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## Sorption of Copper Ions from the Nitric Acid Solution of Electrolytic Refining of Silver with Using Chelating Resin XUS 43605

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**Abstract.** The article is devoted to the sorption of copper ions from a silver electrolyte solution onto a chelating resin with hydroxypropylpicalylamine functional groups. The ion exchange capacity was determined under batch static and dynamic conditions, the effect of flow rate on the ion exchange capacity was shown, the possibility of desorption of copper ions by 1M and 2M sulfuric acid was investigated, the coefficient of separation of copper and silver under static and dynamic conditions is determined.

**Keywords:** electrolyte, refining, silver, copper, extraction, sorbent.

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# Сорбция ионов меди из азотнокислого раствора электролитического рафинирования серебра на хелатирующую смолу XUS 43605

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**Аннотация.** В статье исследуется сорбция ионов меди из раствора серебряного электролита на хелатный сорбент с гидроксипропилпикалиламиновыми функциональными группами. Определена рабочая емкость сорбента в статических и динамических условиях, показано влияние скорости подачи рабочего раствора в колонку на сорбцию ионов меди, исследована возможность десорбции меди 1М и 2М серной кислотой, определен коэффициент разделения меди и серебра в статических и динамических условиях.

**Ключевые слова:** электролит, рафинирование, серебро, медь, извлечение, сорбент.

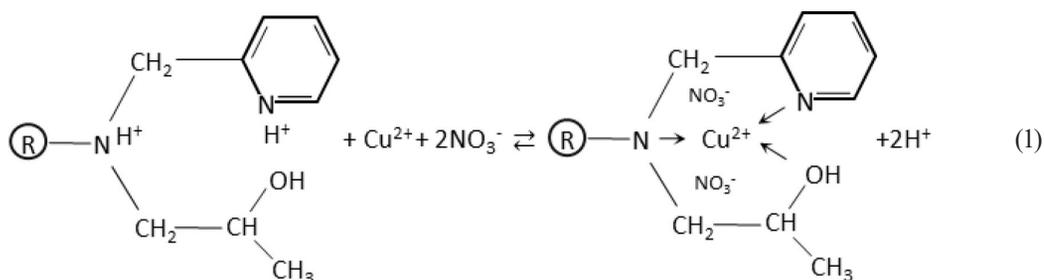
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## Introduction

One of the problems of silver refining is the need to purify the recycled silver electrolyte from non-ferrous metal ions, in particular, from copper ions, which makes up the largest proportion of impurities. At the moment, the most cost-effective way to remove copper from a silver electrolyte is hydrolytic purification. But the pH of hydrate formation of copper and silver hydroxides are similar, some part of silver passes into the hydrate cake together with silver. According to [1], during the hydrolytic purification of the silver electrolyte, up to 3 % of silver passes into the hydrate cake, and the mass fraction of silver in the cake is up to 25 %.

One of the possible ways to solve this problem is sorption. As is known, cation exchange resins are able to absorb metal ions from neutral and alkaline solutions. However, there are several chelating sorbents that are able to absorb metal ions from acidic solutions. Such sorbents include ionite with hydroxypropylpicalylamine functional groups (HPPA). The structure of the HPPA group is shown in Fig. 1.

The sorption of copper ions onto a resin of this type is carried out by the formation of a chelated complex of a copper ion with a molecule of pyridine and hydroxyl, as well as with a central nitrogen atom. The reaction of copper sorption from nitric acid solutions to HPPA can be represented in the following form:



An ion exchange resin based on HPPA functional groups was first developed by The Dow Chemical Company and was labeled as XFS 43084, but later it was renamed to XUS 43605. Robert Grensted [2], was one of the creators of this type of sorbents, established the dependence of the absorption constant on pH for some metals (Fig. 2).

Desorption of copper with HPPA is possible in an acidic solution when hydrogen ions displace copper ions from functional groups. Desorption is also possible with an ammonia solution, when more stable ammonia copper complexes are formed.

