2	27.5	4.4	6.9	176	10.7	51	8.6	345	8.6
Flotation I									
Froth F-1-1	43.6	29.5	74.1	622	59.9	232	62.4	1510	59.6
Tailings T-1	11.8	4.2	2.8	261	6.8	193	10.1	1162	12.4
Cleaner flotation									
Froth F-1-2	39.1	32.2	72.6	664	57.3	240	58.0	1540	54.5
Underflow M-1-1	4.5	5.9	1.5	264	2.6	166	4.4	1246	5.1
Froth F-1-3	34.3	36.0	71.2	709	53.7	253	53.5	1561	48.5
Underflow M-1-2	4.8	5.2	1.4	341	3.6	153	4.5	1381	6.0
Concentrate C-1	12.9	61.5	45.7	1008	28.7	325	25.8	1790	20.9
Underflow M-1-3	21.4	20.7	25.5	527	25.0	210	27.7	1423	27.6
Flotation II									
Froth F-2-1	10.8	22.1	13.8	607	14.5	200	13.3	1289	12.6
Tailings T-2	6.3	6.6	2.4	587	8.1	145	5.6	1192	6.8
Cleaner flotation									
Froth F-2-2	4.5	36.6	9.5	731	7.3	229	6.3	1342	5.5
Underflow M-2-1	6.3	11.8	4.3	519	7.2	180	7.0	1251	7.1

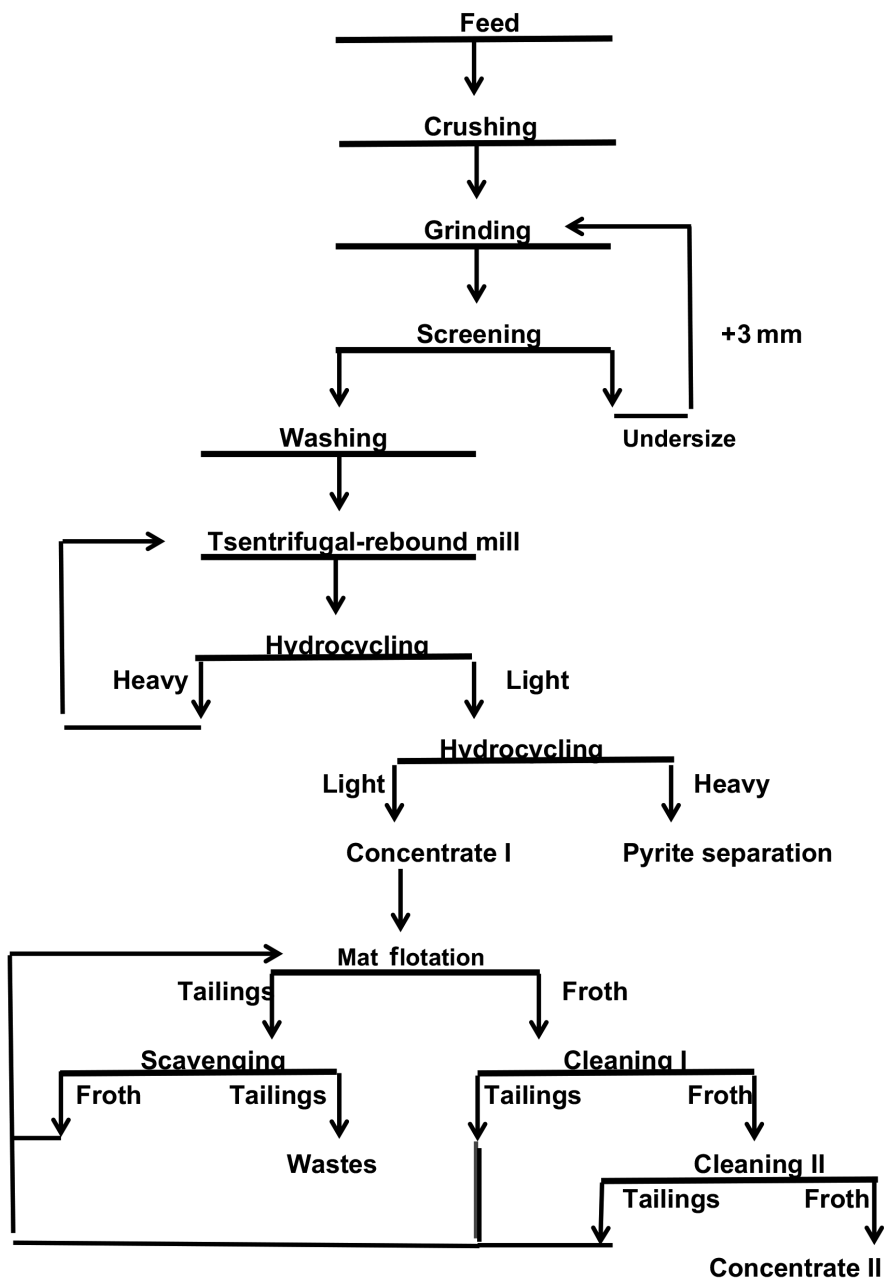


Fig. 2. A basic flowsheet for the process of separation of organic matter from argillite.

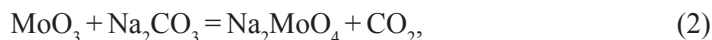
The results obtained show that the beneficiation process can afford a product with an enhanced content of rare metals at their recovery of 70–75%. The amount of material for further treatment was significantly decreased, to 20–30% of the feed material. A basic flowsheet for the process of separation of OM from argillite is shown in Figure 2. However, possibilities of using beneficiation in argillite processing, particularly with regard to complete metals recovery, had to be additionally investigated and economic analysis of the whole process had to be performed. Therefore, the further processing of argillite was carried out without prior separation of OM.

5. Combustion of argillite with salt roasting

As an alternative to organic matter separation during argillite processing, further its combustion with salt roasting prior to leaching was used. The ground argillite of –6+0 mm was mixed with 20 wt% sodium chloride or sodium carbonate and roasted under oxidizing conditions in the fluidized bed at 800–850 °C [15]. An oxidizing roast converts the oxides of vanadium, molybdenum and uranium via the addition of sodium chloride or sodium carbonate to a soluble form as follows:



By using a carbonate, the conversion can be expressed as follows:



Temperature control is critical because the recovery of metals into a leaching solution decreases when the combustion temperature exceeds 850 °C [16]. It should be noted that NaCl and Na₂CO₃ may be used in combination in the roasting process, but their additional amounts need optimization.

The yield of the roasted residue after combustion of OM was 80–85% and the contents of rare metals were increased. The average contents of rare metals in the combustion residue were the following: Mo 566 g/t, U 202 g/t and V 1380 g/t.

