A processing method of the goldsmith's and electronic Au-Ag-containing wastes

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Spôsob spracovania zlatníckych a elektronických Au-Ag odpadov

Veľké množstvá odpadov z elektrických a elektronických zariadení sa hromadia v celej Európe. Každý spotrebiteľ vyprodukuje priemerne 16 kg tohto odpadu za rok, čo v Európe predstavuje celkovo šesť miliónov ton za rok. Ide o obrovské plytvanie zdrojmi. Znamená to taktiež veľké ekologické nebezpečenstvo, keďže elektrické spotrebiče a elektronické zariadenia obsahujú vysoko toxické ťažké kovy a organické znečisťujúce látky. Podľa nových predpisov EÚ budú musieť výrobcovia odteraz platiť za zber a likvidáciu týchto výrobkov.

Odpady ušľachtilých kovov Au-Ag predstavujú širokú škálu typov a foriem odpadov s rôznymi balastnými prvkami aj zložkami. Problematika spracovania odpadov s obsahom Au a Ag je vysoko aktuálnou v celosvetovom meradle z hľadiska hodnoty a špecifických vlastností týchto kovov ako aj ich nenahraditeľnosti v oblasti bankovníctva, zdravotníctva, priemyslu a v neposlednom rade aj v samotnej výrobe a predaji zlatníckych výrobkov. Predkladaný návrh možnosti spracovania Au-Ag zlatníckych a elektronických odpadov si kladie za cieľ získať zlato a striebro v kovovej forme. Aplikácia navrhovaného procesu spracovania uvedených Au-Ag odpadov predstavuje pre spoločnosť praktický, ekonomický a zároveň ekologický význam pri ich spracovávaní. Získavanie zlata, resp. striebra z Au-Ag odpadov je mimoriadne dôležité v podmienkach inflačného vývoja, kedy tieto ušľachtilé kovy sú stabilným zdrojom pokrývania potrieb spoločnosti.

Kľúčové slová: *zlato, striebro, odpad, lúhovanie, elektrolýza*

Introduction

The secondary gold sources are the most abundant, cheapest and the most available ones. The effective reprocessing of secondary sources and their quick recycling reduces the pressure on the gold exploitation and processing from primary sources (deposits). The character and substantially high content of precious metals in the secondary sources enables to use more simple procedures than in the primary metallurgy, and the realization of the repurchase is fundamentally cheaper than the prospecting, survey and exploitation of the deposits (Tomášek et al., 1999).

The secondary gold sources are generated, by the craftsmanship and industrial processing of gold and alloys thereof (jewellery fractions and fillings, used abrasives, clad clock waste and used melting crucibles), by the amortization of products (old jewels and fractions thereof, dental alloys, graded electrotechnical and electronical scrap, non-graded electronical scrap); by hoarding (medals, coins, bank alloys, sacral and museum treasures, gold submerged in the seas and oceans, buried in the graves and in the left deposits).

The individual raw materials include a various content of metals and, therefore, they are processed separately. Gold and accompanying metals (Ag, Ni, Zn, Cd, platinum group elements, etc.) from these sources are returned to the circulation in the so-called "mini metallurgical plants". They are companies focusing on the repurchase, processing (recycling) and the production of semi-finished products made of precious metals. These are sold for the further processing in the form of bars, metal sheets, wires, and other products especially to jewellers, stomatological laboratories, and e. g. also to the mint in Kremnica. In Slovakia, it is especially the Zlatá Huta in Trenčín, AGNO in Nové Zámky, SAFINA in Bratislava, and the Faculty of Metallurgy Technical University in Košice, where the "mini metallurgical plant" PLATAURUM works on the laboratory base. A lot of recycled precious metals is not officially published due to the fact that the individual mini metallurgical plants are the private companies. In the realization centre PLATAURUM 150 kg of Au and 500 kg of Ag were reprocessed in 1998.