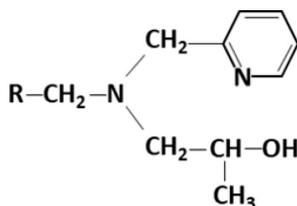


Fig. 1. Structure of the hydroxypropylpicalylamine functional group

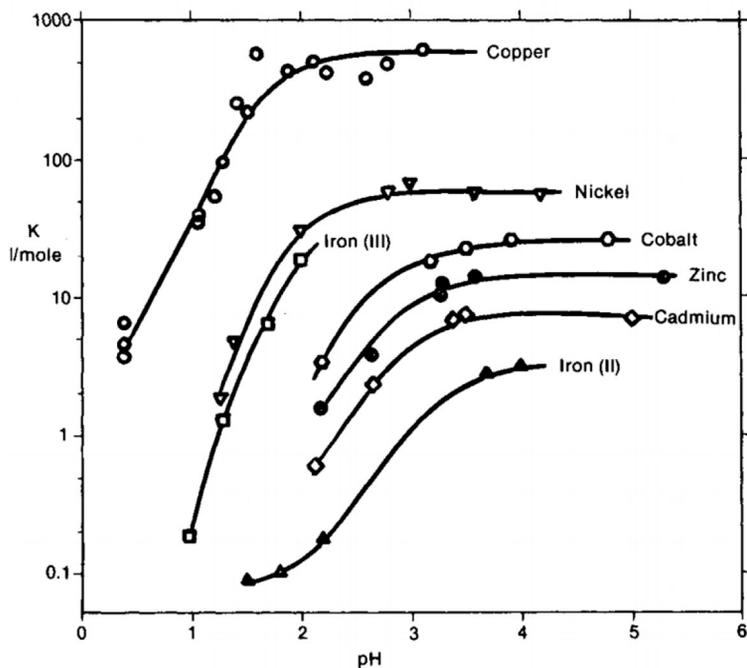


Fig. 2. The dependence of the absorption constant of some transition metals as a function of pH for XFS 43084

The possibility of copper desorption by sulfuric acid with HPPA under dynamic conditions was investigated by the authors [3–6] with using XUS 43605 resin. The experimental results showed that copper is most effectively desorbed by 2M H<sub>2</sub>SO<sub>4</sub>, and at a flow rate of 2 BV/h (bed volumes per hour) and 10 BV/h, the desorption kinetics is almost the same [3] and for a full desorption, no more than 3–3.5 column volumes of a solution of 2M sulfuric acid are required.

Researches [7] shows that copper can be reduced by electrolysis from the obtained sulfuric acid desorbates. Copper desorption from XUS 43605 was carried out with 20 % sulfuric acid. After reaching the concentration of copper in the desorbate – 50 g/l, the solution was reinforced with concentrated sulfuric acid and sent for copper electrolysis.

The objectives of this work: to investigate the possibility of purification of silver electrolyte from copper ions by sorption onto ionite with hydroxypropylpicalylamine functional groups, to determine the capacity of the sorbent under static and dynamic conditions, to determine the coefficient of separation of copper and silver by sorption under static and dynamic conditions, to select the optimal parameters of sorption and desorption for a more complete separation of copper and silver.

### Materials and methods

A sample of a resin with HPPA functional groups XUS 43605 from The Dow Chemical Company was used for copper sorption studies. The model solution was prepared using silver nitric acid and copper nitric acid. To simulate a real electrolyte, free nitric acid was added to the model solution. Based on Fig. 2, for the deepest extraction of copper, the pH of the electrolyte was adjusted to pH 2, using an ammonium hydroxide solution and pH measurements were carried out with a portable pH meter.

Copper concentration in solutions was measured by inductively coupled plasma mass spectrometry (ICP-AES) on an atomic emission spectrometer iCAP RQ (Thermo Fisher Scientific) model. The concentration of silver was determined by gravimetric method, by precipitation of insoluble AgCl precipitate from the solution of the analyzed sample, as well as by the ICP-MS method. In dynamic sorption and desorption experiments a Masterflex L/S 7519–06 pump was used to supply the solution to the column, and a C 660 fraction collector (Buchi) was used to select fractions of the solution. In sorption experiments under static condition a vibrating shaker Heidolph Vibramax 100 was used for constant mixing. The resin suspension was weighed using CAUW-220D analytical scales, and an automatic pipette Eppendorf Research Plus 1–10 was used to select the working solution. The sorbent moisture was measured using the Ohaus MB 23 humidity analyzer. To measure the pH of solutions, the Mettler Toledo SevenGo pH meter was used.