The roasted residue was further processed by the acid and alkaline leaching of the soluble forms of rare metals. In the former case, a 20% sulfuric acid solution and in the latter case, a 20% sodium carbonate solution was used. The leaching was carried out by agitation and sedimentation-filtration under the following conditions: solid input-liquid ratio 1:3, temperature 100 °C for 30 min. The recovery of metals in both cases was approximately 70–80%. The acid leaching method takes advantage of the increased recovery of metals, though the alkaline (carbonate) leaching is inherently more selective than the acid one, while the majority of ions of other metals, such as iron, are insoluble

in this case. By using sodium carbonate for salt roasting, it is possible to carry out the water leaching of the residue. The possibility of utilizing the recycling of residual salts for the roasting process needs to be studied.

6. The recovery of rare metals from salt-roast leaching solutions

Rare metals can be recovered from leaching solutions by using a variety of methods, including chemical precipitation and ion exchange. As rare metals molybdenum, uranium and vanadium were present in leaching solutions in low concentrations and their selective recovery was needed, the ion exchange method in column mode was applied. This enabled a high enrichment of metals in the eluent to be achieved.

As is known, the type of molybdenum ions in a leachate depends on the concentration of hydrogen ions [17]. In the pH range 1–6 molybdenum species exist as polyanions, at pH lower than 1 molybdenyl species MoO_2^{2+} and at pH above 7 molybdate ions MoO_4^{2-} predominate. Vanadium exists in a leachate of low pH, < 1 , as vanadyl species VO_2^+ , in the pH range 2–10 as polyanions and at pH above 10 mostly as metavanadate anions VO_3^- . Uranium is present in sulphuric acid solutions as an anionic sulfate complex $[\text{UO}_2(\text{SO}_4)_3]^{4-}$ and in carbonate solutions as a carbonate complex $\text{UO}_2(\text{CO}_3)_3^{4-}$. In a sodium hydroxide solution uranium exists in the form of an insoluble diuranate $\text{Na}_2\text{U}_2\text{O}_7$.

In the recovery and separation of U and V the use of anion exchangers takes advantage of the following factors: 1) the ionic state of metals in leaching solutions; 2) high adsorption capability; 3) high concentration of cationic iron species. Model solutions were used to study the possibilities of recovering and separating Mo, U and V from anion-exchange resins, considering the large excess of sulfate ions and the presence of other ions such as ferric cations. A strongly basic anion-exchange resin AB-17 with a polystyrene matrix and a functional group R_4N^+ was used in the OH^- form. The adsorption experiments were carried out on ion-exchange columns of 80 or 165 cm in height and 2–3 cm in diameter, with an average resin volume of 4.4 ml. The solution was fed in at the top of the column at a rate of $10 \text{ cm}^3/\text{min}$. The concentrations of metals in the effluent were continuously determined during sorption and elution.

According to literature, molybdenum and uranium form anionic complexes in both strong and weak acid solutions, which have a high selectivity in terms of anion-exchange resins [18]. In contrast, the adsorption of vanadium on the anion-exchange resin is possible only from a very weak acid solution, the maximum loading of the resin occurring at pH 6–8. Therefore, at first, the exchange adsorption of V from the acid leachate was investigated. Laboratory tests were carried out using an orthogonal main-effect plan (Table 2) [19–21]. The effects of different parameters on the ion exchange process of vanadium were determined using the following formula:

Table 2. Orthogonal main-effect plan to evaluate the effects of parameters on the vanadium sorption process

	x_0	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	y_v	y_v^2
Basic level (x_1^0)		200	3.5	0.5						
Unit of variance (1_i)		150	2.5	0.4						
Lower level (-)		50	1.0	0.1						
Upper level (+)		350	6.0	0.9						
Test 1	+	-	-	-	+	+	+	-	1.0	0.9
2	+	+	-	-	-	-	+	+	9.4	88.9
3	+	-	+	-	-	+	-	+	52.2	2723.8
4	+	+	+	-	+	-	-	-	47.1	222.2
5	+	-	-	+	+	-	-	+	0.6	0.3
6	+	+	-	+	-	+	-	-	1.7	2.7
7	+	-	+	+	-	-	+	-	35.5	1260.3
8	+	+	+	+	+	+	+	+	52.5	2557.5
$\sum x_{ij}y_j$	200.0	21.5	174.7	-19.5	2.4	14.7	-3.2	29.5		
Effect ($2N\sum x_{ij}y_j$)	4998.0	5.4	43.7	-4.9	0.6	3.7	-0.8	7.4		
$Q = 1/N(\sum x_{ij}y_j)^2$		57.8	3815.9	47.4	0.7	26.9	1.3	108.5		9056.4

Note: x_1 – concentration of vanadium (50–350 mg/l); x_2 – pH value (1.0–6.0); x_3 – concentration of sulphate ions (0.1–0.9 M); y_v – sorption capacity of resin towards vanadium, mg/g.

$$x_{i \text{ main-effect}} = 2/N \sum x_{ij} y_j, \quad (4)$$

where x_i is the concentration of metal; y_j is the sorption capacity of resin (complete) towards metal, mg/g air dry resin, N is a test number; $x_{ij} y_j$ is the interaction between x_{ij} and y_j . The experimental results are presented in Table 2.

The error of variables may be evaluated, assuming that interactions between the factors are negligible:

$$s^2 = \frac{0.7 + 26.9 + 1.3 + 108.4}{4 \text{ (degrees of freedom)}} = 34.4. \quad (5)$$

where s^2 is error variance (dispersion).

$$Q = s^2 F = 34.4 \times 7.71 = 265.2, \quad (6)$$

where Q is total variability (e.g. failure to reproduce treatment combinations exactly) and F is F -criterion, whose values depending on the degree of freedom for a 5% risk can be obtained from Table 2 [19, 22]. Effects $Q_i > Q$ are significant.

From Table 2 it can be seen that the pH factor has the most significant effect on the sorption capacity of the anion exchanger:

$$Q_2 = 3815.89 > 265.2, \quad (7)$$

where Q_2 is the variability of the sorption capacity of resin y_j due to the change in x_i . The sorption capacity of the resin increases by 43.7 mg/g with pH increasing from -1 to $+6$, while values of other factors remain on basic level.

The increase of the concentration of V increases the sorption capacity of the resin and the increase of the content of sulphate ions decreases it, but these effects are insignificant in a statistical sense.

