Leaching of gold from a mechanically and mechanochemically activated waste

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The intensification of leaching of gold from a waste using mechanical activation (milling in water) and mechanochemical activation (milling in thiourea solution) were studied as the pretreatment steps. The leaching of "as-received" sample in an acid thiourea solution resulted in 78 % Au dissolution, after mechanical activation 98 % and mechanochemical activation up to 99 % of the gold was leached during 120 min. The mechanochemical activation resulted in an increase of the specific surface area of the waste from 0.6 m^2g^{-1} to a maximum value of 20.5 m^2g^{-1}. The activation was performed in an attritor using variable milling times. The physico-chemical changes in the waste as a consequence of mechanochemical activation had a pronounced influence on the subsequent gold extraction.

Keywords: *waste, gold, thiourea, mechanical activation, mechanochemical activation.*

Introduction

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 [5, 12, 14, 15, 18].

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 jewelry and fractions thereof, dental alloys, graded electrical and electronic waste, non-graded electronic waste) [10]; by collecting (medals, coins, bank alloys, sacral and museum treasures) [9].

Gold is impractical connected on 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 [4].

Hydrometallurgical processes are especially suitable for the treatment of gold-bearing and goldsmith′s waste materials. Modern 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 [13, 20].

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 [1, 3, 6, 8].

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 [2, 16]. In this process which is called mechanical activation the minerals are subjected to intensive milling. This milling results in particle disintegration and chemical or physicochemical transformations which significantly affect the subsequent mineral processing operations.

Mechanochemical activation integrates milling and leaching operations into a single step. In addition to an improvement in milling performance (the leaching agent also acts as a milling additive) there are operational benefits relating to the economy of the overall process. Generally, the mechanochemical activation of solids (minerals, wastes, etc.) leads to positive influence on the hydrometallurgical operations [2, 19].

The mechanochemical approach has been applied for refractory materials with the aim of changing the chemical composition and/or the particle sizes of the gold-bearing raw materials, thus facilitating the subsequent leaching in order to increase the recovery of noble metals [7, 11].

The aim of this work was to examine the possibility of recovering gold from the golden waste using thiourea leaching. A mechanical and mechanochemical activation was applied in order to determine its effect on the recovery of gold.

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Experimental

Material

Golden waste (Slovakia) was selected as input material for testing mechanical and mechanochemical activation and subsequent thiourea leaching of gold. The chemical composition of the waste was as follows: 0.68 % Au, 0.05 % Pd, 36.5 % Cu, 15.4 % Fe, 3.12 % Zn.

Mechanical activation (milling in water)

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 (200 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.

Mechanochemical activation (milling in thiourea solution)

Mechanochemical 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 (200 g of 2 mm diameter) as milling means, milling medium 200 ml of thiourea solution consist of 10 gl^{-1} $CS(NH_2)_2$, 5 gl^{-1} $Fe_2(SO_4)_3.9H_2O$ and 10 gl^{-1} H_2SO_4; 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 ground 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 golden 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.

Results and discussion

Physico-chemical changes of mechanically and mechanochemically activated waste

The mechanical and mechanochemical activation of golden waste is characterized by an increase in specific surface area. The effect milling of the waste on its surface area is shown in Fig. 1. The original value of surface area (0.6 m^2g^{-1}) increased rapidly to 19 m^2g^{-1} and finally to a maximum value of 20.5 m^2g^{-1}, with increase milling time.

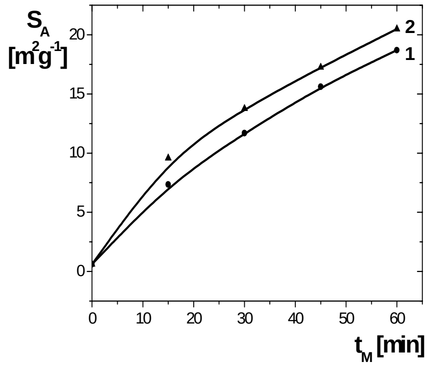

Fig. 1. The specific surface area, S_A as a function of milling time, t_M. 1-mechanically activated sample, 2-mechanochemically activated sample.

Increases in the fraction of fine particles and specific surface area are changes which are frequently observed as the consequence of intensive milling [7]. This manifold new surface area formation correlates with the particle size analysis of the milled samples (Fig. 2). The "as-received" sample has a 100 % abundance of particles with a diameter under 30 μm (1) but only 10 % of particles with diameter less than 10 μm. For the mechanically and mechanochemically activated samples (2, 3) the particles are relatively smaller than those of the "as-received" sample.

