Mechanical activation and electrolysis of gold from goldsmith's waste

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The intensification of the thiourea leaching of gold from goldsmith's waste (Košice, Slovakia) using mechanical activation as the pretreatment step. The leaching of "as-received" sample in an acid thiourea solution resulted in 77 % Au dissolution, after mechanical activation 98 % of the gold was leached during 120 min. The activation was performed in an attritor using variable milling times. The physico-chemical changes in the waste as a consequence of mechanical activation had a pronounced influence on the subsequent gold extraction. Maximum recovery of gold was reached behind 60 minutes at optimum conditions of electrolysis.

Keywords: *waste, gold, mechanical activation, leaching, electrolysis.*

Introduction

Au-Ag wastes represent the important source of precious metals. The problem of recycling secondary resources containing noble metals is in the centre of interest of all developed economies of the world. Therefore, this problem is being tackled as one that is not only a technological, legislative or economical problem, but also one related to the environmental protection. Obtaining of these metals from waste materials and lowering the environmental load by recycling is a very complex issue that requires an all-round strategy and the application of a number of methods [1, 2, 3].

The secondary resources of gold are generated by craftsmanship and industrial processing of gold and alloys thereof (goldsmith's fractions and fillings, abrasives tailings, clad clock waste and used melting crucibles), by amortization of products (ceramic waste, old jewellery and fractions thereof, dental alloys, graded electrical and electronic waste, non-graded electronic waste), by collecting (medals, coins, bank alloys, sacral and museum treasures) [4].

Gold is wired in with the component of Au-wastes included with accompanying elements and cannot come in contact with leaching solutions. Leaching of Au-wastes without pretreatment remitted in low Au extraction [5].

Hydrometallurgical processes are especially suitable for the treatment of gold-bearing and goldsmith′s waste materials. Contemporary hydrometallurgy of gold is based on the application of cyanide leaching. The cyanide process is indeed a highly toxic technology. Gold is sometimes finely disseminated in waste materials and cannot come in contact with cyanide solution [6, 7].

The thiourea process of gold extraction from wastes consisting of gold leaching into the thiourea solution, and consequent precipitation of these metal from the solution is, with regard to the ecological character of thiourea, the perspective alternative hitherto the most used cyanide method. Thiourea leaching has more rapid kinetics for gold solubilization than classical cyanide leaching [8, 9, 10, 11, 12, 13, 14].

The chemical, biological and physical pretreatments are applied as intervention steps directed to the solid phase the goal of which is to change the composition and particle size of the gold bearing substances and thus to facilitate the subsequent leaching. Simultaneously with examination of chemical, biological and physical pretreatment the new processes of mechanochemical pretreatment are being successfully applied in fundamental research as well as in plant operations [15]. In this process are the minerals subjected to intensive milling. This milling results in particle disintegration and chemical or physicochemical transformations, which significantly affect the subsequent mineral processing operations.

The aim of this work was to examine the possibility of recovering gold from the goldsmith's waste using thiourea leaching. A mechanical activation was applied in order to determine its effect on the recovery of gold. The additional intent was to examine the possibility of recovering gold from the thiourea waste solution in metallic form.

Experimental

Material

Goldsmith's waste (Košice, Slovakia) was selected as input material for testing mechanical activation and subsequent thiourea leaching of gold. This input material is also called as a goldsmith's shoddy goods.

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The chemical composition of the waste was as follows: 0.67 % Au, 0.54 % Ag, 0.05 % Pd, 34.5 % Cu, 15.4 % Fe, 28.9 % Ni, 13.6 % Sn, 3.1 % Zn.

Mechanical activation

Mechanical activation was performed in a stirring ball mill (attritor) Molinex PE-075 (Netzsch, Germany) under the following conditions: volume of milling chamber 500 ml, weight of sample 50 g, steel balls (2000 g of 2 mm diameter) as milling means, milling medium 200 ml water, milling time 15, 30, 45 and 60 min, revolutions of the milling shaft 600 min^{-1}, ambient temperature.

Physico-chemical characterization

The specific surface area, S_A was determined by the low temperature nitrogen BET adsorption method using a Gemini 2360 sorption apparatus (Micromeritics, USA). The particle size distribution of the milled goldsmith′s waste was measured by a laser beam scattering in a Helos and Rodos granulometer (Sympatec GmbH, Germany). The mean particle diameter was calculated as the first moment of the volume size distribution function.