Statistically insignificant are effects:

$$\text{for factor } x_1: \quad Q_1 = 57.8 < 265.2, \quad (8)$$

$$\text{for factor } x_3: \quad Q_3 = 47.4 < 265.2. \quad (9)$$

As seen from Table 2, the sorption capacity of the anion exchanger with respect to vanadium at a minimum pH of the leaching solution is very low, approximately 1 mg/g (tests 1, 5, 6).

The breakthrough curves for the sorption of V at different pH values of the leaching solution are shown in Figure 3 and elution profiles for V sorption with different stripping solutions are depicted in Figure 4.

Figure 3 shows the sorption of V to be highly dependent on the solution pH. The adsorbed vanadium was completely eluted with both eluents (Fig. 4) and the best strip gave a satisfactory concentration factor, about 10.

By the sorption of vanadium from the acid leaching solution one must take into account its high content of Fe^{2+} and Fe^{3+} ions. The sulphate complex of

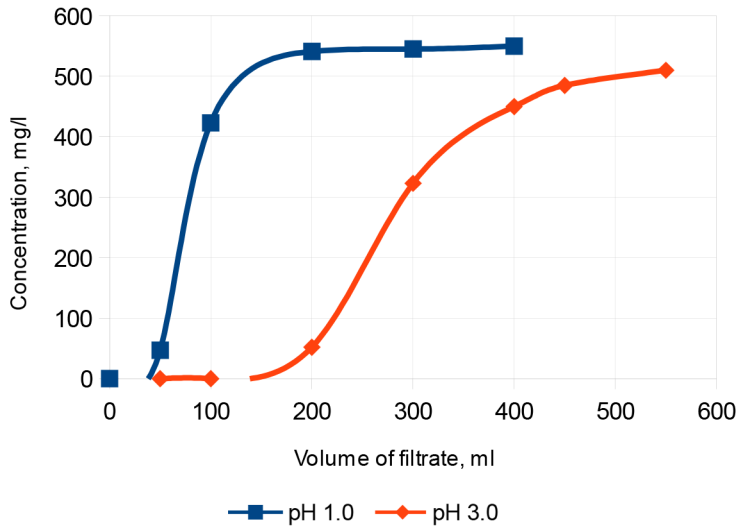


Fig. 3. Breakthrough curves for the sorption of vanadium by anion exchanger AB-17 at different pH values of the leaching solution.

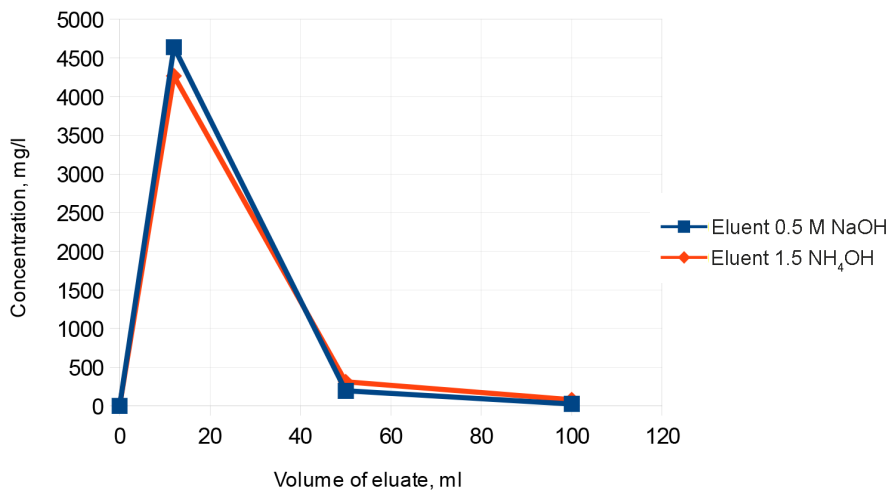


Fig. 4. Elution profiles of vanadium from anion exchanger AB-17.

iron(III), $[\text{Fe}(\text{SO}_4)_2]^-$, may be adsorbed on the anion exchanger together with vanadium anions, which may significantly influence the adsorptivity of V. To avoid the precipitation of iron hydroxide, the effect of iron ions at pH 1.5 was examined. The results are presented in Table 3.

Table 3. Determination of the effect of iron(III) ions on the sorption of vanadium

	x_0	x_1	x_2	x_1x_2	y_v	y_v^2	y_{Fe}	y_{Fe}^2
Basic level (x_0^0)		200	7.0					
Unit of variance (1_j)		150	5.6					
Lower level (-)		50	1.4					
Upper level (+)		350	12.6					
Test 1	+	-	-	+	0.7	0.5	5.6	31.4
2	+	+	-	-	21.0	441.0	11.0	121.0
3	+	-	+	-	0.8	0.7	24.0	576.0
4	+	+	+	+	1.1	1.2	21.0	441.0
$\sum x_{ij}y_{vj}$	23.6	20.6	-19.8	-20.1				
Effect ($2/N\sum x_{ij}y_{vj}$)		10.3	-9.9	-10.1				
$Q_i = 1/N(\sum x_{ij}y_j)^2$	138.8	106.0	98.0	101.2		442.6		
$\sum x_{ij}y_{Fej}$	61.6	2.5	2.8	-8.3				
Effect ($2/N\sum x_{ij}y_{Fej}$)		1.3	1.4	-4.2				

Note: x_1 – concentration of vanadium, mg/l; x_2 – concentration of iron, g/l; y_v – sorption capacity of resin towards vanadium, mg/g; y_{Fe} – sorption capacity of resin towards iron, g/g.

Table 3 reveals that the sorption capacity of the resin towards vanadium depends strongly on the concentration of iron (effect is -9.9 mg/g) and that its sorption at a high concentration of iron ions is negligible, approximately 1.0 mg/g (tests 3, 4). Tests 3 and 4 also give evidence of a marked sorption of iron on the anion exchanger. The presence of iron(II) ions causes vanadium to appear in its tetravalent state, VO^{2-} , which exhibits no adsorptivity on the anion exchanger.

Based on the results presented in Tables 2 and 3, it can be concluded that at low pH and in the presence of iron in high concentrations, the sorption of vanadium from acid solutions on the anion exchanger is insignificant.

Thereafter, the sorption of uranium and molybdenum from acid solutions on the anion exchanger was first investigated in a wide range of pH values, 1.0 – 4.0 . The effects of various parameters, namely the concentrations of molybdenum (x_1) and uranium (x_2) as well as solution pH (x_3), were evaluated. The results obtained on the basis of the factorial main-effect plan presented in Table 4 show that the effects of uranium concentration (x_2) and pH value (x_3) on the sorption of U are significant and relatively close, -49.6 mg/g and 48.5 mg/g, respectively. The concentration of Mo has a considerably higher influence on the sorption of U, effect $x_1 = -69.6$ mg/g.

