

# Study of Sorption Properties of Anion Exchangers with Long-Chained Cross-Linking Agents for Tungsten Hydrometallurgy

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**Abstract** The macroporous anion exchangers with long-chained cross-linking agents were investigated for the tungsten recovery from salt solutions. The physical-chemical characteristics of these sorbents were studied by means of sorption-desorption experiment as well as electron and IR-spectroscopy. The anion exchangers on the basis of macroporous copolymers of methylacrylate and divinyl-ester of diethyleneglycol or tetravinyl-ester of pentaerythritol possess the exchange capacity to tungsten 2—5 times greater than the porous anion exchangers on the basis of styrene and divinylbenzene, therefore they can be used for selective tungsten recovery from complex salt solutions.

**Keywords** anion exchangers, macroporous structure, long-chained cross-linking agents, tungsten recovery, salt solution

## 1 INTRODUCTION

Tungsten-containing raw materials are complex mineral systems in their physical-chemical composition, from which tungsten is converted by chemical-metallurgical methods into  $\text{Na}_2\text{WO}_4$ ,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  solutions with the background of  $\text{NaX}$  ( $\text{Na}_2\text{X}$ ,  $\text{Na}_3\text{X}$ ),  $\text{HNO}_3$  (where  $\text{X}=\text{OH}^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ )<sup>[1-6]</sup>. The subsequent tungsten transition in to  $[(\text{NH}_2)_2\text{WO}_4\text{-H}_2\text{O-NH}_4\text{OH}]$  solution is carried out by means of sorption and extraction<sup>[1,3,6-11]</sup>. The extraction process is already in industry but is ecologically dangerous under certain conditions<sup>[1,3,10,11]</sup>. It is known<sup>[3,7]</sup> that the cation exchange processes are applied for the  $[(\text{NH}_4)_2\text{WO}_4\text{-H}_2\text{O}]$  production but they can be carried out only for the  $(\text{Na}_2\text{WO}_4\text{-NaOH-H}_2\text{O})$  solution with the minor salt background ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ). However, the anion exchange process for the ammonium tungstate production, for realization of which anion exchangers with high exchange capacity to tungsten are needed, is free from these limitations.

The earlier investigated anion exchangers on the basis of gel and porous copolymers of styrene and vinylpyridine types were used for the tungsten recovery from waste solutions<sup>[1,7,9]</sup>. The macroporous anion exchangers on the basis of acrylic copolymers with long-chained cross-linking agents synthesized by TOKEM-Company (Kemerovo, Russia) are more appropriate in conversion from sodium tungstate into ammonium tungstate<sup>[12-15]</sup>.

The present work is devoted to the selective tungsten recovery from salt systems on macroporous methylacrylate anion exchangers with long-chained crosslinking agents in comparison with the porous anion exchangers on the basis of styrene.

## 2 Experimental

The physical-chemical properties of anion exchangers investigated were studied by means of sorption-desorption experiment, mercury porometry as well as electron and IR-spectroscopy<sup>[13,16-19]</sup>. The common anion exchangers mass ( $\sim 50$  g) was previously prepared in the  $\text{Cl}^-$  form (the average bead diameter is 0.3—0.5 cm) and was kept in air-dry storage.

The initial tungstate solutions with the concentration of 0.0001—0.1 mol·L<sup>-1</sup> and with the given pH and salt background were previously stocked for 10 days. The common volume of these solutions was 10—20 L. The distribution coefficients  $D$  calculated from:  $D=\text{mmol of W sorbed per g resin}/\text{mmol of W per ml of solution}$  were determined under batch experiment conditions (the resin used  $\sim 1.0$  g, the solution volume was 0.2 L). The equilibrium time was 24 h.

The tungsten sorption was also investigated under the dynamic conditions in the thermostated glass column (15 mm diameter, 160 mm height, porous filter). The resin (0.2 g) was first swollen for 4 h and then transferred into the column. The tungsten-containing solution with the definite pH value and

Received 1999-05-31, accepted 1999-12-13.

