EXPERIMENTAL STUDY OF KINETICS AND MECHANISM OF SEPARATION OF PALLADIUM BY THIOUREA FROM NITRIC ACID SOLUTIONS WHILE SOLVING THE PROBLEMS OF SEPARATION OF LIQUID RADIOACTIVE WASTE (RAW)

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A large experience on problem of utilization of radioactive waste of AEPS activity is accumulated (see Review on Purex-process [1]) where at treatment of (RAW) a use of different methods of fractionation is recommended, in particular, an isolation of fractionation of noble metals (NM), creating certain difficulties at hardening and reduction in the further process before the burial.

Solving the problem of fractional separation of noble metals (NM) in [2], we showed that at activated coal, modified by thiourea - $\{CS\ (NH_2)_2\}$- (TU) we managed to have palladium (one from NM of radioactive waste mass) from liquid nitric acid (6 N HNO_3) up to 10 mg / 1g of coal. However, there was a problem on rate of sorption and mechanisms of transformation of palladium complexes with (TU) in the medium of HNO_3.

In a number of papers devoted to the investigation of coordination properties of (TU) [3] the interaction of (TU) with HNO_3 is not reflected in detail, though nitric acid cannot only give up proton, but also oxidize thiourea, what in its turn, can effect the steadiness of its complexes with Pd. The present paper is devoted to study of the behavior of palladium complexes in the system [Pd - HNO_3 - CS $(NH_2)_2$], where by the assumption several parallel-sequentional processes with different rates can take place.

Using the method of potentiometric titration in the cell with the platinum indicator and chloride-silver electrode of comparison with the bridge from 1M of KNO_3, placed into the solutions, where titration conditions on thiourea, nitric acid and palladium content varied, we watched the process of formation of palladium complexes with thiourea (TU) in stages.

The initial potential Pt in the system [HNO_3 - (TU)] is determined by the concentrations of the components, as well as, by the adsorption of the products of their interaction in the process of titration [4]. It was shown by the change of the potential that the first to precipitate quickly was brown sediment, where the relation of Pd to (TU) {H} = 1:1 and 1:2. To get a soluble complex with the ratio of = 1:3 of orange color while adding the soluble (TU) the potential changes still more slowly, i.e. a displacement of the third acido-ligand is difficult. At (H) = 1:4 and higher a complex of the light-yellow color is formed. At the excess of (TU) the potential of the Pt-electrode drops abruptly corresponding to the adsorption on the surface of the product of the first stage of oxidation of thiourea [5].

The first stage of oxidation of (TU) by nitric acid can be written in the form of the equation:

$$2\{[H\text{-}SC\ (NH_2)_2]^+\} + 2\ HNO_3 + 2NO_3 = \{C_2S_2N_4H_6\}*\ 2NO_3 + 2\ HNO_2 + 2H_2O,$$

where the initially took up a proton thiourea at oxidation gives ion associate with formamidindisulfide (FMDS) - the product of its oxidation at the first stage. Spectrophotometrically it is difficult to fix, since the region of its absorption is in the ultraviolet (190-240nm) [5], where nitric acid also absorbs. However, in this system the product of interaction in the first stage is also a nitrous acid, which has a typical spectrum for its molecular form in the region of 350-400nm in the form of 4 peaks [6]. By the rate of appearance, growth and disappearance of this spectrum the process of interaction of pure thiourea (TU) with HNO_3 depending on HNO_3 concentration and the time of their contact was investigated. A two-ray spectrophotometer UV - VIS with the cells of 0,1 and 0,5 cm was used. It proved that pure thiourea (under our conditions it can considered as a redundant after the formation of the complex with Pd) accumulates HNO_2 with a different rate depending on HNO_3 concentration and the time of their contact. At the same concentration of (TU) in 4 N HNO_3 the spectrum nearly appears in 20 minutes, in 3 N – in an hour, in 2 N – in 2 hours. Process of accumulation of (FMDS) and HNO_2 in 1 N acid ends at this stage, but in 3-4 N HNO_3 (FMDS) oxidizes or decomposes [4,7] in 2-3 days. Thus, thiourea oxidation taking place in stage is a slow process and can be interrupted at different stages by a rapid process of complex formation with palladium depending on the order of discharge of reagents and their concentration. Characteristics of precipitates and their solubility depending on mole relationship (H), palladium weight (nitric acid salt) and thiourea in the initial state, reaction medium-6n HNO_3, volume -50ml are given in table 1.

