Isolation of Precious Metals Contained in a Gold and Silver Alloy

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Abstract

Studies were performed concerning the process of obtaining noble metals (gold, silver, platinum, palladium) and tellurium, involving the following process stages: dissolving the gold and silver alloy in nitric acid solutions in the presence of ammonium nitrate under the gas phase pressure; purifying the leaching solutions via sorption (from platinum and palladium) and via hydrolytic precipitation (from copper and tellurium); electrochemical extraction of silver-containing solutions to produce cathode silver; conditioning and refining the gold sludge; an electrochemical extraction of eluates containing platinum group metals; obtaining tellurium concentrate. The number and type of linearly independent reactions have been found out for the dissolution of the parent alloy, key components for the stoichiometric description of chemical reactions in the system have been identified. A mathematical evaluation of quantitative changes in the complicated heterogeneous system with polyvalent nitrogen is presented.

Key words: gold, silver, platinum, palladium, nitric acid, ammonium nitrate, nitric oxide, molecular nitrogen, chemical reaction, stoichiometric factor, electrochemical extraction, refining

INTRODUCTION

Precious metals being not subject to corrosion and oxidation are widely used in mechanical engineering. Gold coatings with the thickness less than 1 µm are applied onto the surface of the spacecraft and satellites in order to reflect infrared radiation, as well as onto some internal parts in order to protect them against overheating and corrosion. The thinnest films of noble metals are applied inside and outside onto the covers of aircraft engines of high altitude airplanes. As an anti-corrosive coating, precious metals are used in the manufacture of pipes, valves and vessels for special purposes. A wide range of gold-containing pigments was developed for coating the metals, in particular or cladding steel pipes to transport corrosive materials. A very light, not darkening over time 80 % Pd + 20 % Ag alloy composition is used for manufacturing the scales used in astronomical and navigational instruments. For scientific and industrial purposes, one uses about 90 % of all the platinum metals, the rest is used in the jewelry industry [1–3]. The manufacture of precious metals is highly profitable [4], which encourages the modernization of the existing processing technologies and the development of novel ones, including the refining of a gold and silver alloy.

The purpose of the present work consisted in improving the technology of obtaining silver, gold, platinum, palladium and tellurium in the processing of the gold and silver alloy to extend the scope of using the precious metals in mechanical engineering.
EXPERIMENTAL

In order to optimize the silver refining process and to reveal regularities in the system of NO(g) – N₂(g) – H⁺(l) – NH₄⁺(l) – NO₅(l) – H₂O (system I) concerning the defixation of the bound nitrogen in the course of interaction between nitric oxide and ammonium ions in nitric acid solutions under hydrothermal conditions, we used a setup that consisted of two autoclaves connected with a gas transmission pipeline [5]. One of the autoclaves was purposed for producing nitric oxide NO, the other one was purposed for investigation. The autoclaves were made of VT 1-0 grade titanium; the volume of the liquid phase was equal to 0.7 dm³, the volume of the gas phase amounted to 1.0 dm³. The autoclave for investigation was equipped with an electrical heater and a driver for stirring the solution therein. The solution temperature as automatically maintained at a preset level (T±1.5 K) using a contact thermometer.

For NO to obtain, the first autoclave was loaded with M00K grade copper, a solution of nitric acid with the concentration of 4 mol/dm³, and then the system was heated up to 373 K [6]. The second autoclave with the solution un-der investigation was sealed, evacuated and heated to a preset temperature. After reaching a level of pressure equal to 1.65–1.7 MPa in the first autoclave, the second autoclave was fed with a gaseous mixture of the following composition (%): NO 96.8–97.0, NO₂ 3.0–3.2. Experimental conditions were as it follows: initial concentration of NH₄⁺ 0.182, that of HNO₃ 0.185 mol/dm³, the partial pressure of NO 0.378 MPa, temperature 373 K, stirrer rotation speed 18 s⁻¹. Using a sampler, every 15 min the solution was taken to analyze for NH₄⁺ [7] and HNO₃ [8].