Static exchange capacity (SEC) was calculated by the formula (2):

$$SEC = \frac{(C_0 - C_1) \times V}{V_r}, \text{ mg/ml} \quad (2)$$

where  $C_0$  – initial concentration of the element in solution, mg/l;  $C_1$  – equilibrium concentration of the element in solution, mg/l;  $V$  – volume of solution, l;  $V_r$  – resin volume, ml.

To determine the exact volume of the sorbent in experiments on the sorption of copper under static conditions, the bulk density ( $\rho$ ) of the resin was previously calculated by the formula:

$$\rho = \frac{m_r}{V_r}, \text{ mg/ml} \quad (3)$$

where  $m_r$  – resin weight, mg;  $V_r$  – resin volume, ml.

Since desorption with sulfuric acid with HPPA proceeds completely, the ion exchange capacity (IEC) of the resin under dynamic conditions for a specific element was calculated based on the concentration of the element in the desorbate and the volume of the desorbate:

$$IEC = \frac{\Sigma(C \times V_{desorbate})}{V_r}, \text{ mg/ml} \quad (4)$$

where  $C$  – the concentration of the element in the desorbate, mg/l;  $V_{desorbate}$  – desorbate volume, l;  $V_r$  – resin volume, ml.

To assess the selectivity of resin by copper and silver ions, the separation coefficient calculated by the formula (5):

$$D_{Cu,Ag} = \frac{Kd_{Cu} \bar{C}_{Cu} C_{Ag}}{Kd_{Ag} \bar{C}_{Ag} C_{Cu}} \quad (5)$$

where,  $Kd_{Cu}$  and  $Kd_{Ag}$  – coefficients of distribution of copper and silver ions, respectively, between the sorbent-solution phases;  $\bar{C}_{Cu}$  и  $\bar{C}_{Ag}$  – the concentration of copper and silver ions, respectively, in the sorbent (desorbate);  $C_{Cu}$  и  $C_{Ag}$  – the concentration of copper and silver ions, respectively, in the initial solution.

## Experimental

### *Sorption under static conditions*

The sorption of copper under static conditions was carried out from a model solution (Table 1). An XUS 43605 suspension with a known humidity was added to a 50 ml flask filled with 10 ml of the model solution. Saturation occurred within 24 hours with constant stirring on a shaker. Solutions before and after saturation of resin were analyzed for copper and silver content. Based on the bulk density calculated by formula (3), the volume of the suspension was determined. The capacity of the sorbent for copper was calculated according to the formula (2). Due to the high concentration of silver in the initial silver electrolyte, the determination of the silver capacity by formula (2) gives a large error, therefore the sorbent was dissolved in concentrated sulfuric acid with the addition of an oxidizer, and silver chloride was precipitated from the resulting solution by the action of dilute hydrochloric acid.

### *Sorption under dynamic conditions*

To measure the sorption characteristics of the sorbent under dynamic conditions, a 40 ml column filled with 30 ml of sorbent was used.

In experiments to study the effect of the ionic form of the resin on the sorption of copper ions, XUS 43605 was used in the free base form and H form (Fig. 4). To bring the sorbent into the free base form, it was first washed with 5 % ammonia solution (1.5 BV), and then with water (1.5 BV). To bring

Table 1. Model solution for the sorption of copper (pH 2)

Concentration, g/l		
Ag <sup>+</sup>	Cu <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>
160	13.7	40.0

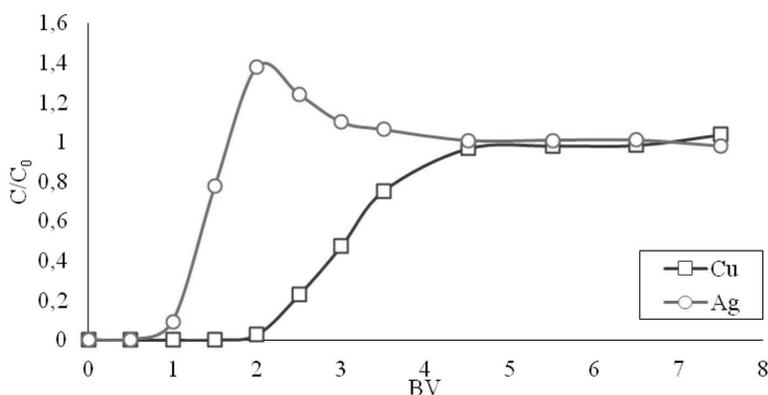


Fig. 3. Output curves of copper and silver sorption to HPPA (free base form). 1 BV/h