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background was filtered through the sorbent with the flow rate 0.07—0.1 L·h<sup>-1</sup> in a period up to the equilibrium time (24 h). The tungsten desorption from anion exchangers was carried out by 20% ammonia solution or by solution of NaOH and NaCl mixture (10% each). The eluent volume was ~100 ml. The tungsten content in solution and eluate was determined spectrophotometrically<sup>[20]</sup>. From the experimental data, the exchange capacity (EC) of anion exchangers to tungsten was calculated (amount of W sorbed in the resin, mmol·g<sup>-1</sup>).

Experiments were repeated 3 or 4 times. The average experimental error is below 6%.

The identification of tungsten ionic state was obtained from electron spectroscopy data at the wavelength range of 200—400 nm using the Specord UV Vis spectrophotometer (Germany). The absorption layer thickness was 0.2—0.8 cm.

The anion exchanger samples for IR-spectroscopy were prepared according to the following procedure. After the saturation of samples with tungsten ions at the definite pH values, the sorbents were dried by filter paper (no washing with water in order not to change the tungsten ionic state in the resin phase). Then the air-dried samples were ground in a vibration mill. The resins tableting was carried out with KBr (0.3 mg resin to 200 mg KBr). The IR-spectra were registered using IR-spectrometer Specord M80 (Germany). The electron and IR-spectra were identified in accordance with the works<sup>[21-23]</sup>.

### 3 Results and Discussion

Need for application of anion exchanger with macroporous structure is caused by tungsten ionic state. The polymeric ions HW<sub>7</sub>O<sub>24</sub><sup>5-</sup>, W<sub>7</sub>O<sub>24</sub><sup>6-</sup>, W<sub>12</sub>O<sub>40</sub><sup>8-</sup>, W<sub>12</sub>O<sub>40</sub>(OH)<sub>2</sub><sup>10-</sup>, W<sub>12</sub>O<sub>38</sub>(OH)<sub>2</sub><sup>6-</sup> are formed from WO<sub>4</sub><sup>2-</sup> ions by polycondensation in the solution with tungsten concentration 0.001—0.01 mol·L<sup>-1</sup> at pH<8. These polymeric ions are larger than the monomeric tungstate ions<sup>[15-17]</sup>. That is why aminopolymer beads with open pores (the pore size should be about 150—200 nm) are necessary for the ion exchange recovery of large polymeric ions<sup>[1,4,5,7]</sup>.

#### 3.1 Effect of anion exchanger structure on tungsten sorption

The synthesis of methylacrylate copolymers and aminopolymers on their basis was carried out according to methods in Ref. [18,19] using long-chained cross-linking agents and porogene isooctane (30% to monomer mass). These copolymers were aminated by ethylene diamine (EDA), diethylene triamine (DETA) and triethylene-tetramine (TETA). The physical-chemical characteristics of the resins are shown in Table 1. The anion exchangers synthesized on the basis of porous copolymers of styrene and divinylbenzene (DVB) and aminated by the same amines (EDA, DETA, TETA) were taken for comparison.

The physical-chemical structure of anion exchangers investigated is improved with the increase in cross-linking agent length (going from DVB to TVEPE): the

Table 1 Physical-chemical properties of ion exchangers investigated

Trade name	Copolymer	Cross-linking agent, %	Resin structure	Aminating agent	Static exchange capacity in Cl <sup>-</sup> -form, mmol·g <sup>-1</sup>	Filled mass, g·cm <sup>-3</sup>	Specific surface, m <sup>2</sup> ·g <sup>-1</sup>	Total pore volume, cm <sup>3</sup> ·g <sup>-1</sup>	Average pore diameter (maximal pore diameter), nm
AN-108P	MA	DVEDEG, 7	MP	EDA	6.3	0.36	44—55	0.45—0.67	42—105 (700—1900)
AN-108TP	MA	TVEPE, 3	MP	EDA	6.8	0.39	39—44	0.50	51—80 (700—2200)
AN-221	St	DVB, 10	P	EDA	4.1	0.48	41—47	0.80	23—80
AN-106P	MA	DVEDEG, 7	MP	DETA	6.8	0.39	34—39	0.34	22—85 (400—1800)
AN-106TP	MA	TVEPE, 3	MP	DETA	8.6	0.38	43—51	0.49—0.56	57—130 (500—2100)
AN-511	St	DVB, 10	P	DETA	4.6	0.49	23—28	0.61	24—30
AN-1P	MA	DVEDEG, 7	MP	TETA	9.6	0.34	38—43	0.44	47—95 (700—900)
AN-1TP	MA	TVEPE, 3	MP	TETA	10.6	0.36	37—45	0.51—0.68	65—130 (1200—1800)
AN-521	St	DVB, 10	P	TETA	5.1	0.51	27—34	0.69—0.84	25—35