The effects of concentrations x_1 and x_2 on the sorption of molybdenum are significant, 74.2 mg/g and -64.7 mg/g, respectively, but the effect of pH value (x_3) is essentially higher, 125.5 mg/g.

The results of tests showed the adsorptivity of Mo and U to be highly dependent on the solution pH value. Considering also the fact that the pH of acidic leaching solutions was low, the subsequent studies were focused on the metals adsorptivity at lower pH values, in the range of 1.0 – 2.0 (factor x_3). The values of the levels for the factors of Mo (x_1) and U (x_2) concentrations were low, 100 mg/l⁻ (minus), and high, 500 mg/l (plus), respectively (Table 5).

In assessing the error variance, it was assumed that interactions between the factors were close to zero. Based on 4 degrees of freedom, the error variance (s^2) with respect to molybdenum sorption is:

$$s^2 = (163.8 + 0.08 + 66.1 + 2.2)/4 = 58.0, \quad (10)$$

$$Q_{Mo} = s^2 F = 58.0 \times 7.71 = 447.2, \quad (11)$$

where F-criterion is 7.71 [19, 22].

The error variance with respect to uranium sorption is:

$$s^2 = (1851.4 + 313.8 + 53.6 + 475.8)/4 = 673.7, \quad (12)$$

$$Q_U = s^2 F = 673.2 \times 7.71 = 5193.8. \quad (13)$$

The results presented in Table 5 give evidence of that the concentration factor has the highest effect on the ion exchange sorption of molybdenum:

$$Q_{1Mo} = 9166.6 > 447.2. \quad (14)$$

Table 4. Estimation of the effects of various parameters on the adsorptivity of uranium and molybdenum in the pH range of 1.0–4.0 of the leaching solution based on the factorial main-effect plan

	x_0	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	Y_{M_0}	Y_U
Basic level (x_i^0)		300	100	2.5						
Unit of variance (1)		250	90	1.5						
Lower level (-)		50	10	1.0						
Upper level (+)		550	190	4.0						
Test 1	+	-	-	-	+	+	+	-	164.3	10.7
2	+	+	-	-	-	-	+	+	177.1	1.5
3	+	-	+	-	-	+	-	+	137.1	40.6
4	+	+	+	-	+	-	-	-	146.2	20.6
5	+	-	-	+	+	-	-	+	297.9	53.5
6	+	+	-	+	-	+	-	-	367.2	5.6
7	+	-	+	+	-	-	+	-	127.1	204.9
8	+	+	+	+	+	+	+	+	332.7	3.5
$\sum x_{ij}y_{M_{0ij}}$	1749.6	296.8	-258.9	500.2	132.6	253.0	-147.2	140.0		
Effect ($2/N\sum x_{ij}y_{M_{0ij}}$)		74.2	-64.7	125.5	33.2	63.2	-36.8	35.0		
$Q_i = 1/N(\sum x_{ij}y_{M_{0ij}})^2$		11011.3	8378.7	31275.0	2197.8	8001.1	2708.5	2450.0		
$\sum x_{ij}y_{Uij}$	340.9	-278.5	198.3	194.1	-164.3	-220.1	100.3	142.7		
Effect ($2/N\sum x_{ij}y_{Uij}$)		-69.6	49.6	48.5	41.1	-55.0	25.1	35.7		
$Q_i = 1/N(\sum x_{ij}y_{Uij})^2$		9695.3	4915.4	4709.4	3374.3	6055.5	1257.5	2545.4		

Table 5. Estimation of the effect of various parameters on the adsorptivity of uranium and molybdenum in the pH range of 1.0–2.0

	x_0	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	Y_{Mo}	Y_{Mo}^2	Y_U	Y_U^2
Basic level (x_1^0)		300	300	1.5								
Unit of variance (1)		200	200	0.5								
Lower level (-)		100	100	1.0								
Upper level (+)		500	500	2.0								
Test 1	+	-	-	-	+	+	+	-	106.6	11363.6	20.9	436.2
2	+	+	-	-	-	-	+	+	166.5	27722.3	13.4	179.6
3	+	-	+	-	-	+	-	+	80.7	7020.9	91.3	8335.7
4	+	+	+	-	+	-	-	-	156.6	24523.6	53.8	2894.4
5	+	-	-	+	+	-	-	+	90.0	8100.0	33.1	1095.6
6	+	+	-	+	-	+	-	-	147.4	21726.8	31.4	985.9
7	+	-	+	+	-	-	+	-	73.5	5394.9	124.0	15376.0
8	+	+	+	+	+	+	+	+	151.1	22831.2	30.6	936.4
$\sum x_{ij}Y_{Moij}$	972.4	270.8	-48.6	-48.4	36.2	-0.8	23.0	4.2				
Effect ($2/N\sum x_{ij}Y_{Moij}$)		67.7	-12.2	-12.1	9.1	-0.2	5.8	1.1				
$b_i = 1/N\sum x_{ij}Y_{Moij}$		0.17	-0.03	-12.1	$1.1 \cdot 10^{-4}$	-0.001	0.028					
$Q_i = 1/N(\sum x_{ij}Y_{Moij})^2$	118195	9166.7	295.2	292.8	163.8	0.08	66.1	2.2		128680		
$\sum x_{ij}Y_{Uij}$	398.5	-140.1	200.9	39.7	-121.7	-50.1	-20.7	-61.7				
Effect ($2/N\sum x_{ij}Y_{Uij}$)		-35.0	50.2	9.9	-30.4	-12.5	-5.2	-15.4				
$b_i = 1/N\sum x_{ij}Y_{Uij}$		-0.09	0.13	9.9	$-3.8 \cdot 10^{-4}$	-0.063	-0.026					
$Q_i = 1/N(\sum x_{ij}Y_{Uij})^2$	19850	2453.5	5045.1	197.0	1851.4	313.8	53.6	475.8				30240

The increase in molybdenum concentration from 100 to 500 mg/l increases the sorption capacity of the resin towards Mo to 67.7 mg/g. The increase of uranium concentration in the same range increases the sorption capacity of the resin towards U to 50.2 mg/g. The resin's sorption capacity with respect to Mo is nearly independent of the concentration of uranium (effect -12.2 mg/g):

$$Q_{3U} = 295.2 < Q_{Mo} \quad (15)$$

At the same time, the resin's sorption capacity towards U depends on the concentration of molybdenum (effect -35.0 mg/g). The effect of the pH factor on the sorption of both metals is insignificant. Tests 2, 4, 6 and 8 demonstrate that the resin's sorption capacity with respect to Mo is higher, approximately 150 mg/g, at its high concentration in the solution (+). The resin exhibits a maximum sorption capacity towards uranium, approximately 120 mg/g, in test 7 where the U concentration is high (+) and that of Mo low (-). Due to the high values of Mo and U concentration effects, their interactions x_1x_2 are also high, respectively 36.2 and -30.4 mg/g.