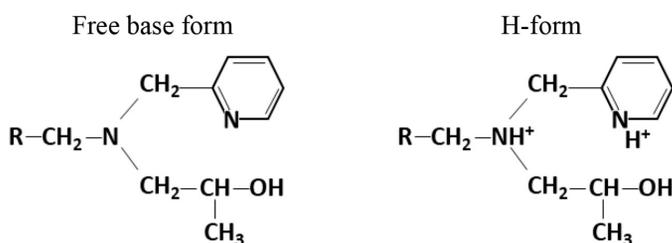


Fig. 4. The structure of the XUS 43605 functional group in free base and H form

the sorbent into H-form, it was washed with a solution of 2 %  $\text{HNO}_3$  with the addition of  $\text{NH}_4\text{OH}$  to pH 2 (3 BV). At the sorption stage, the working solution of the silver electrolyte was passed through a column with a resin with flow rate of 1 BV/h. The output curves are shown in Fig. 5.

In experiments to study the effect of the flow rate on copper sorption, saturation was carried out at a flow rate of 1 and 0.5 BV/h. The output curves are shown in Fig. 7, the capacity indicators are presented in Table 4. The capacity of XUS 43605 for copper, depending on the solution flow rate passed through the column (free base form). In these experiments, the resin was washed with 10 BV of water, after which desorption with sulfuric acid was carried out. The capacity of the sorbent was calculated by the copper content in the desorbate (according to formula 4).

### Washing

To increase the separation of copper and silver, the washing of the sorbent after sorption was investigated in two ways. In one case, the sorbent was washed with water, in the other case with a solution of 2 % nitric acid with pH adjustment with a solution of ammonium hydroxide to pH 1.5. To adjust the pH, an ammonia solution was added to the nitric acid solution. For more complete washing, 10 BV of the washing solution was passed through the column with flow rate 6 BV/h. The fractions of the washing solution coming out of the column were analyzed for the content of the main elements. A comparative washing table is presented in Table 5. To evaluate the separation coefficients of copper and silver depending on the washing solution, after washing, desorption with 10 % sulfuric acid was carried with flow rate 5 BV/h. According to the concentration of copper and silver in desorbates, the

capacity of the resin by copper and silver ions was determined, and according to formula (4), the separation coefficients of copper and silver were calculated depending on the washing solution used. The results of these calculations are presented in Table 6.

### *Desorption*

A solution of sulfuric acid was chosen as a desorbing system for copper desorption. Copper sulfate desorbate can be used for subsequent electrolysis of copper. Studies of copper desorption by sulfuric acid with XUS 43605 consisted in the selection of optimal parameters for the concentration of sulfuric acid and the flow rate of sulfuric acid solution through column. To do this, two experiments were conducted on the desorption of copper using 1M and 2M sulfuric acid, which was fed into a column with a saturated sorbent at a feed rate of 5 BV/h, as well as another experiment on the desorption of copper with 2M sulfuric acid at a feed rate of 10 BV/h. At the exit of the column, the desorbate was fractionated using a fraction collector. The obtained fractions were analyzed for copper and silver content, and the output desorption curves were constructed based on the results of the analysis (Fig. 8, Fig. 9 and Fig. 10). Also, according to the content of copper and silver in the initial solution and desorbates, the separation coefficient of copper and silver was calculated according to the formula (5).

## Results and discussion

### *Sorption under static conditions*

Static sorption experiment has shown that the XUS 43605 sample is able to selectively extract copper ions from a model solution of a silver electrolyte (pH 2). Table 2 shows the obtained values of the static exchange capacity for copper and silver for this sample, as well as the coefficient of separation of copper and silver ( $D_{CuAg}$ ) under static conditions.