MA—methylacrylate; St—styrene; DVEDEG—divinyl-ester of diethyleneglycol; TVEPE—tetravinyl-ester of pentaerythritol; DVB—divinylbenzene; EDA—ethylene diamine; DETA—diethylene triamine; TETA—triethylene-tetramine; P—porous; MP—macroporous.

pore size as well as total pore volume and chemical activity (exchange capacity) grow substantially (Table 1). The swelling of polymer network of the anion exchangers beads grows in the hydrated state at the expense of great amount of ester bonds and flexibility of long-chained cross-linking agents. That is why the ionic permeability of anion exchanger beads to tungsten polyanions grows (Table 2).

The effect of aminating agent on sorption properties of anion exchangers investigated depends on copolymer physical structure (porosity) and its type (on the basis of methylacrylate or styrene) as well as on the tungsten polyanion size in the salt solution.

The anion exchangers with the same functional groups (EDA, DETA, TETA) and with various physical structure of the beads (MP, P, MN or LB) absorb the tungsten ions depending on resin porosity and on pH value of the solution (Table 2).

The styrenated anion exchangers AN-221, AN-511, AN-521 (porous samples) and AN-406, AN-467, AN-466 (large-beaded samples) absorb the tungsten polyanions 2–5 times less than the macroporous anion exchangers on the basis of methylacrylate and long-chained cross-linking agents. The macronetwork anion exchanger AN-106T (it is analogous to AN-106P but was synthesized without isoctane as a porogene) absorbs the tungsten polyanions only by surface functional groups because of porosity absence.

Between the macroporous anion exchangers with long-chained cross-linking agents DVEDEG (AN-108P) and TVEPE (AN-106TP, AN-1TP), AN-1TP shows the highest values of exchange capacity to tungsten (Table 2, Fig. 1). These anion exchangers are the most applicable to  $\text{Na}_2\text{WO}_4 \rightarrow (\text{NH}_4)_2\text{WO}_4$  conversion.

### 3.2 Effect of solution salt composition on anion exchanger saturation degree

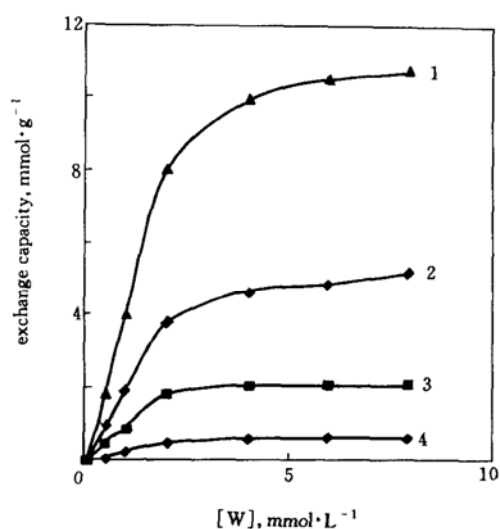
The tungsten concentration in solution varies

**Table 2** Tungsten sorption on anion exchangers of different porosity from  $(\text{Na}_2\text{WO}_4\text{-H}_2\text{O-HCl})$ -solution (The initial tungsten concentration is  $3 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ )

Trade name	Aminating agent	Porosity	Static exchange capacity in the $\text{Cl}^-$ -form, $\text{mmol}\cdot\text{g}^{-1}$	<i>D</i>	
				pH=2.5	pH=5.1
AN-108P	EDA	MP	6.4	304	251
AN-221	EDA	P	4.1	124	87
AN-467	EDA	LB	4.1	71	47
AN-106TP	DETA	MP	8.6	387	282
AN-511	DETA	P	4.6	171	142
AN-406	DETA	LB	4.1	62	47
AN-106T	TETA	MN	7.9	18	24
AN-1TP	TETA	MP	10.6	417	290
AN-521	TETA	P	5.1	203	164
AN-466	TETA	LB	4.8	68	54

MP—macroporous; P—porous; LB—large-beaded; MN—macronetwork;

*D*—distribution coefficient

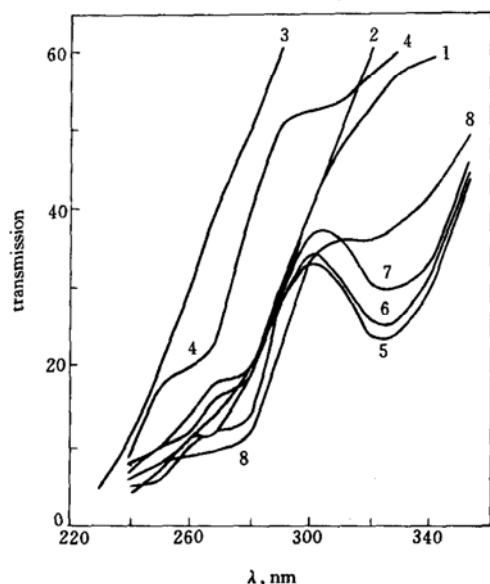


**Figure 1** Isotherms of tungsten sorption on anion exchangers in the system  $\text{Na}_2\text{WO}_4\text{-NaNO}_3\text{-H}_2\text{O}$  (pH=2.5±0.1) (The  $\text{NaNO}_3$  concentration is  $1.5 \text{ mol}\cdot\text{L}^{-1}$ ; The data are obtained under dynamic conditions) 1—AN-1TP; 2—AN-521; 3—AN-466; 4—AN-106T

from the maximum to about zero during the technological process of ion exchange conversion  $\text{Na}_2\text{WO}_4 \rightarrow (\text{NH}_4)_2\text{WO}_4$ . That is why the exchange capacity value of anion exchangers depends on tungsten ion concentration in equilibrium solution (Fig. 1). The isotherms of tungsten sorption at pH=2.5 are convex (*i.e.* selective sorption of tungsten polyanions). The increase in EC to tungsten is also associated with its ionic state change in the  $(\text{Na}_2\text{WO}_4\text{-HCl-H}_2\text{O})$ -system (pH=2.5) in dependence on tungsten concentration:  $\text{WO}_4^{2-} \rightarrow \text{W}_7\text{O}_{24}^{6-} \rightarrow \text{W}_{12}\text{O}_{40}(\text{OH})_2^{10-} \rightarrow \text{W}_{12}\text{O}_{38}(\text{OH})_2^{6-}$  [16,17].

With the increase in tungsten concentration from  $10^{-5} \text{ mol}\cdot\text{L}^{-1}$  up to  $10^{-2} \text{ mol}\cdot\text{L}^{-1}$ , the polyanions of

para-, hydrometa- and metatungstates are formed. The similar change of tungstate ionic state takes place in dependence on solution aging time at the definite pH values (Fig. 2): with the acidification of the system to pH 5.1 or 2.5 the polyanions  $W_7O_{24}^{6-}$  (spectrum 8) and  $W_{12}O_{40}(OH)_2^{10-}$ ,  $W_{12}O_{38}(OH)_2^{6-}$  (spectrum 3) are formed.