In the particular secondary sources the following Au-content is present: dental alloys – 66 % Au, old jewels and fractions 39-73 % Au, jewellery fractions and fillings 19-52 % Au, earth waste 0,1-9 % Au, used crucibles 0,8-5 % Au, used abrasives (grindings, papers and cloths) 0,1-5 % Au, clock clad waste 0,25-5 % Au, graded electronical scrap (contacts) – approximately 1 % Au, non-graded electrotechnical and electronical waste 0,007-0,03 % Au (Bakoš and Chovan, 2004).

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(Recenzovaná a revidovaná verzia dodaná 14. 9. 2005)

In 1990, there were 2.799 tons Au realized on the world markets, and almost 16 % of them came from the secondary sources there. The biggest source of secondary gold for the recycling is jewellery. From the total amount of 441 tons Au, up to 71 % represent jewels and artistic articles.

The second most important source was the electronical waste (Fig. 1), from which 5 % recycled Au was produced. The electrotechnical waste however graded, unlike other raw materials containing a many-times higher Au content, is not suitable for the recycling in the small extent. In the future, this source can become a common part of the raw material inputs for the primary metallurgy of concentrations with the noble metals content, because the gold consumption grows constantly in the electrotechnical industry (Hoffmann, 1992). There is more than 20 tons of Au spent yearly for these purposes in USA, 17 tons in Japan, and 9 tons in Germany.

Relatively small amount of Au was gained by recycling of various kinds of technical alloys (2,5 %) and dental metals (1,8 %). Important article is, however, the hoarded gold in the international trade. Bank commercial alloys formed 8,4 % of total amount of gold, state interventions 6,5 % and coins up to 4,8 %.

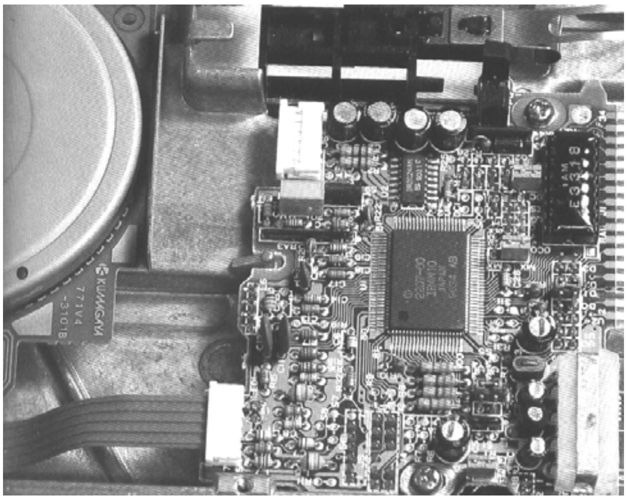


Fig. 1. Electronic waste
Obr. 1. Elektronický odpad

Most of the recycled gold in Slovakia is again used for the jewellery purposes. The approximate picture about the amount of recycled gold on the Slovak market can be created according to the official statistics of the Assay Office of the Slovak Republic, which is the authority of the state administration for hallmarking and testing of precious metals. In practice the Assay Office's activity means that all legally tradeable products made of precious metals come through the Branches of the Assay Office (Trenčín, Bratislava, Košice and Levice), which affix the relevant mark-hallmark on them. In the first half of the year 2002, there were 933.724 kg of gold jewels hallmarked (36 % came from export), and this totally amounts to 404.677 pieces of golf jewels there.

Method of goldsmith's and electronical Au-Ag-contained wastes processing

The thiourea process of gold and silver extraction from ores, concentrates, or goldsmith's and electronical wastes, consisting of gold and silver leaching into the thiourea solution and consequent precipitation of these metals from the solution is, with regard to the very low toxicity of thiourea, the perspective alternative hitherto the most used cyanide method (Baláž et al.,1996; Baláž et al., 2003; Ficeriová, 1996; Ficeriová et al., 2004; Habashi, 1993; Marsden an House, 1994).