### *Sorption under dynamic conditions*

An experiment on copper sorption on HPPA under dynamic conditions at a flow rate of 1 BV/h showed that silver ions are first sorbed together with copper ions, but with gradual saturation of the resin, copper ions displace silver ions. The average concentration of copper ions in the raffinate in this experiment was 0.7 mg/l.

### *The effect of the ionic form on the ion exchange capacity*

Since copper ions replace hydrogen ions in the sorption process by the reaction (1), and the capacity of the sorbent depends quite strongly on the pH of the solution (Fig. 2), copper sorption was carried out in two working forms of resin: in H form and in the form of a free base (Fig. 4).

Table 2. Static copper exchange capacity for XUS 43605

Resin name	Resin weight ( $m_r$ ), g	Resin volume ( $V_r$ ), ml	Capacity (Cu), mg/ml	Capacity (Ag), mg/ml	$D_{CuAg}$
XUS 43605	0,5035	1.41	23,9	8,0	34,9

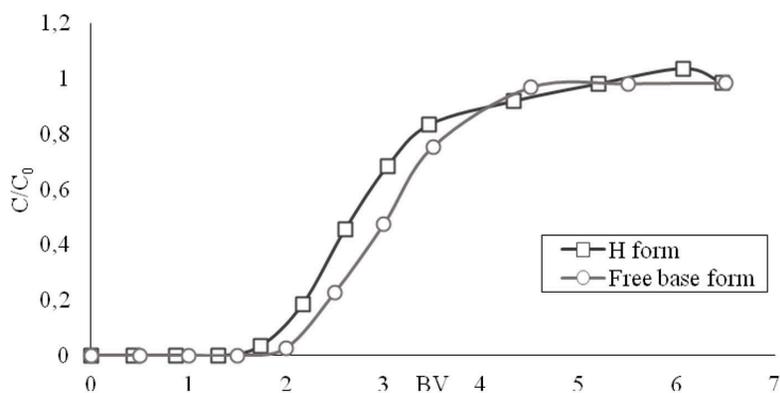


Fig. 5. Output curves of copper sorption on XUS 43605 in free base and H form

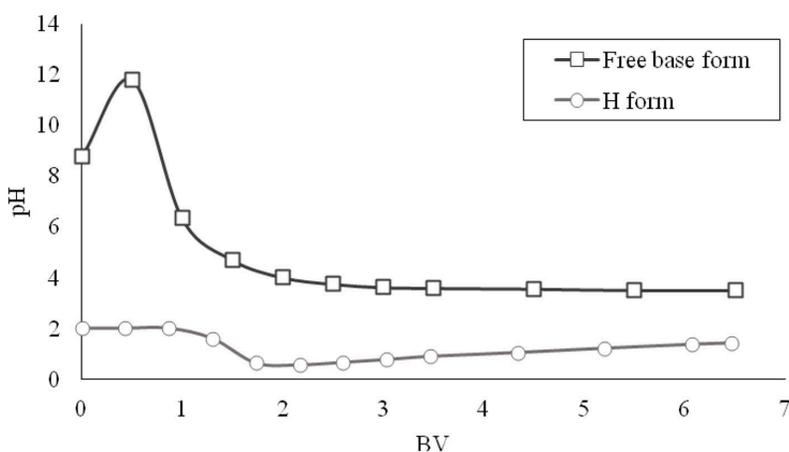


Fig. 6. Output pH curves of sorption Cu (II) to XUS 43605 in H-form and free base form

As can be seen from Fig. 6, when copper is sorbed onto the resin in the free basic form, protonation of functional groups occurs first, and therefore the pH of the outgoing solution increases. It is also worth noting the precipitation of silver hydroxide in the first fractions of the raffinate.

Also, in this experiment, pH was measured for each raffinate fraction. Fig. 6 shows the output curves of pH changes during sorbent saturation.

Thus, the use of a sorbent in the form of a free base allows to increase the capacity, but also contributes to the precipitation of metal hydroxides in the first fraction of the raffinate.

#### *Effect of the solution flow rate on copper sorption*

Reducing the flow rate of the solution in the dynamic sorption experiment from 1 to 0.5 BV/h increases the resin capacity (Cu) (Table 4). This is explained by the fact that with an increase in the flow rate, the selectivity of absorption of copper ions decreases, therefore silver is sorbed from the solution to the sorbent, thereby reducing the copper capacity.