RESULTS AND DISCUSSION

Known silver refining patterns [10, 11] using the technique of electrochemical refining (soluble anode) exhibit a number of disadvantages: an intense evolution of nitric oxide in the course of preparing the initial electrolyte; a large amount of metal (~15 %) in spent electrolytes, anode residues etc. An alternative with respect to the “classical” refining could be presented by an electrochemical extraction recovery of silver from nitric acid solutions (insoluble anode) in the technology of the complex processing of a gold and silver alloy [12]. After the dissolution of silver from the gold and silver alloy, the leach solution is subjected to two-stage purification: first of all, there is carried out sorption purification from platinum meals and a hydrolytic purification from copper and tellurium, with the further silver electrical extraction from silver-containing electrolyte to obtain branded silver. After the regeneration of the sorbent from the eluate via electrical extraction, a concentrate of platinum group metals is isolated. The gold sludge from leaching the silver goes to the refining operation to obtain branded gold. The hydrated cake obtained after hydrolytic treatment of the silver-containing electrolyte is used for the isolation of tellurium concentrate.

In order to realize the reaction of defixation the bound nitrogen aimed at suppressing the of nitrogen oxide emission, the dissolution of silver is carried out in the presence of ammonium nitrate. 0.723 mol/dm³ of NH₄NO₃. Then the system was sealed, evacuated and heated up to 378 K. At an overpressure in the 0.05 MPa, initial sampling was performed, whereas subsequent sampling for the analysis for NH₄⁺, HNO₃, and Ag⁺ [9] was carried out at the time intervals of 15 min.
isolation of the number and type of linearly independent reactions and major components for stoichiometric describing the chemical reactions in the course of dissolving the gold and silver alloy in nitric acid solutions with ammonium nitrate could allow optimizing the process of preparing the silver-containing solution for electrical extraction.

In the case when one cannot unequivocally predict the staged character of chemical reactions basing on theoretical assumptions, a corresponding kinetic model is constructed for each proposed mechanism. Basing on the experimental results, a model should be chosen that reflects in the best manner the experimental data within the chosen field of experimentation. Thus, the mechanism and kinetics of a complicated chemical reaction could be determined according to the following scheme [13, 14]:

− The formation of possible mechanisms for a complicated multi-stage reaction and the construction of a kinetic model for each of them;
− The qualitative analysis of competing reaction mechanisms and the evaluation of the properties of solutions for kinetic models;
− Planning the starting and precision experiments in order to obtain estimates for the kinetic constants of the models with the required accuracy;
− The discrimination of the models; planning a discriminatory experiment; choosing the reaction mechanism and the kinetic model those reflect most closely the results of the experiment.

In the course of the studies, it was found that the possible chemical interactions in the system I can be described by a stoichiometric reaction equation for defixation the bound nitrogen:

\[ \begin{align*}
8NH_4^+(l) + 4NO_3^-(l) & \rightarrow 4H^+(l) \\
+ 7N_2(g) + 14H_2O & \\
3NH_4^+(l) + NO_3^-(l) & \rightarrow 2H^+(l) \\
+ 3N_2(g) + 5H_2O
\end{align*} \]

The thermodynamic probability of reactions (1) and (2) is determined by the negative values of changing the Gibbs free energy: $-\Delta G = 2454$ and 1014 kJ/mol, respectively.

Chemical reactions \((r = 1, \ldots, R)\) are characterized by a conversion level $\xi_r$, an increment of the number of moles $\Delta n_k$ and stoichiometric coefficients $v_{k,r}$ for all the components \((k = 1, \ldots, K)\) in each of the reactions $r$. In order to calculate the conversion level of linearly independent reactions $\xi_r$, it is enough to have information concerning the number $R$ of increments $\Delta n_k$ for key components $k$. Basing on data concerning the value of $\xi_r$ on can calculate all the increments $\Delta n_k$ [15].