Regarding the aim of gold and silver precipitation from the thiourea solutions, which is the maximum extraction of these metals with the possibility of thiourea solution regeneration, the way of electrolytic precipitation of gold and silver proves to be a perspective way.

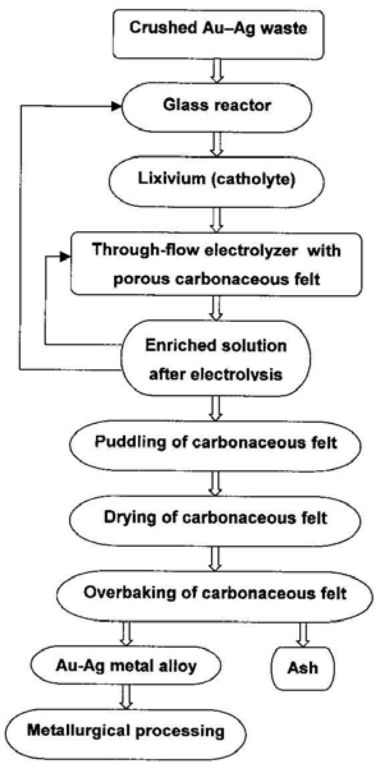
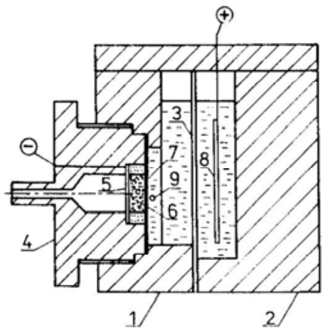


Fig. 2. Flowsheed of Au-Ag-contained jewellery and electronical waste processing
Obr. 2. Technologická schéma spracovania Au-Ag zlatníckeho a elektronického odpadu

From the published data and theoretical knowledge about the electrolytic gold and silver precipitation from thiourea solutions it follows that two types of electrodes (as a of surface with the aim of its enlargement, and at the same time, the inertness of electrode material against acid thiourea solutions) can be used for this electrolysis. It is an electrode made of titan plates and a porous electrode made of carbonaceous felt. Due to the more unrolled surface and the intertwined higher electrolyzer production capacity, as well as the more easy processing of cathodic product, the porous electrodes are made from the carbonaceous felt, which in addition to the full resistance against acid solutions, good electric conductivity and a considerable internal active surface distinguish them by an ability to precipitate 20 to 30 grams per one gram of carbonaceous felt. This material seemed to be the most suitable for precipitalinty electrolytic gold and silver from thiourea solutions (Maslij et al., 1986).

For a constant metal precipitation on the porous electrode from the carbonaceous felt from solutions is necessary to provide the symmetric distribution of potential on this electrode. The given condition is fulfilled on condition that the carbonaceous felt conductivity is comparable with the electrolyte conductivity (Gašpar, 1992).

Figs 2. and 3. show the proposal of a flowsheet of processing of the Au-Ag-contained jewelry and the electronical waste, and a scheme of the laboratory circulating electrolyzer. The presented technological scheme (Fig. 2) includes the extraction of gold and silver from jewelry gold and electronic Au-Ag wastes with the use of the flow electrolyzer with a porous carbon felt (Fig. 3) and thiourea acting as an ecologically appropriate lixiviating chemical agent for precious metals.