**Figure 2** Electron absorption spectra of  $(Na_2WO_4-NaNO_3-H_2O)$ -solutions at  $pH=2.5\pm 0.1$  (1—4) and  $pH=5.1\pm 0.1$  (5—8)

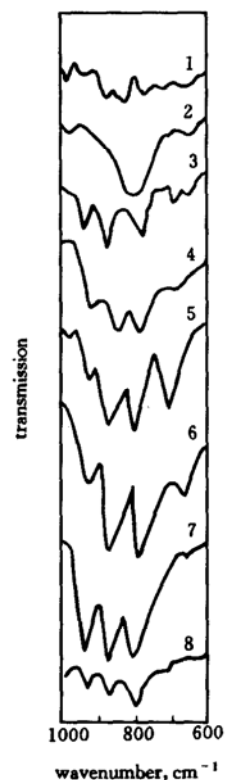
The solution aging time at constant pH: 3,8—15 min; 2,7—5 h; 1,6—72 h; 4,5—144 h

The change of tungsten ionic state has effect on type of ions sorbed.

The IR-spectroscopic data obtained for anion exchanger AN-1TP saturated in the solution with  $pH=2.5\pm 0.1$  and with varying tungsten concentration in the initial anion exchange system corroborate the above-mentioned (Fig. 3). IR-spectrum 2 presents the anion exchanger saturated in the solution with tungsten concentration  $10^{-4} mol\cdot L^{-1}$ . The absorption band at  $650-850 cm^{-1}$  is characteristic for  $WO_4^{2-}$  ions sorbed on the resin<sup>[21-23]</sup>.

With the increase in tungsten concentration in solution, the polyanionic systems changing gradually over to the equilibrium state are formed (Fig. 2, spectra 1, 2, 4 for  $pH=2.5$  and spectra 5—7 for  $pH=5.1$ ). It should be noted that the equilibrium state is attained practically after 72 h for the ionic system with  $pH=5.1$  (spectrum 6 in Fig. 2 changes slightly and becomes spectrum 5 after 144 h). In the system with  $pH=2.5$ , the equilibrium state is not established after 72 h. There are several ionic forms of tungsten polyanions in the solution in this case. The equilib-

rium state is attained only after 144 h (Fig. 2, spectrum 4 which has two shoulders at 240—260 nm and 280—300 nm). Therefore the ionic system changes in the direction of formation of stable metatungstate polyanions  $W_{12}O_{40}(OH)_2^{10-}$  or  $W_{12}O_{38}(OH)_2^{6-}$ .



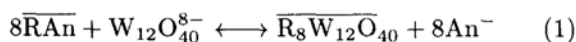
**Figure 3** IR-spectra fragments of anion exchanger AN-1TP (2—7) saturated in  $(Na_2WO_4-NaNO_3-H_2O)$ -solutions ( $pH=2.5\pm 0.1$ ) with various tungsten concentration

Spectrum	Tungsten concentration, $mol\cdot L^{-1}$	Solution aging time before the sorption, h
2	$10^{-4}$	0.5—2
3	$2 \times 10^{-4}$	0.5—2
4	$10^{-3}$	0.5—2
5	$3 \times 10^{-2}$	0.5—2
6	$3 \times 10^{-2}$	72
7	$3 \times 10^{-2}$	144

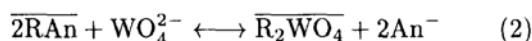
Spectrum 1—anion exchanger AN-1TP in the  $Cl^-$ -form.  
Spectrum 8—anion exchanger AN-106T after the tungsten sorption from the solution with the tungsten concentration  $3 \times 10^{-2} mol\cdot L^{-1}$

Thus the anion exchanger AN-1TP is saturated with different polyanions after the tungsten sorption from solutions with  $pH=2.5$  (Fig. 3, spectra 3—7), just as the equilibrium in solutions is shifted in the direction of  $WO_4^{2-}$  ions formation with the decrease in tungsten concentration. Under the same conditions, the macronetwork anion exchanger AN-106T absorbs the tungsten ions only by surface groups (Fig. 3, spectrum 8).