The average concentration of copper ions in the raffinate in all copper sorption experiments does not exceed 10 mg/l.

Table 3. Copper capacitance characteristics of XUS 43605 obtained under dynamic saturation conditions (0.5 BV/h)

Ion exchange resin (ionic form)	Capacity, g/l
XUS 43605 (H-form)	23.9
XUS 43605 (Free base form)	26.0

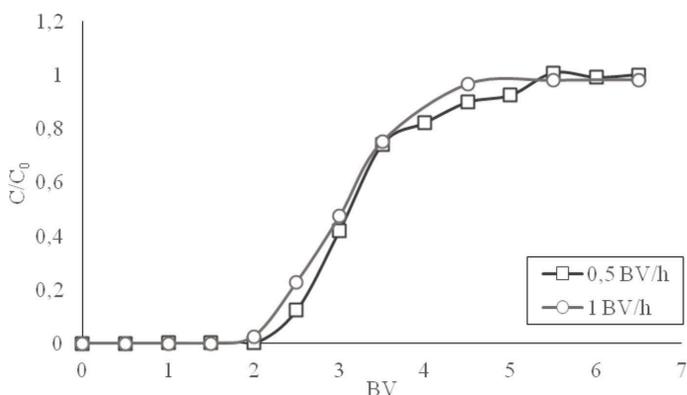


Fig. 7. Output curves of copper sorption on XUS 43605 (free base form) at a flow rate of 1 and 0.5 BV

Table 4. The capacity of XUS 43605 for copper, depending on the solution flow rate passed through the column (free base form)

Flow rate sorption	Capacity (Cu), g/l
1 BV/h	26.0
0.5 BV/h	26.4

### Washing

Table 5 shows the silver ions concentration in the washing water fractions. The washing experiment shows that even after passing 10 column volumes of water, it is not possible to completely wash the silver from the sorbent. It indicates the collective sorption of copper and silver by resin. This makes it possible to purify recycled washing water from copper and silver ions for reuse in subsequent washing cycles.

Table 5. Silver concentration in washing solutions

Washing solution type	Water		20 g/l NO <sub>3</sub> <sup>-</sup> (pH 1.5)	
	Cu, mg/l	C Ag, mg/l	Cu, mg/l	Ag, mg/l
Volume, BV				
2	7112,5	76611.9	12955.0	80593,2
4	917.0	674.7	2064.0	2010,4
6	536.0	1137.2	1848,4	1310,0
8	348,7	575.2	1265.0	50,25
10	347,5	126.3	948,2	47,25

Table 6. Resin capacity and separation coefficients depending on the type of washing solution

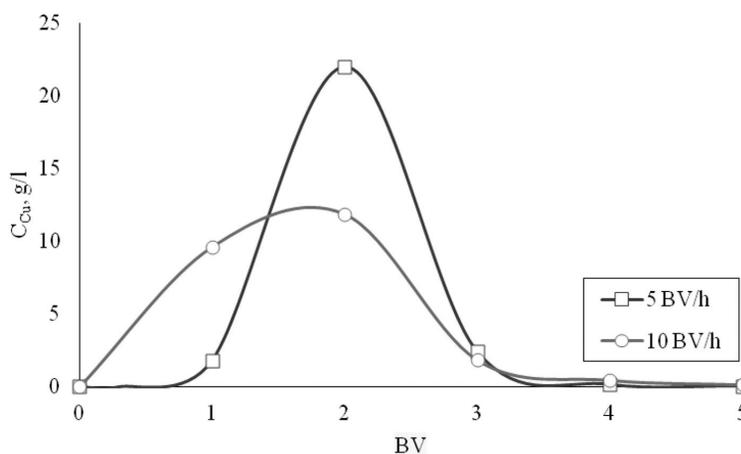
Washing solution type	Water		20 g/l NO <sub>3</sub> <sup>-</sup> (pH 1.5)	
	Cu	Ag	Cu	Ag
Capacity, g/l	26,4	1,2	19,8	0,1
Ratio	0,956	0,044	0,995	0,005
$D_{CuAg}$	244		1931	

At the same time, during acid washing, silver is more completely desorbed and copper is partially washed out. In the case of acid washing, 6 BV is sufficient to wash the sorbent from silver ions. Table 6 shows the sorbent capacities for copper and silver, depending on the washing solution used, as well as the corresponding separation coefficients of copper and silver.