In the studied range of parameters the sorption capacity of the anion exchanger towards molybdenum can be calculated on the basis of the data presented in Table 5 by using the following formula:

$$y_{Mo} = 121.5 + 0.17(x_1-300) - 0.030(x_2-300) - 12.1(x_3-1.5) + 1.1 \times 10^{-4}(x_1-300)(x_2-300) - 0.001(x_1-300)(x_3-1.5) + 0.028(x_2-300)(x_3-1.5) \quad (16)$$

Analogously to the above formula, the sorption capacity of the anion exchanger with respect to uranium can be calculated.

Figures 5, 6 and 7 depict the breakthrough curves for the sorption of Mo and U at their different concentrations in feed solutions. From the figures it can be seen that regardless of these concentrations, the breakthrough for both metals began at the same time.

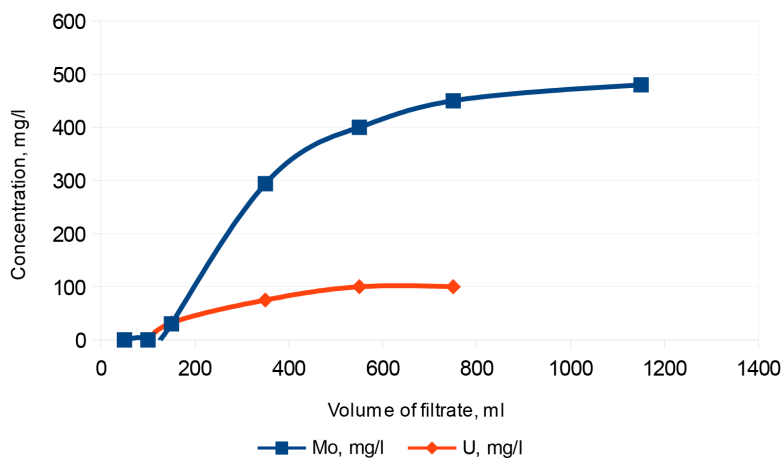


Fig. 5. Breakthrough curves for the sorption of molybdenum and uranium by anion exchanger AB-17 at their different concentrations in feed solutions, pH 2.0 (test 6, Table 5).

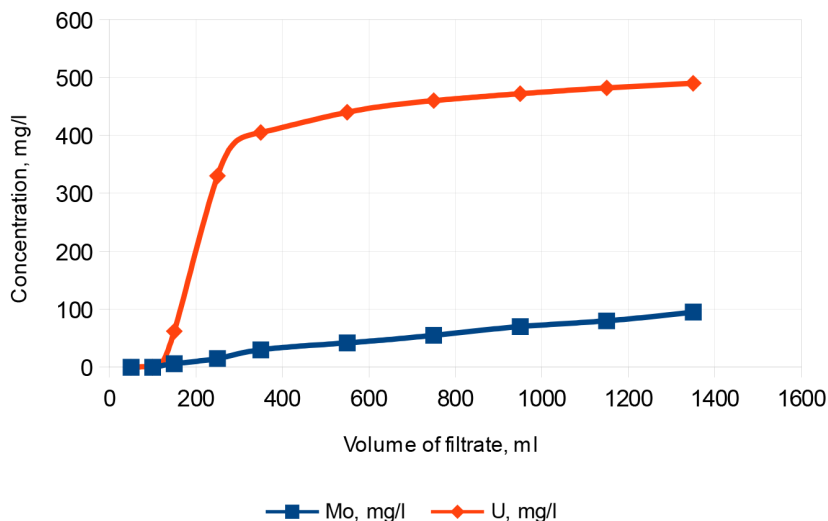


Fig. 6. Breakthrough curves for the sorption of molybdenum and uranium in significant excess of U ions in the feed solution, pH 2.0 (test 7, Table 5).

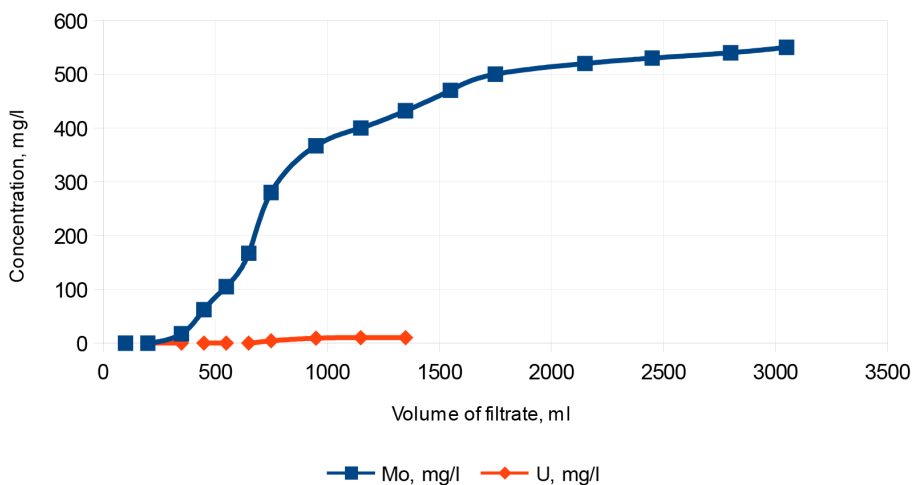


Fig. 7. Breakthrough curves for the sorption of molybdenum and uranium in significant excess of Mo ions in the feed solution, pH 4.0 (test 6, Table 4).

The dependence of the anion-exchange resin's sorption capacity with respect to U on the concentrations of molybdenum and uranium in feed solutions is illustrated in Figure 8.

