# Extraction of Ag(I) ion traces from aqueous solutions using inorganic thin film and nanocrystalline sorbents

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# Abstract

In this paper, we have presented experimental data and the theoretical basis for the extraction of silver ions from aqueous solutions, using metal sulfides (PbS, ZnS, MnS, CuS, FeS) in the form of thin films, nanocrystals in gel matrices, and precipitates. A mathematical model, taking into account the sorption of Ag(I) due to a three-stage ion exchange in the occurence of solid-liquid phase contact, containing complexing entities (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>H<sub>4</sub>CS, N<sub>3</sub>H<sub>5</sub>CS, NH<sub>3</sub>, EDTA, TEA). This model was applied in the technology of equipment design.

Keywords: Silver (I) ions, ion exchange, metal sulphide, thin film, gel matrix, equilibrium processes

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### Introduction

# a. Description of the kinetics of ion exchange in thin film and nanocrystalline inorganic materials as a multistage process

The fundamental basis for extracting Ag(I) ions from aqueous solutions, using inorganic thin film and nanocrystalline sorbents is there are three known stages of diffusion of metal ions in solids: on the surface of solid–aqueous solutions phase contact; along the boundaries of grains (crystals) of the solid; inside the crystallites. The most important of these are: diffusion by random movement of atoms; diffusion of tracer atoms (self-diffusion and hetero–diffusion); chemical diffusion; mutual diffusion of charged particles <sup>[1]</sup>. Atoms of a solid body, as well as, those of impurity materials are subject to random movements. In <sup>[2]</sup>, the process of ion exchange (of Ag, Cu, Mn, Ni, Ti, Zr, Ta, Sb, Pb, Hg, Sn ions) in oxides, hydroxides, phosphates, with alkali metal ions, was studied. The importance of equilibrium processes in aqueous solutions, having significant influence on the process of ion exchange, upon phase contact, was shown. In <sup>[1]</sup>, a three-stage diffusion of metal ions in thin polycrystalline films was clearly defined, and the differential kinetic equations of these three stages were presented. However, these equations are cumbersome, describe only a single diffusion stage separately, and contain a large number of parameters. In nanocrystals within gel matrices the process of sorption proceeds in two stages. Non-empirical equations of this process are presented in <sup>[3-10]</sup>. These equations describe the exchange of metal ions in the occurrence of "gel immobilized matrix of a metal sulfide – aqueous solution of a metal ion" phase contact.

# *b.* Sorption, using thin polycrystalline films In thin films, the process occurs in three stages:

$$M_1 = m_1 * (1 - \exp(-W_1 * t)), M_2 = m_2 * (1 - \exp(-W_2 * t * k * m_1/m_2)),$$
  

$$M_3 = m_3 * (1 - \exp(-W_3 * t * m_2/m_3)), M = M_1 + M_2 + M_3;$$

(1)

 $m_1 = a^2 * B * n, m_2 = 6 * a * B * n * l, m_3 = a^2 * B * n * l/b; k_1 = 2 * b/a,$ 

where M – the total specific mass of the sorbed metal ion [ $\mu g/cm^2$ ];  $m_i$  – the cross-sections of ion exchange reactions of the corresponding stages; k – the portion of the cross-section of the second stage diffusion from the cross-section of the first stage diffusion;  $W_i$  – diffusion constants of the corresponding stages [ $s^{-1}$ ]; a – the average crystallite size; b – the average distance between the surfaces of two grains in a polycrystalline film; n – the number of crystallites per 1cm<sup>2</sup> film surface; l – film thickness.

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The experimental curves, showing the dependence of the mass of accumulated metal ion on diffusion time, indicate that the saturation of the outer layer of thin films by sorbed ions occurs in less than 2 minutes, the surface of solid grains (crystals) – more than 6 hours and inside the grains - more than 12 days (fig. 1. Curves of accumulation of Ag(I) ions on thin films).

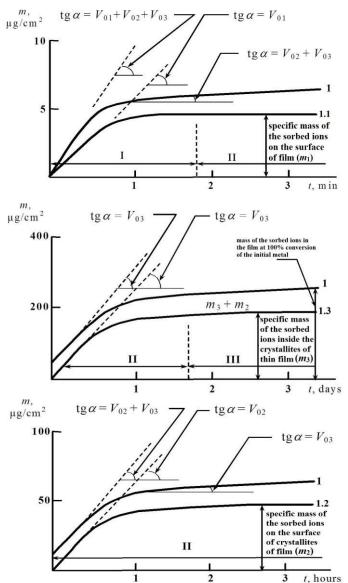


Fig. 1. Curves of accumulation of Ag(I) ions on thin films

1 – curve representing all the stages of the process; 1.1, 1.2, 1.3 – curve of the first, second and third stage correspondly;  $V_{01}$ ,  $V_{02}$ ,  $V_{03}$  – initial sorbtion rates, corresponding to the first, second and third stages.