Using $NH_4^+$ and $H^+$ ions as the key components of the system I, we calculated the conversion level values of the reactions (1) and (2) at different moments of time from the beginning of the process. The values of $\xi_{r(1)}$ decrease during 30 min from 0 to $-0.02$ mol, indicating that the reaction (1) proceeds in the “reverse” direction, when the initial reactants of the reaction (1) exhibit reacting with the stoichiometry of the reaction (2). The values of $\xi_{r(2)}$ increase during 90 min from 0 to $0.08$ mol (Fig. 1).

With the help of experimental data obtained for $NH_4^+$ and $H^+$ ions there was changing the system composition revealed depending on the duration $\tau$ of the process ranged from 0 to

![Fig. 1. Reaction conversion level (ξ) depending on the process duration (τ): 1, 2 – reactions (1) and (2), respectively.](image)

![Fig. 2. Content of system components (n) depending on the process duration (τ): 1 – $NH_4^+$, 2 – $NO_3^-$, 3 – $H^+$, 4 – NO, 5 – $N_2$.](image)
Fig. 3. Gas pressure ($P$) in the system depending on the process duration ($\tau$): 1 – NO, 2 – $N_2$, 3 – $H_2O$, 4 – $\Sigma(NO, N_2)$, 5 – $\Sigma(No, N_2, H_2)$.

105 min (Fig. 2). One can see the content of the components of the system to vary within the following ranges (mol): $NH_4^+$ 0.183–0.092, $H^+$ 0.185–0.239, NO 0.122–0.004, $N_2$ 0.005–0.118, $NO_2^-$ 0.386.

The constant amount of $NO_2^-$ in the system indicates the formal participation of nitrate ions in the processes of interaction between the components.

The total partial pressure of gases in the system was calculated from the amounts of NO and $N_2$ in gas phase at a given moment of time, according to the formula:

$$P = \sum n_i V_i^1RT$$

where $R = 8.3144$ kJ/(mol · K).

The partial pressure of gaseous components in the system was determined depending on time (Fig. 3). It can be seen that for the period 0–45 min from beginning the process the NO pressure exhibits a decrease from 0.4 to 0.001 MPa whereas the pressure of $N_2$, on the contrary, increases from 0 to 0.24 MPa.

The distribution of NO and $N_2$ between the liquid and gas phases is determined by the equilibrium constants (Henry constant $K_H$) characterizing the interaction in the system at a given moment of time:

$$K_{H(NO)} = \frac{P_{NO(g)}N_{NO(l)}}{N_{NO(g)}N_{NO(l)}}$$

where $P_{NO(g)}$, $P_{N_2(g)}$ are the partial pressure values for the gas phase components; $N_{NO(0)}$, $N_{N_2(0)}$ are molar fraction values for the components of the system in the liquid phase.

The conversion level values for the reactions (1) and (2) exhibit opposite signs, so the initial components of the reaction (1) predominantly react according to the mechanism of the reaction (2) because of the lower kinetic complications. The stoichiometric analysis has demonstrated that the number of primary species of the conjugated reaction (1) is lower than that for the coupling reaction, (2) the 2.3-fold [16, 17].

The equilibrium conversion level values for the reactions (1), (2) were determined for the initial concentrations ($C_{i,0}$), and partial pressure values ($P_{i,0}$) of the components with the following composition (g/dm$^3$): $NH_4^+$ 3.3, $NO_3^-$ 22.8, $H^+$ 0.18, NO 0.378, $N_2$ 0.015. For the reactions (1) and (2) these values amounted to −0.077 and 0.3698 mol, respectively, having the same sign with the values of $\xi_n$, calculated from the kinetic characteristics. Basing on the values of $C_{i,0}$, $P_{i,0}$, $\xi_n$ there were determined equilibrium concentrations and partial pressure values for the components of the system (Table 1).

The equilibrium partial pressure of nitrous oxide is close to zero due to the deficiency of the component, which is confirmed by the shift of the reaction equilibrium towards product formation up to a complete consumption of the starting amount of NO.

It was established experimentally that the interaction between nitric oxide and the system components results in decreasing concentration of ammonium ion and increasing the amount of hydrogen ions during 0–90 min from the beginning of the process, which leads to an equilibrium relationship $\Delta n(H^+)/\Delta n(NH_4^+) = 1$.