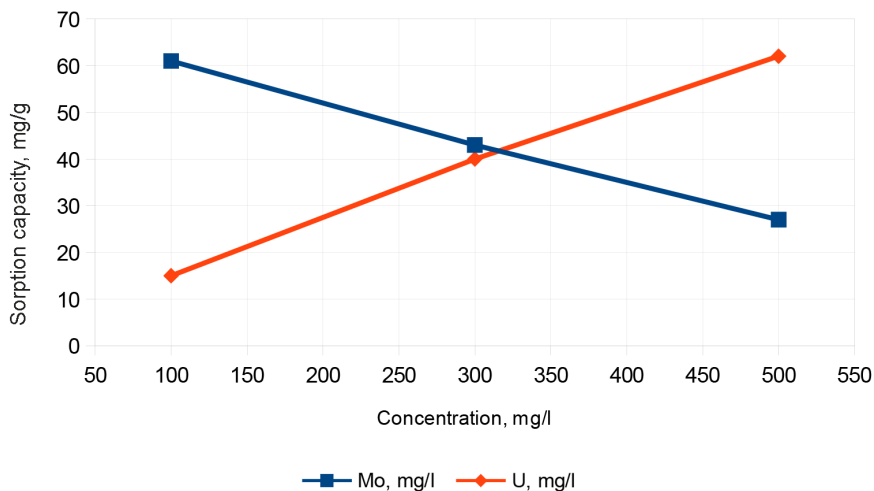


Fig. 8. The dependence of the sorption capacity of anion exchanger AB-17 with respect to uranium on the feed concentrations of molybdenum and uranium.

Considering the large excess of iron(II) ions in acid leaching solutions, the adsorptivity of molybdenum and uranium was examined in the presence of FeSO_4 . In this case, an augmenting factorial plan for determination of main effects was used on an assumption that interactions between the factors were negligible [23]. To the factorial plan with 8 tests (Table 5) a block with the fourth factor x_4 (FeSO_4 concentration 20 g/l) was added (Table 6). The effects of parameters x_1 , x_2 and x_3 calculated on the basis of 12 tests (4 tests in the presence of FeSO_4) were close to those presented in Table 5. However, the presence of FeSO_4 had a strong influence on the resin's sorption capacity towards molybdenum, the effect of x_4 being -61.3 mg/g. At the same time, the effect of x_4 on the adsorption of U was considerably lower, -13.4 mg/g (Table 5, y_u). For example, Table 5 reveals that at low metals concentrations and pH values (test 1) the resin's sorption capacity regarding Mo and U is respectively 106.6 mg/g and 20.9 mg/g, but in the presence of FeSO_4 this capacity is 44.5 mg/g and 21.1 mg/g, respectively (test 9, Table 6). However, the influence of FeSO_4 on the resin's sorption capacity with respect to U is higher at its high concentration, decreasing from 53.8 mg/g (test 4, Table 5) to 33.8 mg/g (test 10, Table 6).

For stripping the selective elution under column loading conditions was used. Figure 9 depicts the selective elution of Mo and U from anion exchanger AB-17 by using respectively HCl and 2.0 M NaOH solutions. Data on the previous sorption of metals are presented in Table 4 (test 7). At first uranium was eluted with dilute hydrochloric acid (0.3 M), then molybdenum was eluted with a 2.0 M NaOH solution. In the elution process the concentration factor of 20 for U and 80 for Mo were achieved.

Table 6. A block of tests for determination of the influence of iron(II) on the sorption of molybdenum and uranium

	x_0	x_1	x_2	x_3	x_4	y_{Mo}	y_U
Test 9	+	-	-	-	+	44.5	21.1
10	+	+	+	-	+	111.8	33.8
11	+	+	-	+	+	57.0	28.9
12	+	-	+	+	+	27.7	61.6
$\sum x_{ij}y_{Moj}$	1213.4	366.6	-10.6	-120.0	-243.1		
Effect ($2/N\sum x_{ij}y_{Moj}$)		61.2	-1.8	-20.0	-60.7		
$\sum x_{ij}y_{Uj}$	543.9	-160.1	246.3	-12.8	-84.7		
Effect ($2/N\sum x_{ij}y_{Uj}$)		-26.7	41.1	-1.1	-21.2		

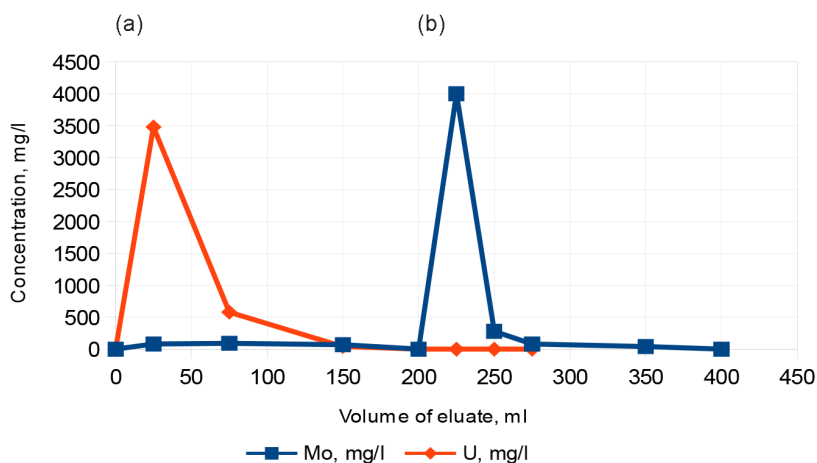


Fig. 9. The selective elution of uranium and molybdenum from anion exchanger AB-17 by using 0.3 M HCl (a) and 2.0 M NaOH (b).

Figure 10 (data on previous sorption from test 3, Table 4) shows the elution profiles of Mo and U under column loading conditions at large excess of Mo ions, indicating their good separation – via the acidic elution approximately 100% of sorbed uranium was removed. Stripping with a weak solution of hydrochloric acid (0.3 M HCl) recovered but an insignificant amount of Mo, approximately 96% of it was eluted with an alkaline eluent. Using a stronger eluent (0.5 M HCl) slightly increased the amount of Mo in an acidic eluent (Fig. 11), however, this depended on its amount sorbed.

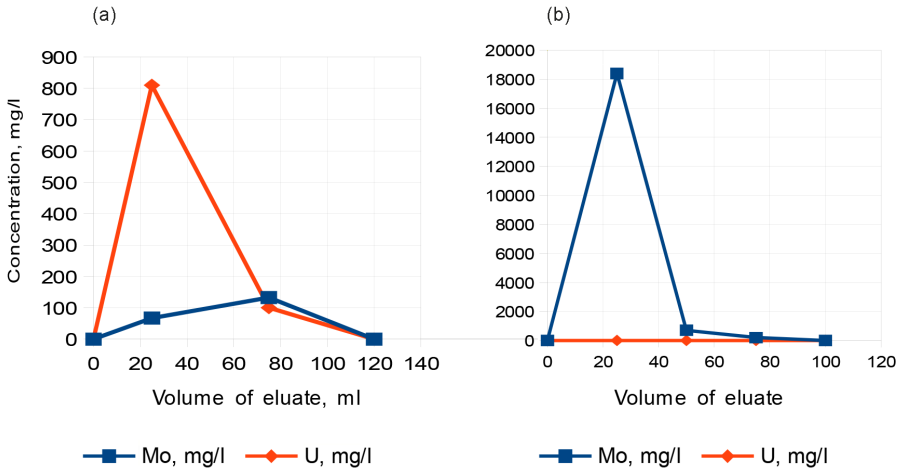


Fig. 10. Elution profiles of uranium and molybdenum under column loading conditions at large excess of Mo ions by using 0.5 M HCl (a) and 2.0 M NaOH (b) as eluates.

