

Gold-silver alloys anodic dissolution research in hydrochloric acid electrolytes

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Relevance of research

- Investments were decreased in the mineral resource base development in recent years and, accordingly, the amount of explored reserves were declined. At the same time, the market maintains a constant demand for precious metals, which shows the increasing supply from year to year.
- The share of process from secondary raw materials tends to grow, and the production cost of precious metals from secondary raw materials is 6-10 times lower than from primary.

- Obtaining refined precious metals is an extremely difficult technological task because it is a multi-stage process, with a significant amount of reverts materials requiring a return to technology.

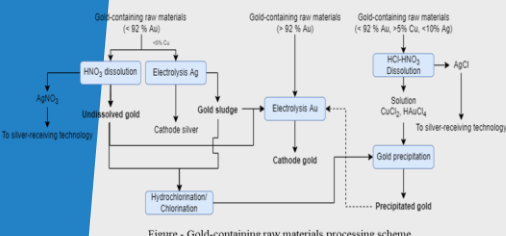


Figure - Gold-containing raw materials processing scheme

Table 1- Gold supply at 2018-2019

Category	2018	2019
Mining	3,509.3	3,463.7
Refining	-12.5	8.3
Secondary processing	1,176.1	1,304.1
Total	4,673.0	4,776.1

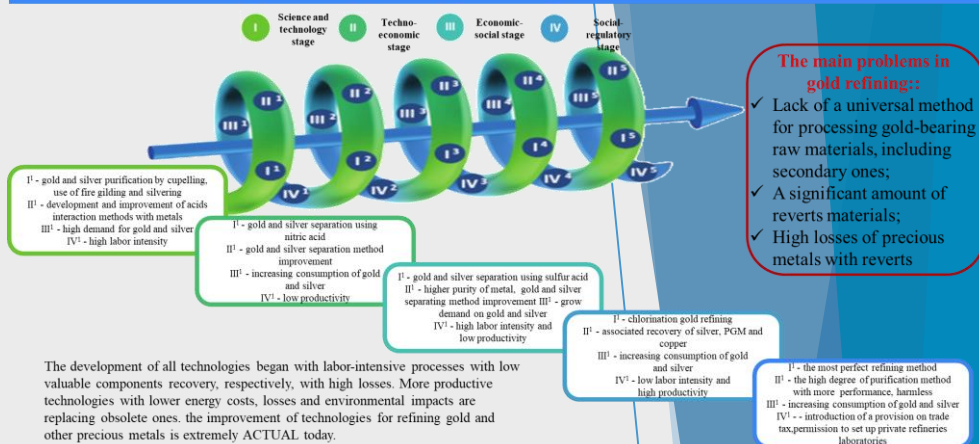
Table 2 -Chronology of technologies origin for the processing of gold-bearing raw materials

Method	Year	Method	Year
Separation Au and Ag at roasting with:		Melting	3500 B.C.E.
• salt (NaCl)	109 B.C.E.	Melting in blast furnace	XIX century
• sulfur	1150...1200	Melting in electric furnace	1920...1940
• arsenic sulfide	1300...1400		
• saltpetre	1556		
• sulfur and ferrom	1758		
Capitation	1400 B.C.E.	Liquid extraction	1970
Acid refinery	1400...1600		
Water chlorination	1833	Electrolysis refinery:	
Milner process	1867	Moskine process	1884
		Wohlwill process	1898

Therefore, one of the most important problems of the industry, including the growing need for recycling of secondary raw materials, is the improvement of existing technologies and introducing the new that provides:

- reduction of the number of stages of the production process;
- reduction of the duration of the processes;
- reduction of the volume of chemical reagents;
- reduction of harmful emissions and production waste.

Gold refining technologies development stages



The development of all technologies began with labor-intensive processes with low valuable components recovery, respectively, with high losses. More productive technologies with lower energy costs, losses and environmental impacts are replacing obsolete ones, the improvement of technologies for refining gold and other precious metals is extremely ACTUAL today.

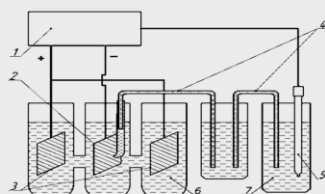
Purpose and research objective

The purpose is establish the possibility of electrochemical dissolution of a gold-silver alloy with an increased silver content (more than 25%) in a hydrochloric acid solution

Research objective:

- Thermodynamic substantiation of the possibility of electrochemical dissolution of a gold-silver alloy with an increased silver content (more than 25%) in a hydrochloric acid solution;
- Definition of features of anodic polarization of a gold-silver alloy (30% Ag) in a hydrochloric acid solution;
- Study of the dissolution specific rate dependence of an alloy in a hydrochloric acid solution on the anodic current density and voltage

Anode: Au-Ag with 30 % of silver
Electrolyte: 100 g/l HCl
Reagents: hydrochloric acid GOST 3118;
potassium chloride GOST 4568;
distilled water GOST 670 .



1 – rectifier; 2 – Au-Ag anode; 3 – cathodes; 4 – salt bridges; 5 – Ag/AgCl electrode; 6 – hydrochloric acid electrolyte; 7 – KCl solution.