If the film thickness is about 500 nm, the replacement of initial metal ions to diffusible ions, which is about 90%, occurs as a result of third-stage diffusion, approximately in about 10 days at  $20-25^{\circ}$ C, and for 6-7 hours at  $70^{\circ}$ C. Upon increasing the thickness of films, the conversion, which is about 100%, occurs in a longer period of time, and the dependence of conversion time on thickness of film is exponential

Table 1: Parameters of ion exchange in the thin films and the precipitates of the metal sulphides

Diffusion nonomotors	Phase contact								
Diffusion parameters	PbS–Ag(I)	CuS–Ag(I)	FeS-Ag(I)						
$m_1 / m_2 / m_3 (\mu g/cm^2)$	5 / 36 / 454	20 / 24 / 260	6/28/113						
$\lg W_1 / \lg W_3 / \lg W_3 (s^{-1})$	-1.3 / -1.9 / -5.7	0.4 / -0.6 / -5.5	-2.8 / -2.8 / -5.4						

Table 1 shows the values of diffusion constants calculated by us for Ag(I), Cu(II) in arrays of PbS, CuS and FeS. As can be seen from the data in Table 1, in the case of diffusion of metal ions on PbS films, the values of  $\lg W_1$  practically do not depend on the nature of cations which diffuses from solution onto the film; this dependence is manifested for the values of  $\lg W_2$  and  $\lg W_3$ . First-stage diffusion of Ag(I) ions on CuS films is characterized by high speed of the process, unlike the above-mentioned types of films, and makes it impossible to determine a constant for FeS thin layers. It is also worth noting that  $\lg W_3$  for the diffusion of Ag(I) does not depend on the nature of cations in the above-mentioned types of films and precipitates. At the same time, the values  $\lg W_1$  very much depend on the initial concentration of diffusible ion in solution; such dependency for  $\lg W_2$  is significantly expressed to a much lesser degree, and for  $\lg W_3$ , it is virtually absent.

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#### c. Sorption by nanocrystals in gel matrices

In gel matrices, with a nanostructured organization of immobilized metal sulfide (average crystal size of 10-50 nm), the process of ion exchange proceeds significantly faster than in thin films due to the isolation of nanocrystals and easy access of metal ions to them <sup>[8-10]</sup>. Furthermore, sorption rate substantially depends on the concentration of metal ions in solution, which is in phase-contact with the sorbent. In this regard, the process takes place in two stages: A – on crystal surfaces, B – inside the crystals. The whole process is described by Eq.(2):

$$M_{\Sigma} = A + B; A = \alpha_* M_* \varphi; B = [1 - \alpha]_* M_* [1 - \exp(-\alpha_* M_* \varphi) * W_3 * t_* (1 - \alpha)^{-1} * M^{-1}];$$
  
$$\varphi = 1 - \exp(-6_* \pi^{-2} * K_* D_* K_{pm} * C_{M^*} A_* t) * r^{-1}; \alpha = 6_* d'/d,$$
(2)

where  $d \ \mu \ d'$  the crystal size and the interplanar distance in the crystals;  $6_*\pi^{-2}$  – parameter which takes into account the spherical form of globules; K – reaction rate constant of the first stage [mg•ml<sup>-1</sup>•s<sup>-1</sup>];

D – coefficient of self-diffusion of water [cm<sup>2</sup>/s];  $K_{pm}$  – correction factor, taking into account the suppression of water diffusion by polymer-binding immobilized matrix;  $C_{M'}$  – concentration of desorbed ions in solution [mol/l]; A – atomic mass of sorbed element; t – reaction time [s]; r – radius of globule [mm]. The parameters of Zn/Ag(I) ion exchange are presented in table 2.

In conclusion of this section, it is worth noting that even in the most recent research works about the diffusion of metal ions in solids carried out by chemists, the phenomenon of multistage diffusion is not well-understood. An attempt to describe the diffusion of metal ions in solids in one stage leads to the use of bulky empirical equations, and the value of the diffusion coefficient varies considerably during an experiment.