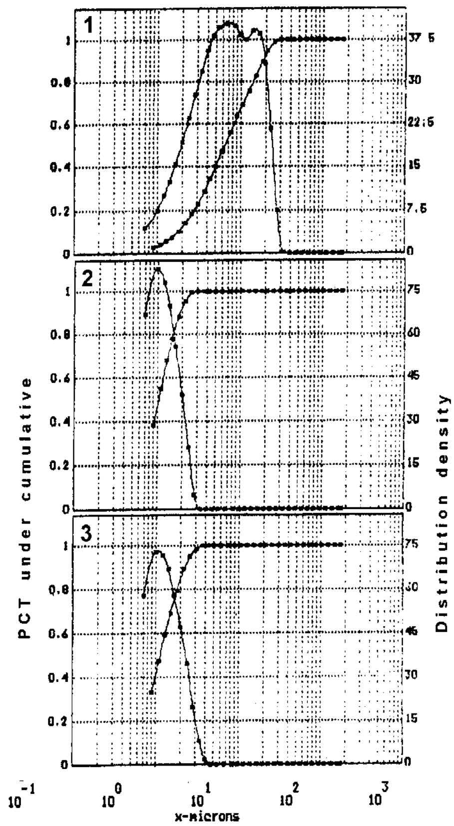

Fig. 2. Particle size analysis of the 1-non-activated sample, 2-mechanically activated sample, 3-mechanochemically activated sample, milling time, t_M = 60 min.

Senna [17] analysed the effect of surface area and the structural disordering on the leachability of mechanically activated minerals. 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 silver 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.

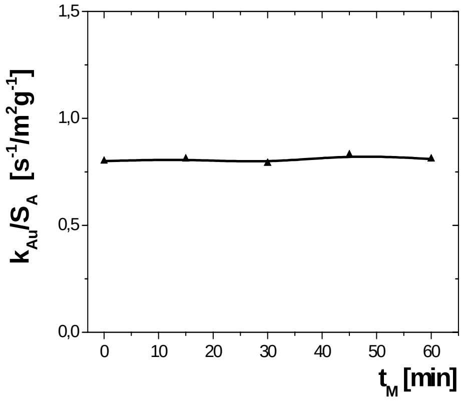

Fig. 3. Specific rate constant of gold leaching, k_{Au}/S_A vs. milling time, t_M for the mechanically activated sample.

This is a case of milling in water medium. In the second case where k_{Au}/S_A increases with increasing milling time, as shown in Figure 4, the surface area S_A, may be again the effective surface area, with an overlapping effect of the structural disorder, as a result of mechanochemical leaching.

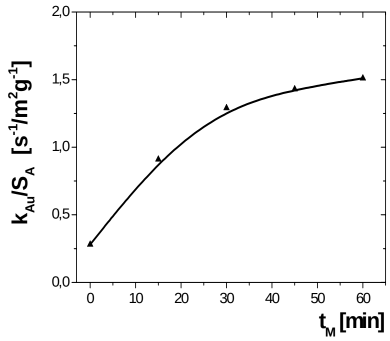

Fig. 4. Specific rate constant of gold leaching, k_{Au}/S_A vs. milling time, t_M for the mechanochemically activated sample.

Thiourea leaching of gold from mechanically and mechanochemically activated waste

The dependence of gold recovery on leaching time is represented for different mechanically activated samples in Fig. 5. While only the recovery of 78 % 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 the physico-chemical changes of the gold-bearing 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).

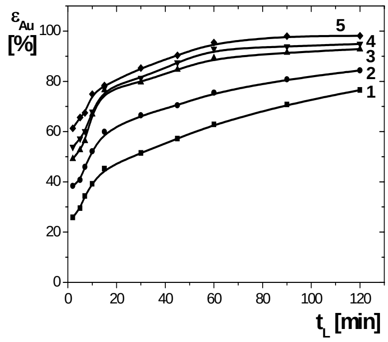

Fig. 5. Recovery of gold, ε_{Au} vs. leaching time, t_L for mechanically activated samples. Milling time, t_M: 1- non-activated sample, 2 – 15 min, 3 - 30 min, 4 – 45 min, 5 – 60 min.

The results for the mechanochemically activated samples Fig. 6 (curves 2-5) showed that the changes concerning of increase a surface area and structural disordering of the gold-bearing waste brought about an acceleration of the process of thiourea leaching. Moreover, it was possible to achieve the gold recovery of 99 % for mechanically activated sample by using leaching time of less than 90 minutes (curve 5).

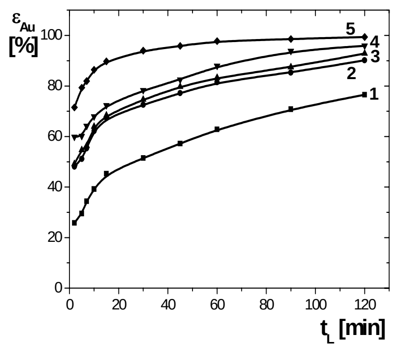

Fig. 6. Recovery of gold, ε_{Au} vs. leaching time, t_L for the mechanochemically activated samples. Milling time, t_M : 1 - non-activated sample, 2 – 15 min, 3 - 30 min, 4 – 45 min, 5 – 60 min.

Conclusion

Mechanical and mechanochemical activation of golden waste has a positive influence on gold leaching. An optimum Au recovery of 99 % was achieved from the mechanochemically treated samples already in 90 minutes of thiourea leaching. The leaching of "as-received" (non-treated) waste resulted in only 78 % Au dissolution. The consumption of milling time has an influence on the physico-chemical changes of gold-bearing waste due to mechanical and mechanochemical 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.

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