The results of the washing experiment show that a more complete separation of copper and silver ions is obtained by acid washing

### Desorption

Desorption experiments have shown that desorption of copper with 2M sulfuric acid at a flow rate of 5 BV/h allows obtaining a more concentrated rich fraction (Cu - 22 g/l) of desorbate than at 10 BV (12 g/l) (Fig. 8).

Fig. 8. Output curves of copper desorption of 2M H<sub>2</sub>SO<sub>4</sub> with flow rate 5 and 10 BV

At the same time, increasing the concentration of sulfuric acid of the desorbing solution from 1M to 2M does not give any advantages (Fig. 9).

Silver ions are also present in the desorbate (Fig. 10). As mentioned earlier, to reduce the concentration of silver ions in copper desorbate, acid washing after sorption is necessary.

From the resulting desorbate, cementation with iron powder is proposed to extract copper and silver, followed by melting and refining of copper, and the mother solution from cementation can be used to obtain iron sulfate.

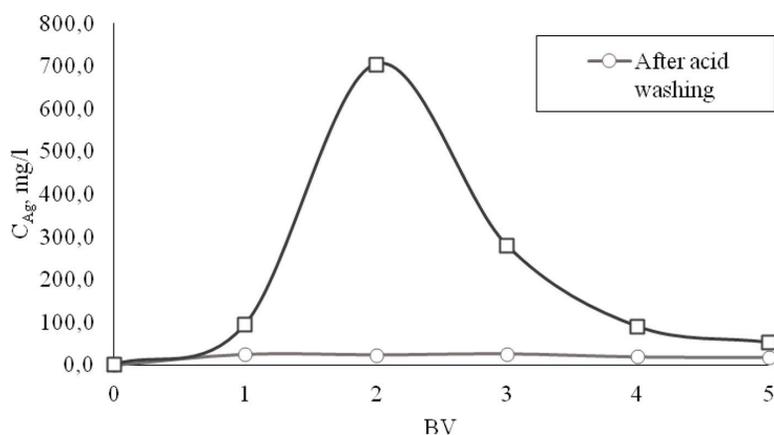


Fig. 9. Output curves of copper desorption of 1M and 2M H<sub>2</sub>SO<sub>4</sub> at a flow rate of 5BV

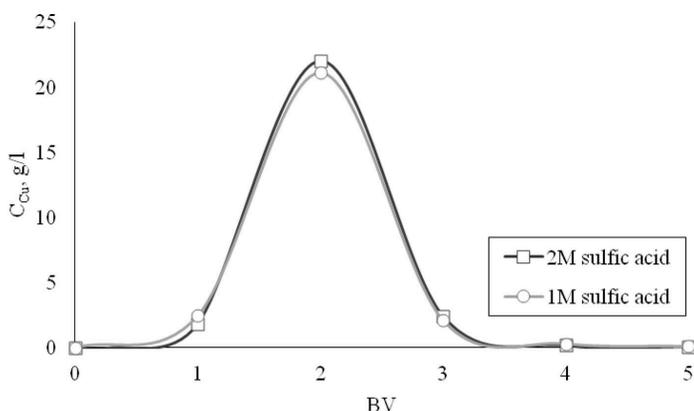


Fig. 10. Output curves of silver desorption from HPPA after water and acid washing. 1M H<sub>2</sub>SO<sub>4</sub>, 5 BV/h

### Conclusion

In this research, XUS 43605 showed the ability to extract copper ions from silver nitrate electrolyte to residual concentrations of no more than 10 mg/l. The capacity of the resin for copper under static conditions was 23.9 g/l, under dynamic conditions 19.8–26.4 g/l, depending on the flow rate of the working solution, on the working form of the sorbent and on the type of washing solution. The possibility of desorption of copper with 10 % sulfuric acid is also shown. The most effective is saturation of HPPA in the basic form at a rate of 0.5 BV/h, acid washing and desorption of 1M H<sub>2</sub>SO<sub>4</sub> at a rate of 5 BV/h. Under such conditions, the separation of copper and silver is ensured with a separation coefficient  $D_{CuAg} = 1931$ .

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