Table 2: Parameters of Zn/Ag(I) ion exchange in agar–ZnS nanocrystals gel matrix. Globule size 0.20 cm; average size of a monocrystal is 15 nm; interplanar distance is 1.086 nm;  $A_{Zn} = 65.4$ ; correction of suppression of self-diffusion of water by gel matrix is 0.8.

pC <sub>Ag(I)</sub>	<i>t</i> (°C)	lgK of the first stage (mg*ml <sup>-</sup> ${}^{1}$ *s <sup>-1</sup> )	$\mathbf{p}W_1(\mathbf{s}^{-1})$	<i>M</i> (μg/ml)	Self-diffusion of water D (*10 <sup>5</sup> cm <sup>2</sup> /s)
2.00	20	2.2	4.0	225	2.1
3.00	20 / 40 /	2.2 / 2.4 / 2.7	4.0/ 3.9 /	152 / 160 /	2.1 / 3.4 / 5.2
60	60	2.272.472.7	3.7	151	2.17 5.47 5.2
4.00	20	2.2	4.0	188	2.1
5.00	20	2.2	4.0	202	2.1

#### d. Effect of complexing agents on the process of sorption

The presence of ligands in the above-mentioned systems causes suppression of sorption in the case of phase-contact surface blocking, or formation of stable complexes. This effect is described by correction G (see the Eq.(3)), which is included in the sorption equation:

$$G = (1+C_{L}/(\Phi_{1}-\Phi_{2}))^{-1}; \Phi_{1} = K_{1*}[M'W] + K_{2*}[M'L] + K_{3*}[M'L_{2}]...; \Phi_{2} = K_{1*}[MW] + K_{2*}[ML] + K_{3*}[ML_{2}] + ...,$$
(3)

where M' and M are sorbed and desorbed metal ions, respectively; W – water molecules in the aquacomplexes; L – ion of complexing agent;  $K'_1$ ,  $K_2$ ... – rate constants of reaction of phase-contact surface with complexes of sorbed and desorbed metal ions, respectively <sup>[4]</sup>.

In the occurrence of phase contact, concentration ranges for the process of ion exchange can be classified into three: dependence on concentration of metal ions in solution, expressed as weak or practically absent if  $pC_{M'} < 5$ , and on the absence of ligands; there is a significant dependence of the process on concentration of metal ions in solution, especially in the presence of ligands at  $pC_{M'} > 5$ , and in the absence of ligands; there is desorption of metal ions at  $pC_{M'} > 12$  and the absence of ligands.

In <sup>[11]</sup>, the importance of the chemistry of equilibrium processes in solution on the sorption of microcomponents at low concentrations (less than  $10^{-8}$  mol/l) by precipitates of neutral hydroxides and metal oxyhydroxides, was presented. The study of the sorption of Ag(I) by metal oxides from borate solutions, in the presence of ammonia, was presented in <sup>[12]</sup>. The authors calculated the ratio of different forms of complexes [AgOH], [Ag(OH)<sub>2</sub><sup>-</sup>], [Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup>] and free Ag<sup>+</sup> in solution in percentages. It was suggested that excess of NH<sub>3</sub> causes a significant decrease in sorption due to reduced tendency of "hydroxyl-ion" bond formation between central metal ions through oxygen or water molecule of a coordinated, more saturated central ion.

In <sup>[3-6]</sup>, the theory of three-stage diffusion of metal ions in thin polycrystalline films at temperature range of  $0-100^{\circ}$ C was developed. This took into account the occurrence of a solid–liquid phase contact, in the presence of complexing agents and compounds, which are capable of blocking the surface of the polycrystalline thin films. The theory includes static and dynamic modes of the process of diffusion and sorption of metal ions. As an example, equations describing the ion exchange process between Pb(II) and Ag(I) upon the phase contact of PbS thin polycrystalline films with aqueous solutions of Ag(I) and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> ions, were presented. The equations take into account the concentration of Ag(I) hydroxycomplexes, oxide Ag<sub>2</sub>O and also concentration of complexes of Ag(I) with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>:

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 $\begin{array}{l} Ag^{+}+OH^{-}\leftrightarrow AgOH (lgK_{1}=3.3, lgK_{1S}=-4.1); \\ AgOH+OH^{-}\leftrightarrow Ag(OH)_{2}^{-} (lgK_{2}=3.1); \\ Ag(OH)_{2}^{-}+OH^{-}\leftrightarrow Ag(OH)_{3}^{2-} (lgK_{3}=2.7); \\ Ag(OH)_{3}^{2-}+OH^{-}\leftrightarrow Ag(OH)_{4}^{3-} (lgK_{4}=2.0); \\ 2AgOH\leftrightarrow Ag_{2}O+H_{2}O (lgK_{0x}=2.5); \\ Ag^{+}+S_{2}O_{3}^{2-}\leftrightarrow AgS_{2}O_{3}^{-} (lgKT_{1}=8.8); \\ Ag^{+}+2S_{2}O_{3}^{2-}\leftrightarrow Ag(S_{2}O_{3})_{3}^{2-} (lgKT_{2}=4.6); \\ Ag^{+}+3S_{2}O_{3}^{2-}\leftrightarrow Ag(S_{2}O_{3})_{3}^{5-} (lgKT_{3}=0.7). \end{array}$ 

 $K_{1S}$  is the constant of molecular solubility, which has the same value for all metal hydroxides with the same oxidation number <sup>[13]</sup>. The calculated values of the ion exchange reaction ability of each complex are as follows:

 $V_0 = 10^{8.4} * [Ag^+]^{1.2}, V_1 = 10^{4.2} * [AgS_2O_3^-]^{1.6}, V_2 = 10^{0.7} * [Ag(S_2O_3)_2^{3-}]^{3.0}, V_3 = 10^{0.5} * [Ag(S_2O_3)_3^{5-}]^{3.4}.$ 

## **Experiment and discussion**

# e. Sorption of Ag(I) ions by PbS thin polycrystalline films

Initially, thin films of PbS needed for carrying out the experiment was synthesized on PET substrates, by hydrochemical precipitation. The thickness of PbS thin films was measured with TEM HITACHI-18 equipment, and was from 0.1 to 0.5  $\mu$ m, corresponding to the mass of PbS from 0.3 to 1.5  $\mu$ g/cm<sup>2</sup>. Aqueous solutions of Ag(I) were then prepared by dissolving AgNO<sub>3</sub> salt (puriss. spec.) in double-distilled water. After this, the synthesized thin films were plunged into the solutions (placed in a thermostat), for a known period of time, for the process of ion exchange to take place. The study of the surface morphology and crystallographic structure of PbS thin films before and after ion exchange, was carried out by SEM on REMMA-202M equipment <sup>[3, 5, 6]</sup>.

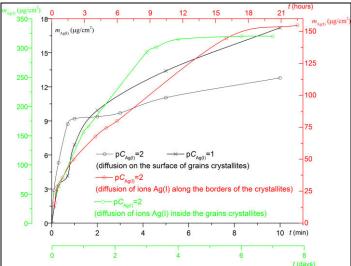


Fig. 2. Experimental curves of accumulation of Ag(I) ions on PbS films at temperature, t°=25°C. The color of data mapping corresponds to the color of X and Y axis, by which data values have been scaled.

Content analysis of Ag (I) and Pb(II) in solid and liquid phases was carried out by AAS (equipment: AAS-IN Carl Zeiss Jena) and XRF (equipment: VRA-20L Carl Zeiss Jena) methods. The results are presented in fig. 2. As seen, in black color, the degree of sorption of Ag (I) on PbS films depends considerably on the concentration of sorbed ions in solution. Also the beginning of any of the three stages is expressed by the emergence of a defined maximum in varying degrees. The cause of this phenomenon, which clearly does not fit in classical understanding of sorption isotherm, is the restructuring of crystalline lattice of the sorbent after about 70% conversion.

Equations of the kinetics of ion exchange across a solid-liquid phase contact, with respect to the effect of the thickness of thin films, are presented in <sup>[3, 5, 6]</sup>. Since the size of monocrystals being studied is about 30 nm, 99% of conversion time in a crystallite is about 40 days, which is much less than the time of ion transport from the phase boundary to the furthest layers from this boundary.

Thus, the total conversion time is determined by the transport time of the sorbed ions, owing to the second stage and to a much lesser extent, the conversion time inside the grains of crystallites. From the equations presented in <sup>[6]</sup>, equation has been deduced for calculating the conversion time of initial metal ions to sorbed ions, depending on the film thickness and a given degree of conversion under conditions of saturation of the surface of the film by the sorbed ions:

where  $\alpha$  is the degree of a given conversion. Time-dependence of a given conversion of metal ions is greatly determined by the thickness of film. Subsequently, at a temperature of 20°C,  $\alpha = 0.95$  and l = 500 nm, conversion time is 30 days, and at the l = 2000 nm, it is about 100 years.