Figure – Schematic electrolysis installation scheme

Thermodynamic substantiation of the electrochemical dissolution possibility of a gold-silver alloy

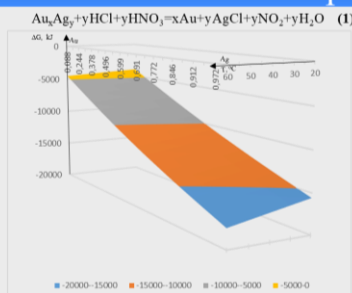


Figure 1- Gibbs energy dependence on the gold-silver alloy composition and the temperature for the reaction (1)

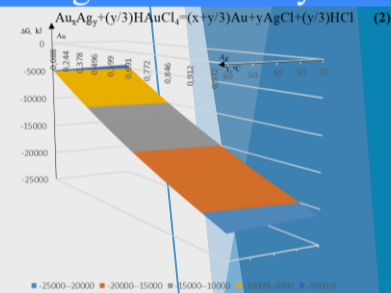


Figure 2- Gibbs energy dependence on the gold-silver alloy composition and the temperature for the reaction (2)

According to the literature analysis and practice, it was found that for the electrolysis process efficiency, a small amount of nitric acid is added to the electrolyte, i.e. oxidizing agent. Silver oxidation in the absence of an oxidizing agent does not occur in hydrochloric acid solutions, because Gibbs energy of reaction (3) is higher than 0



therefore, the formation of a silver chloride passivation layer in the absence of HAuCl_4 and HNO_3 in the hydrochloric acid solution is unlikely.

Anodic polarization variation of gold-silver anode electrochemical dissolution at 0,8 и 1,2 V

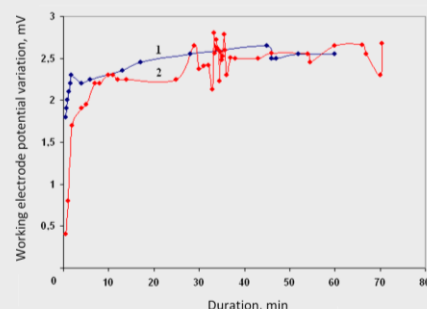


Figure 1 - Anodic polarization variation depending on the duration for test gold-silver alloy at U=0.8 V, ja=100 (1) и 4000 (2) A/m2, t= 60 °C

The production of gold at the cathode did not occur at a voltage of 0.8 V, which may be connected with fact that the potential of reaction (1) is 1 V.

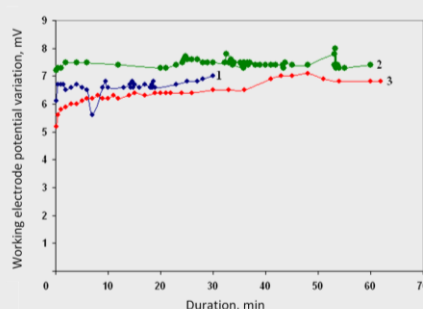
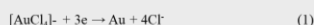


Figure 2- Anodic polarization variation depending on the duration for test gold-silver alloy at U=1.2 V, ja=1000 (1), 2000 (2), 4000 (3) A/m2, t= 60 °C

The electrolysis process was already actively proceeding at a voltage of 1.2 V, the cathodes were covered with a layer of gold, while the higher the current density, the more intensive the electrolysis was. The anode also did not passivate.

Anodic polarization variation (at 1,4 V) and specific rate of gold-silver anode electrochemical dissolution

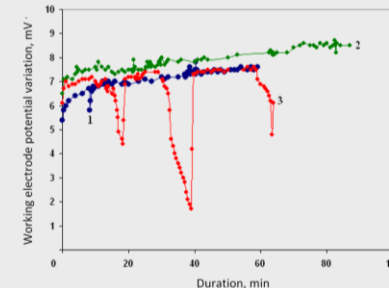


Figure 1 – Anodic polarization variation depending on the duration for test gold-silver alloy at U=1.4 V, ja=1000 (1), 2000 (2) и 4745 (3) A/m2, t= 60 °C

Increasing the voltage supplied to 1.4 V from the current source raised the dissolution rate of the anode, but since the chlorine evolution potential equals 1.359 V at high current densities, the reaction of gold anodic dissolution and chlorine evolution at the anode become competing.

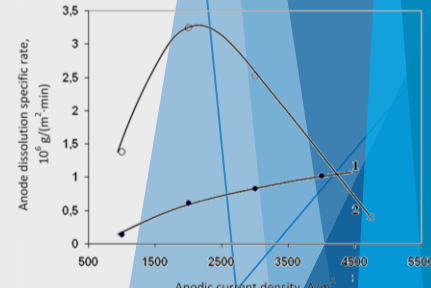


Figure 2 - Anode dissolution specific rate depending on anodic current density for test alloy in hydrochloric solution at the voltage, V: 1) 1.2; 2) 1.4; t= 60 °C

The process mechanism requires additional research in order to establish the reasons for the difference in the dependences of the dissolution rates on the current density and to establish the dependence of the dissolution rate on the silver content in the alloy.

Conclusions

- The thermodynamic evaluation confirmed the possibility of electrolysis of gold-silver alloys in pure hydrochloric acid electrolytes;
- The studies confirmed the absence of the silver chloride layer formation on the gold-silver anode surface during electrolysis from pure hydrochloric acid electrolytes with an HCl concentration of 100 g/l at a temperature of 60 °C;
- The maximum dissolution rate is achieved at U = 1.4 V, ja = 2000 A/m² for Au-Ag alloy with 30% silver content.



The results require testing on copper-gold and Au-Ag-Cu alloys and can form the basis of new technology for processing gold-bearing raw materials in the case of successful experiments.