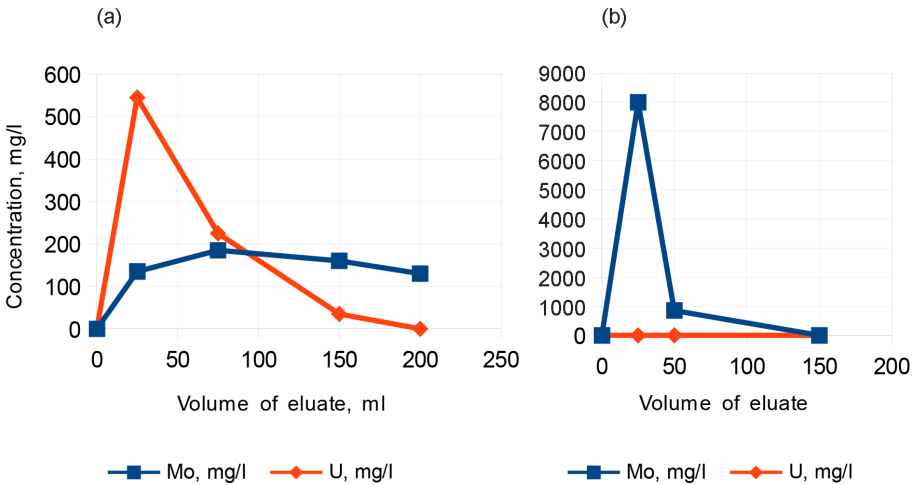


Fig. 11. Elution profiles of molybdenum and uranium from anion exchanger AB-17 by using 0.5 M HCl for the stripping of U.

Considering the large excess of iron ions and the low value of pH, the recovery of molybdenum, uranium and vanadium from acid leachates by anionic resins is very complicated. Two liters of the solution from the percolated leaching of sulphonated argillite ash was passed through a column of the strongly basic anionic resin AB-17 at a resin volume of 80 ml and flow rate of 5.0 ml min^{-1} [5]. The solution contained 65.8 mg/l of U, 85.5 mg/l of Mo, 571.8 mg/l of V and 44.0 g/l of Fe_2O_3 , and its pH was adjusted to 1.5. On the resin, 131.6 mg of U (100%), 98.6 mg of Mo (58%) and 3.71 g of iron

(12.0%) was adsorbed. No vanadium was adsorbed under given conditions. The first stripping with dilute sulfuric acid removed iron ions from the resin. Then uranium and molybdenum were selectively eluted with 1M HCl and 2M NaOH solutions, respectively. The elution profiles of Fe, and of Mo and U are shown in Figures 12 and 13, respectively.

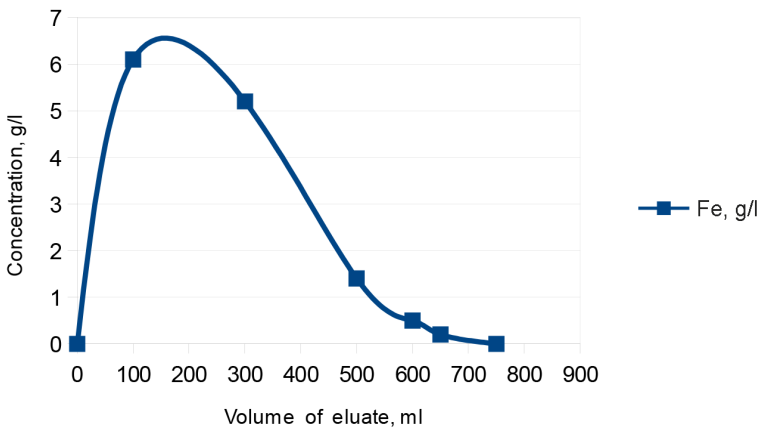


Fig. 12. The removal of iron adsorbed on the anion-exchange resin by using 0.5 M H_2SO_4 .

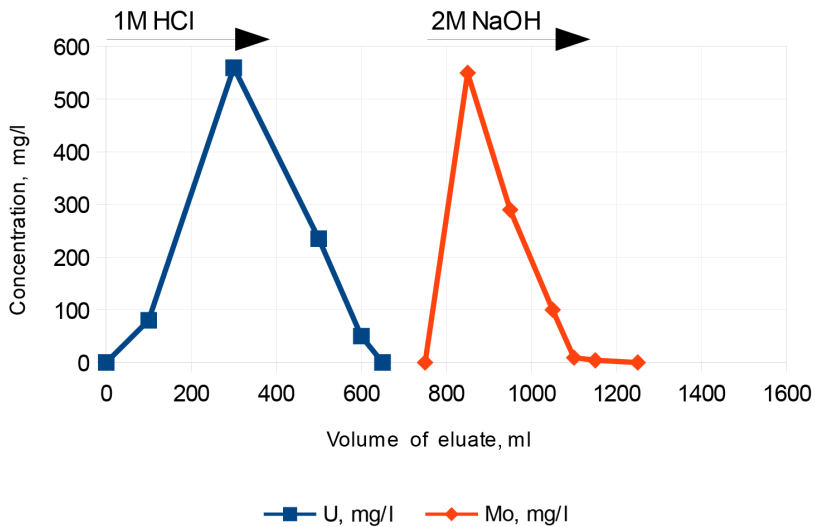


Fig. 13. The recovery of uranium and molybdenum from the sulphonated argillite ash leaching solution by the selective elution [5].

As shown above, the separation of vanadium from acid leachates by using ion exchange is not effective, therefore its precipitation with iron is proposed. For this purpose, the pH of the solution after the recovery of U and Mo by the anion exchanger is raised to 7, followed by the precipitation of iron hydroxide together with V and Mo remaining in the solution. The treatment of the precipitate with alkaline reagents converts vanadium to water-soluble species, unlike iron, which forms an insoluble hydroxide. Optimal conditions for the hot alkaline leaching of the iron precipitate (0.5 h) are given in Table 7.

The data in Table 7 are indicative of a very high efficiency of leaching, up to 95–98.5% for the vanadium contained in iron hydroxide by using the solution of NaOH or Na₂CO₃. Further the separation of V may be performed using the anion exchange method whose optimal conditions are given above.