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#### f. Sorption of Ag(I) by nanocrystals in gel matrices

Synthesis of nanocrystals in gel-matrices was carried out in two steps. In the first step, the gel-forming agent was dissolved in aqueous solution of metal ions, under heat upto 100 °C. Then, the prepared mixture was put dropwise, at a known pressure, in cuvettes with water, at 5-10 °C. In the second step, obtained globules of defined sizes, (which can be changed by changing conditions for the formation of drops), have were added to aqueous solution of Na<sub>2</sub>S; thereby forming gel-immobilized metal sulfide. Studies on the kinetics of Ag(I) sorption in gelatin-gel matrices of PbS, ZnS, CuS, MnS, were conducted in static mode. Samples were placed in solution of AgNO<sub>3</sub> with a concentration of  $1.0 \cdot 10^{-3}$  mol/l. Temperature of solution was 20 °C. The experiments were performed in fixed time. Content analysis of metal ions was performed as in section 2.1. The data is represented in fig. 3-fig. 6 <sup>[7-10]</sup>.

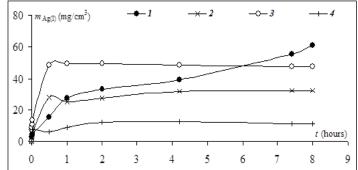


Fig. 3. Experimental kinetics of Ag(I) sorption (pCAg(I) = 3) by PbS (1), ZnS (2), CuS (3), MnS (4).

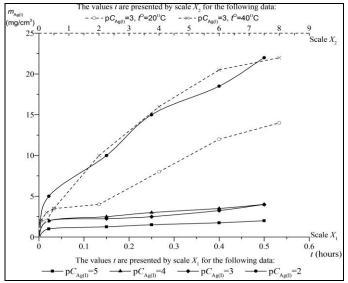


Fig. 4. Experimental kinetics of Ag(I) sorption by PbS-gelatin immobilized matrices at different concentrations of Ag(I) and at temperatures, 20 °C and 40 °C. The data of which t values are shown by the scale, X1, was obtained at 20 °C.

The two-stage process of accumulation of Ag (I) ions is seen in fig. 3 - fig. 6 as two regions on the curve. in the first region, there is a sharp increase of the silver concentration of up to 30 minutes. In the second region, this increase is expressed considerably weaker. By this, the first stage of ion exchange is the surface diffusion of Ag(I) ions and the second stage is the inner diffusion of these ions. Calculations carried out in <sup>[7-10]</sup> by the expression:

$$G_{298}^{0} = -RT_*\ln(K_{S(MS)}/K_{S(Ag2S)}).$$

Using the data of solubility constants of sulfides, MS and  $Ag_2S$ , cited in <sup>[3, 5, 6]</sup> indicated that energy efficiency of the above-mentioned reaction for these metals consist of:

 $\Delta C_{298}^{9}(Pb_{2}S)_{=-128.95 \text{ kJ/mol}}$   $\Delta C_{298}^{9}(Zn_{2}S)_{=-145.01 \text{ kJ/mol}}$   $\Delta C_{298}^{9}(Cu_{2}S)_{=-79.91 \text{ kJ/mol}}$   $\Delta C_{298}^{9}(Cu_{2}S)_{=-226.03 \text{ kJ/mol}}$ 

Λ

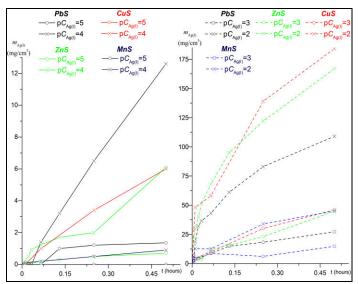


Fig. 5. Experimental kinetics of Ag (I) sorption by PbS, ZnS, CuS, MnS-agar immobilized matrices at different concentrations of Ag (I).