Thiourea leaching

The leaching was investigated in a 500 ml glass reactor into which 400 ml of leaching solution having 10 gl^{-1} $CS(NH_2)_2$, 5 gl^{-1} $Fe_2(SO_4)_3.9H_2O$, 10 gl^{-1} H_2SO_4 and 10 g of milled goldsmith′s waste were added. The leaching was performed at pH = 1 during 120 min at 293 K using a stirring rate of 8.33 s^{-1}. Aliquots (5 ml) of the solution were withdrawn at appropriate time intervals for determination of the content of dissolved gold by AAS method.

The leaching kinetics of gold were best fitted by the kinetic equation:

$$-\ln\left(1-\varepsilon_{Au}\right)=k_{Au}t_L \qquad (1)$$

where ε_{Au} is recovery of gold into the leach solution, k_{Au} is the rate constant (s^{-1}) and t_L is the leaching time (s).

Electrolysis

The electrolysis was performed in a 1300 ml a laboratory electrolyzer (Košice, Slovakia) with carbon cathode and Pt-anode [7]. The following experimental conditions have been selected: total time of electrolysis, t_E = 60 min; catholyte – thiourea with contents of goldsmith′s waste, catholyte volume – 800 ml; anolyte 10 gl^{-1} H_2SO_4, anolyte volume – 500 ml; current density 1000 Am^{-2}; volume of velocity flow of catholyte and anolyte, V_V = 1600 $ml.min^{-1}$; temperature T = 25 °C; pH = 1. The redox potential in optimum leaching conditions was 500-523 mV (versus S.H.E.). Electrochemical redox potential (Pt with fiber with respect to saturated argentochloride electrode) was measured using a VDM-1 milivoltmeter (MESIT Company, Czech republic).

Results and discussion

Physico-chemical changes of mechanically activated waste

The mechanical activation of goldsmith′s waste (gold-bearing waste) is characterized by an increase in specific surface area. The effect milling of the goldsmith′s waste on its surface area is shown in Fig. 1. The original value of surface area (0.5 m^2g^{-1}) increased rapidly to 18.7 m^2g^{-1}.

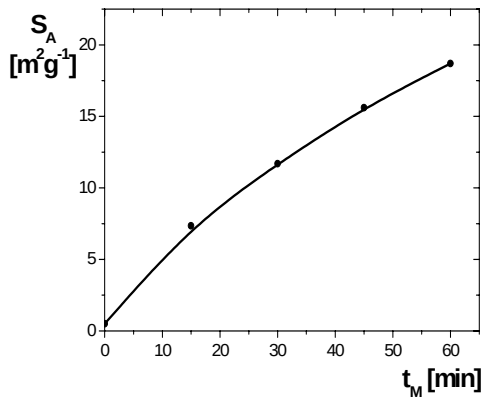

Fig. 1. The specific surface area, S_A as a function of milling time, t_M, mechanically activated sample.

Increases in the fraction of fine particles and specific surface area are changes, which are frequently observed as the consequence of intensive milling [16]. This manifold new surface area formation correlates with the particle size analysis of the milled sample. The "as-received" sample has a 100 % abundance of particles with a diameter under 30 μm but only 10 % of particles with diameter less than 10 μm. For the mechanically activated sample the particles are relatively smaller than those of the "as-received" sample. In Table 1 the percentage of undersized particles is given for these samples.

Tab. 1. The percentage of undersized particles for goldsmith's waste.

Sample	**Milling time** t_M [min]	**Undersize** [%]			
		- 5 [μm]	**- 10** [μm]	**- 40** [μm]	**- 60** [μm]
" as-received "	-	23	68	96	100
mechanical activated	60	100	100	100	100

Thiourea leaching of gold from mechanically activated sample

The dependence of gold recovery on leaching time is represented for different mechanically activated samples in Fig. 2. While only the recovery of 77 % of Au was reached after 120 min leaching for the "as-received" sample (curve 1), this percentage of recovery was attained already at t_L < 15 min for activated samples (curves 3, 4 and 5). The results for the mechanically activated samples (curves 2-5) indicated that surface changes of the goldsmith′s waste brought about an acceleration of the process of thiourea leaching. It was possible to achieve a gold recovery of 98 % after two hours of leaching for mechanically activated sample (curve 5).