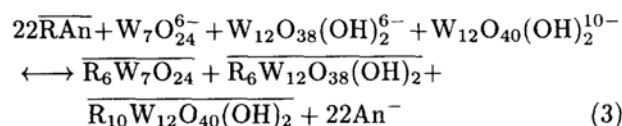
Therefore the data obtained from solution electron spectroscopy (Fig. 2) and IR-spectroscopy of AN-1TP (Fig. 3) testify the complicated ion exchange equilibrium. So the following process takes place during the tungsten sorption from equilibrium solutions with pH=2.5 and W concentration greater than  $10^{-3}$  mol·L<sup>-1</sup>



The sorption of tungstate ions occurs at the tungsten content in solution less than  $10^{-3}$  mol·L<sup>-1</sup>



The polyanions with various charge-to-mass ratios are sorbed from non-equilibrium solutions



The anion charge (An) is equal to 1 for simplicity of representation.

It can be seen from IR-spectra 5—7 (Fig. 3) which define AN-1TP saturated in the solutions with different aging time that with the increase in this time, the various tungsten polyanions are sorbed:  $W_{12}O_{40}^{8-}$ ,  $W_{12}O_{38}(OH)_2^{6-}$ ,  $W_{12}O_{40}(OH)_2^{10-}$ . It can be concluded that the tungsten polyanions with maximal charge-to-mass ratio close to 2 (0.5 for  $WO_4^{2-}$  ions) are recovered simultaneously from the salt solutions at pH=2.5. It should be noted that the tungstate ions sorbed at pH=2.5 are converted in the anion exchanger beads into metatungstate polyanions because of polycondensation process. The exchange capacity of the resin grows in this case<sup>[23]</sup>.

Influence of salt background on the tungsten recovery has remarkable effect at pH≥5.1 (Table 3). It can be seen that AN-106TP (similarly to AN-1TP) recovers effectively tungsten from all salt systems investigated at pH=2.5—5.1.

**Table 3 Tungsten sorption on anion exchanger AN-106TP from different salt solutions** (The salt concentration is  $1.5$  mol·L<sup>-1</sup>; the initial tungsten concentration is  $3 \times 10^{-2}$  mol·L<sup>-1</sup>)

Salt background	Distribution coefficients at pH			
	2.5	4.1	5.1	6.1
	387	381	282	197
Na <sub>2</sub> SO <sub>4</sub>	375	362	280	182
NaCl	367	339	269	73
NaNO <sub>3</sub>	340	297	248	21
Na <sub>3</sub> PO <sub>4</sub>	391	382	387	

The desorption of tungsten polyanions was carried out by aqueous ammonia solutions (20%). The tungsten desorption degree from the resins AN-106TP, AN-1TP, AN-108P exceeds 99%.

#### 4 CONCLUSIONS

The anion exchangers on the basis of macroporous copolymers of methylacrylate and long-chained cross-linking agents (aminating agents DETA, TETA) possess the exchange capacity to tungsten 2-5-times more than the porous anion exchangers on the basis of styrene and DVB. The macroporous ion exchangers can be used for the selective tungsten recovery from complex salt solutions under conversion to the system (NH<sub>4</sub>)<sub>2</sub>WO<sub>4</sub>-NH<sub>4</sub>OH-H<sub>2</sub>O. The pure tungsten salts as well as metal tungsten and its alloys can be obtained from these solutions in accordance with the commercial technology.