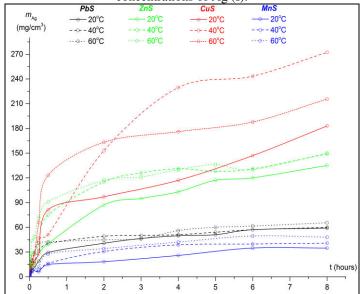


Fig. 6. Experimental kinetics of Ag(I) sorption, (pCAg(I) = 3) by PbS, ZnS, CuS, MnS-agar immobilized matrices at the 20,

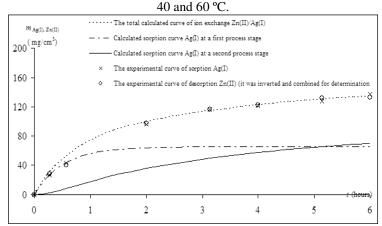
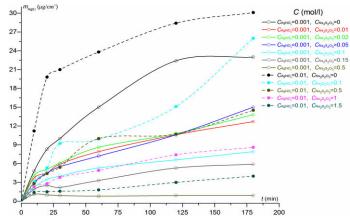


Fig. 7. Kinetic curves of Zn(II)/Ag(I) ion exchange in gel matrix of agar and ZnS nanocrystals; (Cag(I) = 1.00•10-3 mol/l). As an example, a mathematical description of the kinetic curves of Zn(II)/Ag(I) ion exchange has been presented in fig. 7. As can be seen, the calculations correspond well with experiment.

g. Effect of complexing agents on the process of Ag(I)/Pb(II) ion exchange in thin PbS polycrystalline films

The experiment was performed similar to as described in Section 2.1. Additionally, complexing agents were added to the solution (see fig. 8-fig. 14) [4].

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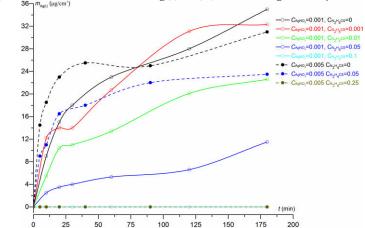


Fig. 9. Experimental kinetic curves of Ag(I)/Pb(II) ion exchange in the presence of  $N_2H_4CS$ , and at *pH*=3.

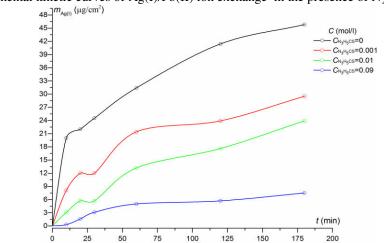
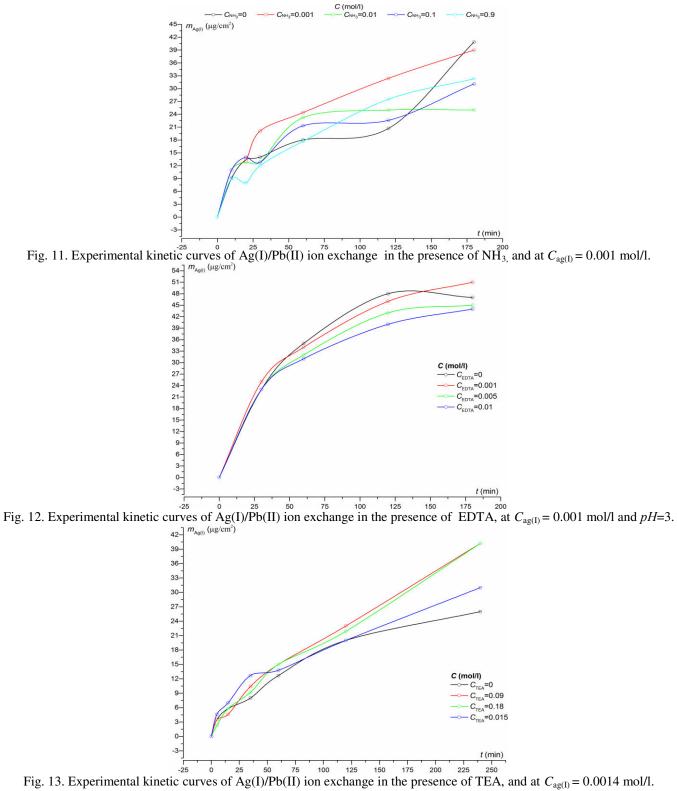


Fig. 10. Experimental kinetic curves of Ag(I)/Pb(II) ion exchange in the presence of  $N_3H_5CS$ , and at  $C_{ag(I)} = 0.001$  mol/l.