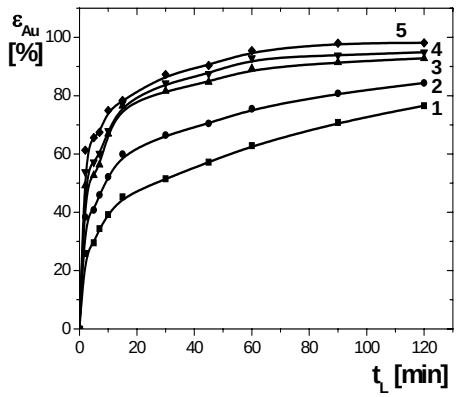

Fig. 2. Recovery of gold, ε_{Au} vs. leaching time, t_L for mechanically activated samples. Milling time, t_M: 1- non-activated sample, activated samples-milling time, t_M: 2 – 15 min, 3 - 30 min, 4 – 45 min, 5 – 60 min.

Senna [17] analysed the effect of surface area and the structural disordering on the leachability of mechanically activated samples. In order to solve the problem – whether surface area or structural disorder are predominant for the reactivity - the rate constant is divided by the proper surface area and plot against the applied energy by activation (or milling time). In our occurrence, if the rate constant of gold leaching is divided by the surface area remains constant with respect to the applied milling time, as shown in Figure 3, then the measured surface area may be the effective surface area and at the same time, the reaction rate is insensitive to structural changes. This is a case of milling in water medium.

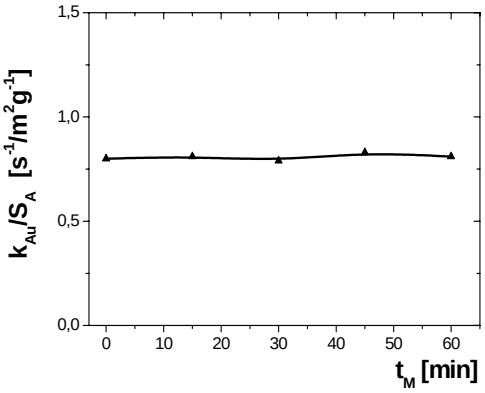

Fig. 3. Specific rate constant of gold leaching, k_{Au}/S_A vs. milling time, t_M for the mechanically activated sample.

The dependence of gold recovery from thiourea solution on the time of electrolysis is represented in Fig. 4 for activated and non-activated samples. Electrolysis enables to obtain from this solution waste up 99 % recovery of gold in time a sixty minutes.

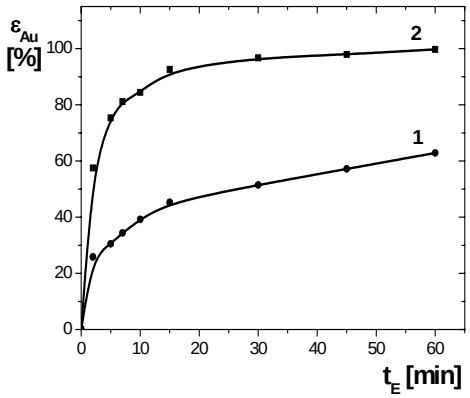

Fig. 4. Recovery of gold from thiourea solution, ε_{Au} vs. time of electrolysis, t_E.
1- non-activated sample, 2- mechanically activated sample, milling time, t_M = 60 min.

Conclusions

Mechanical activation of goldsmith`s waste has a positive influence on gold leaching. An optimum Au recovery of 98 % was achieved from the mechanically activated sample already in 120 minutes of thiourea leaching. The leaching of "as-received" (non-activated) waste resulted in only 77 % Au dissolution. The consumption of milling time has an influence on the physico-chemical changes of gold-bearing waste due to mechanical pretreatment as is evident in the thiourea leaching. Thiourea leaching is non-toxic and has more rapid kinetics for gold solubilization in comparison with the classical cyanide leaching. Elektrolytic process obtaining of gold from solution containing of goldsmith`s waste is suitable and very advantageous kinetic progress for acquirement of gold in metallic form. Over most 99 % recovery of gold was reached behind 60 minutes at optimum conditions of electrolysis.

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