### Table 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Components</th>
<th>$NH_4^+(l)$</th>
<th>$NO_3^-(l)$</th>
<th>$H^+(l)$</th>
<th>NO(g)</th>
<th>$N_2(g)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount, mol</td>
<td></td>
<td>0.102</td>
<td>0.368</td>
<td>0.266</td>
<td>0</td>
<td>0.107</td>
</tr>
<tr>
<td>Concentration, mol/dm$^3$</td>
<td></td>
<td>0.128</td>
<td>0.46</td>
<td>0.333</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Partial pressure, MPa</td>
<td></td>
<td>0</td>
<td>0.407</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
ISOLATION OF PRECIOUS METALS CONTAINED IN A GOLD AND SILVER ALLOY

The interaction in the equilibrium system is described by the following reaction:

$$4\text{NH}_4^+ (l) + 6\text{NO} (g) \rightarrow 4\text{H}^+ (l) + 5\text{N}_2 (g) + 6\text{H}_2\text{O} \quad (5)$$

Equation (5) differs from that obtained earlier basing on analyzing only the equilibrium concentrations of the components [18]:

$$2\text{NO} + 3\text{NH}_4\text{NO}_3 \rightarrow 3\text{N}_2 + 2\text{HNO}_3 + 5\text{H}_2\text{O} \quad (6)$$

The investigation of the system II demonstrated that the dissolution of metallic silver, occurring with the release of the reduction products of ions (mainly NO [19]) via reaction

$$\text{NO}_3^- \rightarrow \text{NO} + \text{N}_2$$

as approaching the equilibrium state, the concentration of ammonium ions and nitric acid exhibit a decrease, whereas the concentration of silver ions increases (Fig. 4).

Ammonium ions react with nitrogen oxide (II) according to the reaction of defixation the bound nitrogen:

$$\text{NH}_4^+ + \text{NO} \rightarrow 2\text{H}^+ + \text{N}_2 + \text{H}_2\text{O}$$

to regenerate the hydrogen ions and to cause the dissolution of additional amounts of metallic silver (Table 2).

As the system approached to the equilibrium state the ratio values of $$\frac{\Delta n_{\text{Ag}^+}}{\Delta n_{\text{NH}_4^+}}$$, $$\frac{\Delta n_{\text{Ag}^+}}{\Delta n_{\text{NH}_4^+}}$$ continuously increased within the ranges of 2.041–2.720 and 2.063–2.834, respectively; the ratio of $$\frac{\Delta n_{\text{Ag}^+}}{\Delta n_{\text{NH}_4^+}}$$ reached a minimum value after 105 min passed from the beginning of the process, which was taken into account in the construction and analysis of the stoichiometric model of chemical reactions, in the course of determining the number and type of linearly independent reactions.

For the system II we obtained the three linearly independent equations of reactions: equations (1) and (2), identical to those inherent in the system I, and equation

$$3\text{Ag}^+ + \text{NO}_3^- (l) + 4\text{H}^+ \rightarrow 3\text{Ag}^+ (l) + \text{NO(g}) + 2\text{H}_2\text{O} \quad (7)$$

corresponding to the reaction between silver and nitric acid. The thermodynamic probability for the reaction (7) to occur is supported by the negative value of changing the Gibbs free energy: $$-\Delta G = 70 \text{kJ/mol}$$.