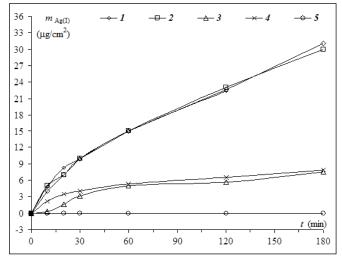


Fig. 14. Experimental kinetic curves of Ag(I)/Pb(II) ion exchange at  $CAgNO_3 = 0.001 \text{ mol/l}$ . Data (1)-absence of complexing agent; data (2)-(5)-presence of complexing agent with concentration,  $C_L = 0.1 \text{ mol/l}$ :TEA (2), N<sub>3</sub>H<sub>5</sub>CS (3), N<sub>2</sub>H<sub>4</sub>CS (4), NH<sub>3</sub> (5).

Fig. 8–14 show complexing agents such as EDTA, ammonia, TEA, have no significant effect on the kinetics of the process, while thiosulphate ion, thiourea, thiosemicarbazide significantly reduce its speed. The experimental data and calculations show decrease in rate of ion exchange in all cases, at initial equilibrium concentrations of free Ag(I) ions below  $10^{-10}$  mol/l or in the presence of complexing agents in solution. Typical in this regard, refer to fig. 14, which shows the kinetic curves of ion exchange at a Ag(I) concentration of  $10^{-3}$  mol/l, and at 0.1 mol/l concentration of various complexing agents. The first step in understanding the reasons for such difference in influence of the ligands under study was the calculation of initial equilibrium concentrations of all forms of coordinated Ag(I) compounds with all the complexing ligands, used in this work. From fig. 8 - fig. 14, it is clearly demonstrated that the greater the difference in stability between Ag(I) and Pb(II) complexes with a specific ligand, the more inhibited the degree of Ag(I)/Pb(II) ion exchange from solutions, containing that ligand.

# Conclusions

A significant difference between the use of thin films and nanocrystals in gel matrices consists of the fact that, in the films, a high degree of conversion of initial metal ions to sorbed ions, is not achieved due to the narrow diffusion front of sorbed ions from the surface phase contact into the inside of the solid. Thus, to achieve deep ion exchange at conditions of room temperature and appropriate reaction time, it is necessary to use films of definite thickness, implanted onto inert substrates or nanocrystals implanted into the polymer mass of matrix. For example, in the case of Ag(I) sorption by ZnS nanocrystals, its speed is high, although the concentration of ZnS in agar-immobilized matrix is not more than 4%. A significant characteristic of thin polycrystalline films is a small surface phase contact, providing only about 1% of the total sorptive capacity. This leads to the absence of dependence of the rate of ion exchange on metal ion concentration in the range of pC<5 and the absence of ligands in solution. In gel matrices with nanocrystals, the amount of metal ions on the surface phase contact is about 40% of the total amount, and the reaction zone is formed in the depth of the gel matrix, which leads to the dependence of the rate of ion exchange at any concentration of metal ions in solution, and a significant intensification of the process. In addition, in thin films of 100 µm, it is impossible to achieve a high degree of conversion for an appropriate experimental time. The shortcoming which impedes wide application of ion exchange was the absence of properties of selective absorption of available stock of ion exchangers and their limited exchange capacity. The latter circumstance in particular, is a very serious obstacle, limiting the use of the ion exchange process only in those cases where a given metal ion is in very dilute solutions, which are inconvenient for ordinary chemical processing <sup>[14]</sup>.

The field of application of inorganic ion exchangers is characterized by high selectivity, chemical, thermal and radiation stability in various conditions of their use. The most universal in terms of sorption, is the zinc sulfide, precipitated as a film on the surface of a granular carrier, whereas for the selective separation of platinum and precious metals, lead and copper sulphides could be used.

Generalized characteristics of sorbents based on thin films, gel matrices and precipitations are shown in table 3.

Sorbent	Thin	Precipitation	For these sorbents in brackets are the sizes of the side of cube													
Paramete rs	film PbS (thickne ss 400±50 nm)	PbS (Diameter of particle10 <sup>4</sup> ÷ 10 <sup>5</sup> nm)	PbS <sup>Agar</sup> (30±6		PbS <sup>Gelatin</sup> (110±34 nm)		ZnS <sup>Agar</sup> (35±5)		CuS <sup>Agar</sup> (42±6 nm)			MnS <sup>Agar</sup> (47±29 nm)				
<i>t</i> (°C)	20	20	20	40	60	20	40	20	40	60	20	40	60	20	40	60
$\frac{pW_{1}/pW_{2}/pW}{3(s^{-1})}$	1,3/1,9/5, 7	2/2,3/5,6	3,4//7, 5	2,4// 8	2,6// 8	2,6//7, 3	2,6// 7	2,7// 8	2,2// 8	2,2//7, 3	2//7, 8	2,3//8, 1	2,4// 8	2//7, 3	2,3//6, 8	1,7//7, 5
$M_1/M_2/M_3/$ (mg/cm <sup>2</sup> )	5/36/45 4	5/30/350	90//135		40//350 160//29		90	210//370			50//320					
t (hours)	2500	2500	48		48	48 48		48		48						
conversion degree	0,95	0,005	0,99		0,9	0,99		0,99		0,95						