Table 1

(H), M / mg	conc. Pd*10^{-3} M	weight, mg, color	atomic relation, Pd: S (#)	conc. Pd mkg/мл in 2 days
1: 4.0 / 4: 12.1	4	8.60, red	1.2 : 1	4.55
1:10.0 / 4: 30.4	4	5.00, yellow	2.0 : 1	0.13
1: 3.9 / 4 :12.0	2	7.00, brown	------	48.00
1: 6.5 / 4 :20.0	2	7.78, orange	1.6 : 1	1.30
1:16.0 / 4 :50.0	2	5.85, yellow	2.1 : 1	0.70
above sediment Pd $(SCN)_2$		orange		2.50
/2.8: 30.4	3	white	2:0.005	3.00

According to the micro- X-ray spectral analysis data (column # in the table) in the obtained precipitates washed to the neutral reaction and dried at room temperature, atomic relationships of Pd to S and solubility in the separated compounds are not the same. The least soluble is yellow sediment. It is known that the presence of the conjugated group - S—S - makes the compound [6] chromophorous. Thus, the analysis performed by the micro-X-ray spectral method confirmed a different relationship of sulfur depending on the color. White sediment obtained at interaction of the oxidized thiourea with Pd is especially compare.

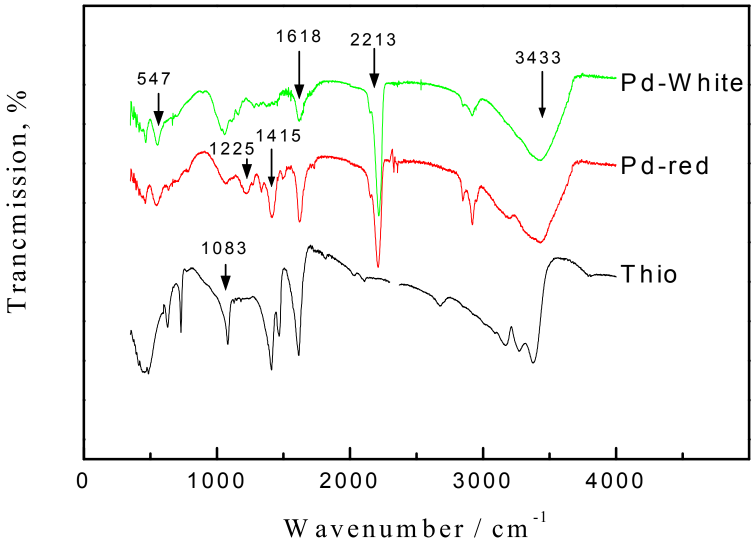

Fig 1 shows IR- spectra of the initial thiourea (Thio) and 2 markedly differing precipitates of red and white colors where the relationship of palladium and sulfur are sharply different.

Yamaguti et al. [8] studying IR-spectra of (TU) and synthesized complexes of Pt and Pd with (TU) think that the metal there is connected with the sulfur atom, because in the complexes spectra one can observe a decrease of the frequency of the stretching vibrations of the bond C—S (696 см$^{-1}$, bonds of S stretch for the metal) and the increase of the frequency of the stretching vibrations of C—N (1520см$^{-1}$, strengthening of the bond) as compared with the thiourea spectrum. From the fig.1 of the spectra of our compounds one can observe a change of the bands of vibrations, relating to the bond C—S (for the white sediment they are absent), and the appearance of the new bands, particularly 2196- 2213 см$^{-1}$ thiourea has not it, as well as weakly marked bands at 1334 см$^{-1}$ and 1225 см$^{-1}$. In the spectra of our red compound frequency (3433 см$^{-1}$) grow related to the vibrations of the bonds nitrogen-hydrogen what testifies about the strengthening of the bonds inside the group and its weakening with the rest mass at compound formation. However, there remains the band 1625 $см^{-1}$ which Yamaguti corresponds to bending vibrations of - NH_2 particle. The marked band in the thiourea spectrum at $1083см^{-1}$ almost becomes smooth. The latter, corresponds to stretching vibrations of N—C—N group, undergoes at complex formation changes related to the increase of bonds C=N (more than 2). It testifies to qualitative structural changes in the compound. By the assumption of a number of authors [9] bridge compounds with the participation of the group N≡C-S - (in the red compound) and N≡C— groups (in the white compound) are formed. The stretching vibration (ν_{CN}) there increases up to 2150-2182 $см^{-1}$ what results in the formation of the bidentate compounds with palladium X-ray phase analysis showed that our compounds with Pd are amorphous.

Thus, while getting practically insoluble compound of Pd with (TU) it is necessary to have the excess of (TU) against the ratio 1:4, after a subsequent oxidation of the thiourea excess and a destruction of its ligands in the complex, which takes place in the medium of 3-6n HNO_3 for 1-3 days.

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