For the case of choosing H+, $$\text{NH}_4^+$$, Ag+ ions as key components, we calculated the conversion level for the reactions (1), (2), (6): the values of $$\xi_{(1)}$$ decrease within the range of 60–150 min from 0 to $$-0.29 \text{ mol}$$, whereas the values of $$\xi_{(2)}$$ and $$\xi_{(6)}$$ permanently increase during 150 min from 0 to 0.76 and 0.97 mol, re-

TABLE 2
Ratio between the increments of components in an open system II

<table>
<thead>
<tr>
<th>Time, min</th>
<th>Increment of the amount of components, mol</th>
<th>Incremental ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$$\Delta n_{\text{NH}_4^+}$$</td>
<td>$$\Delta n_{\text{H}^+}$$</td>
</tr>
<tr>
<td>30</td>
<td>0.333</td>
<td>0.679</td>
</tr>
<tr>
<td>60</td>
<td>0.632</td>
<td>1.341</td>
</tr>
<tr>
<td>90</td>
<td>0.754</td>
<td>1.756</td>
</tr>
<tr>
<td>105</td>
<td>0.786</td>
<td>2.000</td>
</tr>
<tr>
<td>120</td>
<td>0.786</td>
<td>2.013</td>
</tr>
<tr>
<td>150</td>
<td>0.786</td>
<td>2.137</td>
</tr>
</tbody>
</table>
respectively (Fig. 5). Thus, the components of the conjugating reaction (1) interact via conjugated reactions (2) and (6) those occur with lower kinetic complications.

There was the number of system II components experimentally revealed depending on time at the following initial composition of the system (mol): $+4N\text{NH}_4^+$ 0.805, $-3NO_2^- 3.025, H^+ 2.22, N_2 0.005, Ag^0 7.238, NO 0, Ag^{+} 0$ (Fig. 6).

The experimental values for the $H^+, Ag^+$ ions are in a satisfactory agreement with the calculated values (see Table 2): during 90 min from the beginning of the experiment the amount of ammonium ions decreased by 94 %. Within the range of 120–150 min the amount of $NH_4^+$ ions asymptotically approaches zero, whereas the content of $N_2$ within this period of time increases by 9.8 % from the maximum level. After 150 min passed from the beginning of the process, the dissolution of silver occurs according to the reaction described by equation (7) without defixation the bound nitrogen, with NO gas evolution.

Nitrate ions are involved in the dissolution process as an oxidizer of silver. It has been demonstrated that the ratio $\Delta n(Ag^+)/\Delta n(NO_2^-)$ increases from 2 to 3 within the time interval from 0 to 150 min, which indicates that the dissolution of silver, first of all with defixation the bound nitrogen, and then without defixation thereof.

The calculated amounts of NO and $N_2$ allowed us to determine theoretically changing the partial and total pressure of the gases under the conditions of a closed system and constant volume: 1.6 MPa for NO and 3 MPa for $N_2$ (Fig. 7).

In the case of the experiment at a constant pressure of 0.05 MPa, the NO content in the gas phase for a period of 90–120 min from the initiation of the process was equal to 0.02–0.625 mol/dm$^3$, which indicates that defixation the bound nitrogen occurs with no complications within the initial period of silver dissolution (0–90 min), when the amount of $NH_4^+$ ions in the system is sufficient.

For the initial conditions of the system II mentioned earlier, we determined the equilibrium values of the conversion levels for the reactions (1), (2) and (6), those amounted to $-2.305, 0.759$ and $6.174$ mol, respectively, coinciding in the sign with the values of $\xi_i$, calculated from the kinetic characteristics. Basing on the values of the amounts of initial component and from the equilibrium conversion levels for the reactions, we determined the equilibrium concentrations and the partial pressure values for the components of the system (Table 3).
TABLE 3
Equilibrium parameters for the components of system II

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Components</th>
<th>NH₄⁺(l)</th>
<th>NO₃⁻(l)</th>
<th>H⁺(l)</th>
<th>Ag⁺(l)</th>
<th>NO(g)</th>
<th>N₂(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount, mol</td>
<td>0</td>
<td>2.114</td>
<td>0.036</td>
<td>2.278</td>
<td>1.046</td>
<td>0.716</td>
<td></td>
</tr>
<tr>
<td>Concentration, mol/dm³</td>
<td>0</td>
<td>2.349</td>
<td>0.4</td>
<td>2.531</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Partial pressure, MPa</td>
<td></td>
<td>3.55</td>
<td>2.19</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 4
Ratio between the increments of components in an isolated system II