Table 3: Parameters of ion exchange at phase contact of metal sulphide-Ag(I) aqueous solution  $(pC_{Ag(I)} = 2 \div 5)$ 

# References

- 1. Poate J. M., Tu K. N., Mayer J. W. Thin films-interdiffusion and reactions / Eds., Wiley-Interscience, New York, 1978, P.578.
- 2. Yaroslavtsev A.B. Ion exchange on inorganic sorbents // Russian chemical reviews, 1997. V. 66, № 7. P. 579-596.
- 3. Umarova N.N., Movchan N.I., Yusupov R.A., Korolev E.A., Morozov V.P. Ion exchange of silver(I) on thin PbS films as influenced by diffusion // Russian journal of general chemistry, 2003. V. 73. № 7. P. 999-1004.
- Umarova N.N., Movchan N.I., Yusupov R.A., Sopin V.F. The influence of complexing agents on the ion exchange Ag(I)/Pb(II) in thin polycrystalline PbS films// Russian journal of physical chemistry A, 2002. V. 76. № 8. P. 1341-1344.
- 5. Umarova N.N., Movchan N.I., Yusupov R.A., Sopin V.F. Calculation of the diffusion coefficient during the Pb(II)/Ag(I) ion exchange in a PbS thin-film sorbent// Russian journal of physical chemistry A, 2000. V. 74. № 9. P. 1547-1549.
- 6. Yusupov R.A., Tsivunin V.S., Umarova N.N., Abzalov R.F. Calculation of the parameters of a three-stage diffusion of metal ions in thin polycrystalline films// Russian journal of physical chemistry A, 1997. V. 71. № 3. P. 466-468.
- 7. Mikhailov O.V., Gafarov M.R., Yusupov R.A. Synthesis of gelatin-immobilized sulfides of p and d elements // Russian journal of general chemistry, 2000. V. 70. № 11. P. 1821-1822.
- 8. Yusupov R.A., Gafarov M.R., Mikhailov O.V. Ion exchange between an electrolyte aqueous solution and an agarimmobilized nanocrystalline metal sulfide // Russian journal of physical chemistry A, 2003. V. 77. № 11. P. 1827-1831.
- Mikhailov O.V., Gafarov M.R., Yusupov R.A. Lead(II) sulfide synthesis in lead(II) tetraoxophosphate(V) gelatinimmobilized matrix implantates and sorption activity toward silver(I) ions// Russian journal of general chemistry, 2003. V. 73. № 8. P. 1183-1187.
- 10. Gafarov M.R., Mikhailov O.V., Yusupov R.A. Agar-immobilized metal sulfides and their sorption power with respect to Ag(I) ions// Russian journal of general chemistry, 2004. V. 74. № 5. P. 791-792.
- 11. Egorov Y.V., Betenekov N.D. O khimizme sorbtsii mikrokomponentov fazoy tverdogo gidroksida [About the chemistry of sorption by phase of solid micro hydroxide] // Radiokhimiya [Radiochemistry], 1991. V. 31. №3. P. 78-87. (in Russian)
- 12. Ampelogova N.I. Sorbtsiya 110mAg oksidami metallov iz boratnykh rastvorov [Sorption 110mAg by metal oxides from borate solutions]. Сообщение (I) // Radiokhimiya [Radiochemistry], 1983. V. 23. №5. P. 584-589. (in Russian)
- 13. Yusupov R.A., Mikhailov O.V. Correlation between the stability constants and solubility constants of metal hydroxides // Russian journal of inorganic chemistry, 2002. V. 47, № 7. P. 1067-1069.
- 14. Melikhov I.V., Berdonosova D.G., Sigeikin G.I. Sorption mechanism and prediction of sorbents' behaviour in physicochemical systems // Russian chemical reviews, 2002. V. 71, № 2. P. 141-158.