#### REFERENCES

- 1 Reniy, Molibden, Wolfram, Perspektivy Proizvodstva i Promyshlennogo Primeneniya, 1st Russian Sym., Nauka, Moscow (1998). (in Russian)
- 2 Kholmogorov, A. G., Patrushev, V. V., Pashkov, G. L., Russia Pat. 2091487 (1997).
- 3 Li, H., Sun, P., "Hydrometallurgiya wolframa v kitae", 2nd Int. Symp. "Problemy Complexnogo Ispolzovaniya Rud", St. Petersburg, (1996). (in Russian)
- 4 Sun, P., Chen, Z., Li, H., "A new technology for production of high purity paratungstate ammonium from low grade tungsten concentrate", *J. Cent. S. Univ. Technol.*, **3** (2), 171 (1996).
- 5 Sun, P., Chen, Z., Li, H., "Study on treatment of ammonia leaching slag in the metallurgical process of tungsten", *J. Cent. S. Univ. Technol.*, **2** (2), 21 (1995).
- 6 Martins, G. P., "Kinetic of soda leaching of low grade tungsten concentrates", *Hydrometallurgy*, **42** (2), 221 (1996).
- 7 Kholmogorov, A. G., Mokhosoev, M. V., Zonkhoeva, E. L., Modifizirovannye Ionity v Technologii Molibdena i Wolframa, Nauka, Novosibirsk (1985). (in Russian)
- 8 Ohashi, K., Murakami, K., Yamamoto, K., "Absorption behaviour of tungsten (VI) on activated carbon", *Busali Kagaku*, **32**, E313—E319 (1983). (in Japanese)
- 9 Martins, G. P., Costa, C., *Ion Exchange Technology*, Euis Horwood, Chichester, 715—723 (1984).
- 10 Ivanov, I. M., Zayzev, Y. P., "Besothodnaya ekstrakcionnaya tehnologiya pererabotki Wolframovykh ryd i koncentratov", *Zvetnye Metally.*, **7**, 47 (1995). (in Russian)
- 11 Coex, G., Dietz, F., Moris, M., "Solvent extraction of molybdenum and tungsten by alamine 336 and DEHPA", *Hydrometallurgy*, **25** (2), 125 (1990).
- 12 Vdovina, G. P., Kholmogorov, A. G., Russia Pat. 1623219 (1989).
- 13 Kholmogorov, A. G., Kovaleva, M. P., Vdovina, G. P., "Issledovanie sorbcionnykh svoystv aminopolimerov metilacrilata s dlinocepochnym sshivayushchim agentom", *Sibirsky Chim. J.*, **2**, 109 (1991). (in Russian)
- 14 Kholmogorov, A. G., Vdovina, G. P., Kovalera, M. P., Russia Pat. 1287551 (1985).
- 15 Kholmogorov, A. G., Vdovina, G. P., Kovaleva, M. P., Russia Pat. 1526165, (1987).

- 16 Pop, M. S., Heteropoli-i Isopolioxometallaty, Nauka, Novosibirsk (1990).
- 17 Sasonova, O. I., Rozancev, G. M., Kholin, Y. V., "Nekotorye utochneniya sostoyaniya ionov Wolframa (VI) v vodnom rastvore", *J. Neorgan. Chem.*, **43** (11), 1884 (1998). (in Russian)
- 18 Tager, A. A., Balakin, V. M., Vydrina, T. S., "Vliyaniye dliny molekuly sshivayushchego agents i ego prirody na velichinu parametrov poristoy struktury polymernykh sorbentov", *Vysokomolekularnye Soedineniya*, **A32** (4), 727 (1990). (in Russian)
- 19 Zilipotkina, M. V., Balakin, Y. M., Kolmakova, L. K., "Sintez i poristaya struktura ionitov na osnove metilacrylata i divinilnogo efira ethylenglycola", *Vysokomolekularniye Soedineniya*, **A32** (1), 36 (1990). (in Russian)
- 20 Busev, A. I., *Prakticheskoe Rukovodstvo po Analiticheskoy Khimii Redkikh Elementov*, Khimiya, Moscow, (1976). (in Russian)
- 21 Nakamoto, K., *Infrakrasnye Spectry Neorganicheskikh i Koordinazyonnykh Soedineniy*, Mir, Moscow (1966). (in Russian)
- 22 Kazanskiy, L. P., Golubev, A. M., *Kolebatelnye Spectry Heteropolianionov Razlichnykh Strukturnykh Tipov*, Nauka, Novosibirsk (1979). (in Russian)
- 23 Kholmogorov, A. G., Smirnova, I. D., Kirillova, V. P., "O polymerizacii wolframat-ionov v structure anionita", *Zvetsnaya Metallurgiya*, **4**, 58 (1983). (in Russian)