<table>
<thead>
<tr>
<th>Time, min</th>
<th>Increment of the amount of components, mol</th>
<th>Incremental ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>−Δn₅H⁺</td>
<td>Δn₅H⁺</td>
</tr>
<tr>
<td>30</td>
<td>0.538</td>
<td>0.267</td>
</tr>
<tr>
<td>60</td>
<td>0.786</td>
<td>0.390</td>
</tr>
<tr>
<td>90</td>
<td>0.910</td>
<td>0.452</td>
</tr>
</tbody>
</table>

The equilibrium concentration of NH₄⁺ ions is equal to zero; a relatively small residual amount of H⁺ ions could be caused by their participation in dissolution of silver, after the exhaustion of ammonium ions, which is confirmed by shifting the equilibrium of the reaction (7) towards products formation up to a complete consumption of the initial components.

In order to study the behaviour of the components in a closed system we conducted an experiment on dissolving the silver at a temperature of 373–378 K in the solution with the initial concentration, NH₄⁺ 0.99, HNO₃ 0.52 mol/dm³ (Table 4).

One can see that as approaching the equilibrium, the ratio values between the increments for NH₄⁺, H⁺, Ag⁺ ions in different combinations remain almost constant (~2, ~1, ~2, respectively), which allows us to reduce all the interactions in the system to a single reaction. Provided that Δn(H⁺) = Δn(Ag⁺), 2Δn(NH₄⁺) = Δn(Ag⁺), all the interactions in a closed system II could be described by the following equation:

\[
2\text{H}^+(l) + \text{NH}_4^+(l) + \text{NO}_3^-(l) + 2\text{Ag}^+ \rightarrow 2\text{Ag}^+(l) + \text{N}_2(g) + 3\text{H}_2\text{O} \tag{8}
\]

The fact that the nitrogen oxide as the intermediate reaction product is absent in equation (8) is caused by that that being evolved in the course of the dissolution of silver, the nitrogen oxide participates in defixation the bound nitrogen according to equations (1) and (2).

The total interaction between the components in the system II isolated from the environment at any time passed from the beginning of the process can be described by the three linear independent equations for the reactions (1), (2) and (6).

CONCLUSION

1. The fundamental stage of the technology for obtaining the precious metals consists in the dissolution of gold and silver alloy, which occurs in a non-equilibrium system N₂(g) – H⁺(l) – NH₄⁺(l) – NO₃⁻(l) – Ag⁺(l) – Ag – H₂O (system II), includes defixation the bound nitrogen and can be described by the three linear independent reactions:

\[
8\text{NH}_4^+(l) + 4\text{NO}_3^-(l) + 2\text{NO}(g) \rightarrow 4\text{H}^+(l) + 7\text{N}_2(g) + 14\text{H}_2\text{O} \\
3\text{NH}_4^+(l) + \text{NO}_3^-(l) + 2\text{NO}(g) \rightarrow 2\text{H}^+(l) + 3\text{N}_2(g) + 5\text{H}_2\text{O}
\]
3Ag⁺ + NO₂⁻(l) + 4H⁺ → 3Ag⁺(l) + NO(g) + 2H₂O

These reactions are characterized by the negative values of changing the Gibbs free energy, and thus they can proceed with the formation of products up to a complete consumption of initial reagents.

2. In the equilibrium system II the resulting interactions can be described by a single stoichiometric equation of the reaction

2H⁺(l) + NH₄⁺(l) + NO₂⁻(l) + 2Ag⁺ → 2Ag⁺(l) + N₂(g) + 3H₂O

(8)

For the calculation of changing the content of all the components inherent in the system (II) it is enough to monitor the amount of NH₄⁺, H⁺, Ag⁺ ions.

3. The studies performed demonstrated that there is fundamental possibility of obtaining silver-containing solutions (electrolytes) with no formation of environmentally hazardous nitrogen oxides in significant amounts. The technology developed and implemented basing on electrochemical silver extraction provides obtaining the silver and gold of the highest grades, as well as the concentrates of platinum group metals and tellurium in the course of complex processing the gold and silver alloy.

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