Table 7. The recovery of vanadium by the hot alkaline leaching of the iron precipitate

Reagent	Filtrate, ml	Content, mg l ⁻¹	Amount, mg	Recovery, %
5% NaOH				
1. stage	450	220.0	99.0	
2. stage	160	85.3	13.7	
			112.7	95.5
2% NaOH				
1. stage	480	178.2	85.6	
2. stage	480	73.9	35.5	
			121.1	100.0
1% NaOH				
1. stage	480	131.2	63.0	
2. stage	210	0.0	0.0	
			63.0	53.4
10% Na ₂ CO ₃				
1. stage	350	149.1	52.2	
2. stage	210	94.4	19.8	
				61.0
5% Na ₂ CO ₃				
1. stage	420	119.5	50.1	
2. stage	440	105.0	46.2	
			96.3	81.6

A general flowsheet for the process of recovery of Mo, U and V, which was constructed on the basis of the laboratory test results, is shown in Figure 14.

This flowsheet does not include the separation process of OM, whose detailed scheme is shown in Figure 1.

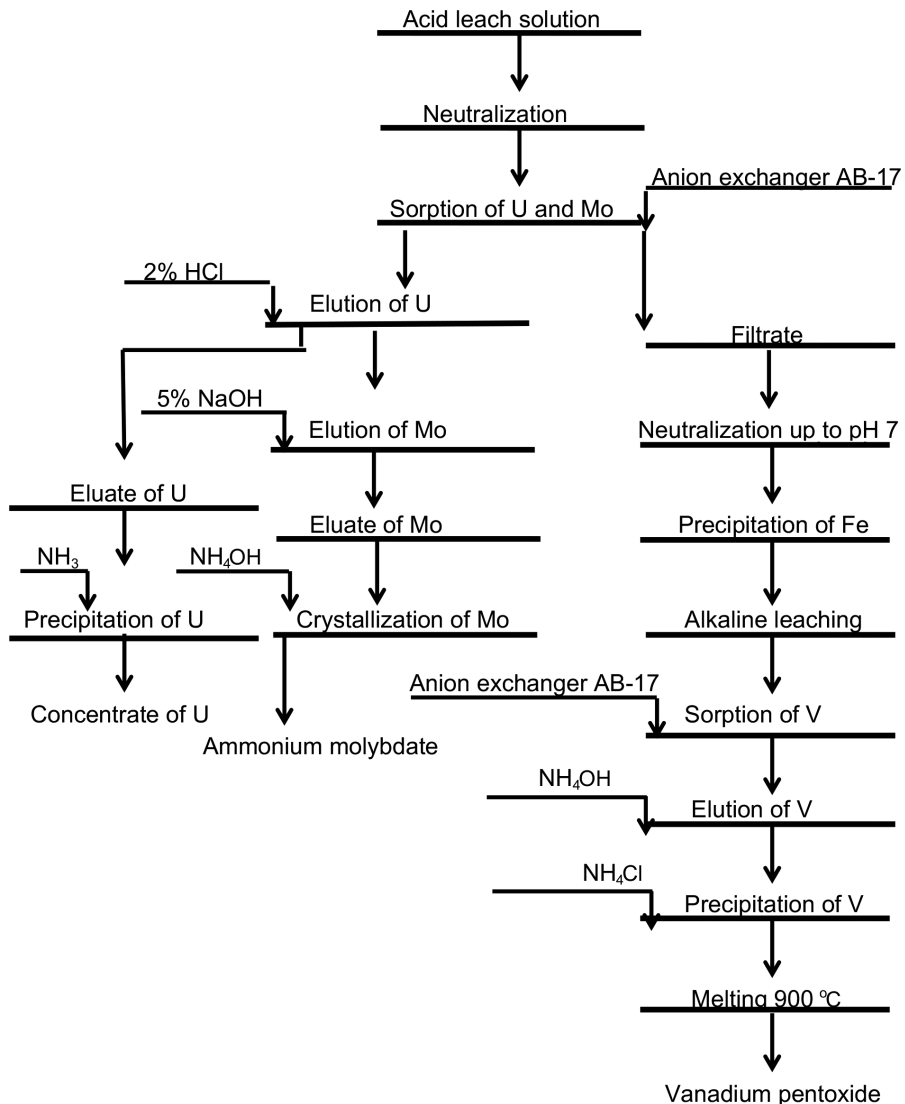


Fig. 14. A general flowsheet for the process of recovery of molybdenum, uranium and vanadium from the argillite leaching solution by anion exchange.

The overall metals recovery process may be divided into the following stages:

1. Combustion with salts. It is offered that in this stage, an additive NaCl or Na_2CO_3 and a temperature range of 800–850 °C be used, while this range may need optimization. As a feed material, ground argillite was used.
2. Leaching with the use of a weak acid or alkaline solution (10–20%).
3. Selective recovery of uranium and molybdenum by the anion exchange process.
4. Precipitation of iron hydroxide with vanadium.
5. Leaching of the iron precipitate with an alkaline solution.
6. Recovery of vanadium by the anion exchange process.
7. Precipitation of molybdenum, uranium and vanadium from elution solutions and refining to high-purity products.

7. Conclusions

Based on the results of the study, the following conclusions are drawn:

1. For the processing of argillite two variants have been presented: 1) separation of organic matter together with allied metals and 2) roasting combustion of ground argillite with salts without prior separation of organic matter.
2. The separation of organic matter allows a significant reduction in the quantity of material to be directed to further processing. Also, it may prove suitable for the recovery of biogas from argillite.
3. Salt roasting combustion of argillite allows weaker acid or alkaline reagents to be used for the further leaching of metals from argillite, which is important in economic terms. Moreover, the method may be taken advantage of in the development of the technology for the further processing of argillite.
4. For the recovery of molybdenum, uranium and vanadium a strongly basic anion exchanger AB-17 was used.
5. The effects of the concentrations of metals and pH of model solutions on the sorption capacity of anion exchanger AB-17 were studied in two pH ranges: 1.0–4.0 and 1.0–2.0. The factorial main-effect plan was used to estimate the effects.
6. For the selective recovery of uranium and molybdenum the selective elution was used.
7. The recovery of vanadium from acid leachates in significant excess of iron ions by the anion exchange process was ineffective. Therefore, a method for the precipitation of vanadium with iron and the subsequent alkaline leaching with its separation by the anion exchange process were proposed.
8. On the basis of the experiments a general flowsheet for the process of recovery of molybdenum, uranium and vanadium from the argillite leaching solution was presented.

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