1-cathodic part
2-anodic part
3-membrane (catex)
4-screwing cover
5-perforated titanium lid
6-porous carbonaceous felt (cathode)
7-non-lead perforated plate
8-platinum net (anode)
9-potential probe

Fig. 3. Scheme of laboratory circulating electrolyzer
Obr. 3. Schéma laboratórneho prietokového elektrolyzéra

Rotoplex-Schneidmühle A20/12 (Fig. 4.) and Omniplex-Hammermühle 40/20 Ha (Fig. 5.) (both Alpine, Germany) crushers can be used for the pretreatment of the goldsmith's and electronic waste. The obtained input material, 8x8 mm for the gold waste and -800 µm for the electronic waste, has been sieved and leached in a glass reactor in the thiourea solution for the gold and silver extraction (Fig. 2.). The thiourea leach from the reactor flows through an electrolyzer where Au and Ag are precipitated on the porous carbonaceous felt. The enriched solution after electrolysis circulates back into the glass reactor as well as into the through – flow electrolyzer, where the content of Au and Ag on carbonaceous felt is increased. The felt after electrolysis is washed and dryied and subsequently baked. The Au-Ag metal alloy and ash with a small amount of waste from the burned carbonaceous felt are the end products from which the alloy is a final product of the goldsmith's and electronic waste processing suitable for a further metallurgical processing.

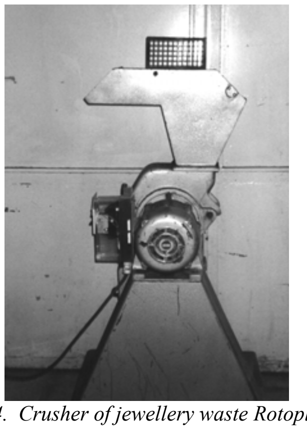


Fig. 4. Crusher of jewellery waste Rotoplex-Schneidmuhle, A20/12 Ro (Alpine, Germany)
Obr. 4. Drvič zlatníckeho odpadu Rotoplex-Schneidmuhle, A20/12 Ro (Alpine, Nemecko)

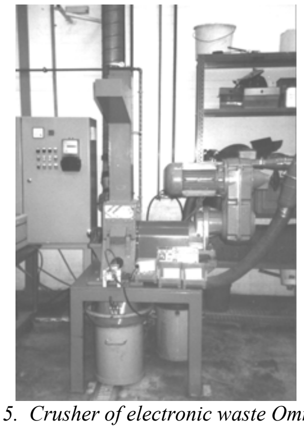


Fig. 5. Crusher of electronic waste Omniplex-Hammermuhle, 40/20 Ha (Alpine, Germany)
Obr. 5. Drvič elektronického odpadu Omniplex-Hammermuhle, 40/20 Ha (Alpine, Nemecko)

Model of the laboratory electrolyzer (Fig. 3.) is formed by the cathodic and anodic parts as well as the catex membrane which is inserted among both electrodes. The porous carbonaceous felt is fixed by a screwing cover. The thiourea solution with a gold and silver content from the goldsmith's and electronic waste is supplied into the cathodic space at a constant rate through a small tube. Perforated titanium lid serves as an current collector. The cathode is placed between the collector and the non-lead perforated plank. The platinum net serves as an anode. The potential probe is used for the cathode potential measurement.

Regarding the fact that the electrolytic gold and the silver precipitation process from the thiourea solutions is limited by the diffusion of individual complex gold and silver cations in the thiourea solution to the electrode (Fleming, 1992), the transfer coefficient of the gold and silver thiourea complex mass is the important and necessary kinetic factor of the electrolysis process for a possible industrial application of the electrolysis with the aim of its optimization.

Conclusions

The process of goldsmith's and electronic Au-Ag waste treatment is important from a view-point of ecology and environment because it is practically a waste-free and closed technology.

There are two important aspects for the application of the carbonaceous felt for the electrolytic precipitation of Au and Ag from thiourea solutions:

1. the homogeneous potential distribution throughout the carbonaceous felt is required where the level expulsion of gold and silver on the felt takes place,
2. thiourea gold and the silver solution of fixed volume circulate with a known velocity through the through-flow electrolyzer with the carbonaceous felt untill the proper efficiency of gold and silver precipitation is obtained.

Acknowledgements:This work was supported by the Slovak Grant Agency for Science (Grant No. 2/5151/5) and APVT-20-018402.

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