Leaching of Gold and Silver from Crushed Au-Ag Wastes

Jana Ficeriová*,[a], Peter Baláž[a], Erika Dutková[a] and Eberhard Gock[b]

[a]*Institute of Geotechnics of the SAS, Watsonova 45, 043 53 Košice, Slovakia*

[b]*Institute of Mineral and Waste Processing and Dumping Technology, Technical University Clausthal, Walther-Nernst Strasse 9, 38 678 Clausthal-Zellerfeld, Germany*

Abstract: Au-Ag noble metal wastes represent a wide range of waste types and forms with various ballast elements and components. The thiourea process of gold and silver extraction from ores, concentrates or secondary raw materials consists of gold and silver leaching into the thiourea solution and the consequent precipitation of these metals from the solution. Due to the non-toxic character of thiourea it is the perspective alternative to the up to now most frequently used cyanide method. The thiourea leaching of gold and silver from electronic waste, goldsmith's waste and ceramic waste using crushing as the pretreatment step was investigated. For electronic waste, it was possible to achieve 97 % gold and 94 % silver recovery within 120 minutes of thiourea leaching. Up to 98 % of gold and 96 % of silver were recovered from goldsmith's waste after 60 minutes of leaching. In the case of ceramic waste, we achieved up to 98 % gold and 97 % silver extraction efficiency after only 45 minutes of leaching. In comparison with the classical cyanide leaching, thiourea leaching acts faster and without a harmful environmental impact.

Keywords: Waste, Gold, Silver, Crushing, Leaching.

1. INTRODUCTION

Electronic waste comprises electric waste and includes an extremely complex mixture of electric, electronic and other components. Sources are production waste from the electric and electronic industry as well as defect or technically obsolete devices for which there is a legal obligation for disposal on trade and municipalities [1].

The main components of electronic waste are approximately: 45 % ferrous metals, 10 % non-ferrous metals (mainly Cu and Al), 22 % plastics and 9 % glass.

In contrast, the average fraction of electronic components is only 3 %. Most utilization firms call the circuit board including the attached elements and the frame electronic components. From this viewpoint, the fraction of electronic waste is usually between 20 and 30 % [2, 3].

There are considerable differences between the composition of the individual groups of electronic waste and even within one group. For assistance, washing machines and refrigerators consist almost completely of ferrous metals and contain a very small fraction of electronics. Computers and entertainment electronics, however, have a high fraction of electronics. The percentage of noble metals is much higher in computers than in the other categories of electronic waste. The following examples give some general indications: low value (< 100 ppm Au) TV-boards, monitor boards, (cordless) phones, calculators, shredded bulk material after Al-Fe-separation; medium value (100 to 400 ppm Au) PC-boards, laptop- and handheld-computers, some mobile phones; high value (> 400 ppm Au) Circuit boards from main-frames, some mobile phones, multi-layer ceramic capacitors [4].

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); by collecting (medals, coins, bank alloys, sacral and museum treasures), gold lost in the seas and oceans, buried in the graves and in the decommissioned deposits [5].

Gold and silver is impractical connected on the component of Au-Ag wastes included with abundance of accompanying elements and cannot come in contact with leaching solutions. Leaching of Au-Ag wastes without pretreatment remitted in low Au and Ag extraction [6].

Physical pretreatment by crushing have been applied to Au-Ag wastes with the aim of changing the part sizes of the gold and silver-bearing wastes, thus facilitating the subsequent leaching in order to increase the recovery of noble metals [7, 8]. Crushing induces changes size of component parts of Au-Ag wastes. It increases the fraction of components and improves their contact with leaching reagents.

Modern hydrometallurgy of gold and silver is based on the application of cyanide leaching. The cyanide process is a highly toxic technology. The thiourea process of gold and silver extraction from wastes or concentrates 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. Thiourea leaching has more rapid kinetics for gold and silver solubilization than classical cyanide leaching [9-13].

The aim of this work was to examine the possibility of recovering gold and silver from electronic, goldsmith's and ceramic wastes using thiourea leaching. Crushing was ap-

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*Address correspondence to this author at the Institute of Geotechnics of the SAS, Watsonova 45, 043 53 Košice, Slovakia; Fax: + 421-55-7922604; E-mail: ficeri@saske.sk

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Table 1. Chemical Composition of Au-Ag Wastes Under Study

Waste	Components (%)										
	Au	Ag	Cu	Pb	Zn	Fe	Br	Sn	Ni	Sb	Mn
Electronic (Germany)	0.25	0.18	0.85	0.0003	0.24	0.35	0.52	0.41	0.13	0.016	0.002
Goldsmith's (Slovakia)	0.8	0.45	0.53	0.041	0.012	0.008	-	-	0.005	0.004	0.0003
Ceramic (Czech Republic)	0.4	0.35	0.6	0.0007	-	-	-	-	0.003	-	-

plied in order to determine its effect on the recovery of gold and silver.

2. EXPERIMENTAL

2.1. Materials

The electronic waste (PC-boards, Germany), goldsmith's waste (abrasive papers, Slovakia) and ceramic waste (pink porcelain, Czech Republic) were selected as materials for testing the thiourea leaching of gold and silver. The chemical composition of the studied wastes is given in Table **1**.

2.2. Physicochemical Characterization

The X-ray fluorescence spectroscopy (XRF) was done using a Philips PW 1404 (X-tal LiF 200) spectrometer equipped with a source operating at 40 kV and 30 mA. Data were collected every second and the detector was moved at a rate of 0.1° min^{-1}.

2.3. Crushing of Au-Ag Wastes

Rotoplex-shredder crusher A20/12 Ro and Omniplex-hammer crusher 40/20 Ha (both Alpine, Germany) were used for treatment of electronic, ceramic and goldsmith's wastes. After crushing, the material was 8x8 mm in size in case of goldsmith's waste and -800 μm in case of electronic/ceramic waste. Before leaching the waste has been sieved.

2.4. Thiourea Leaching of Au-Ag Wastes

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 50 g

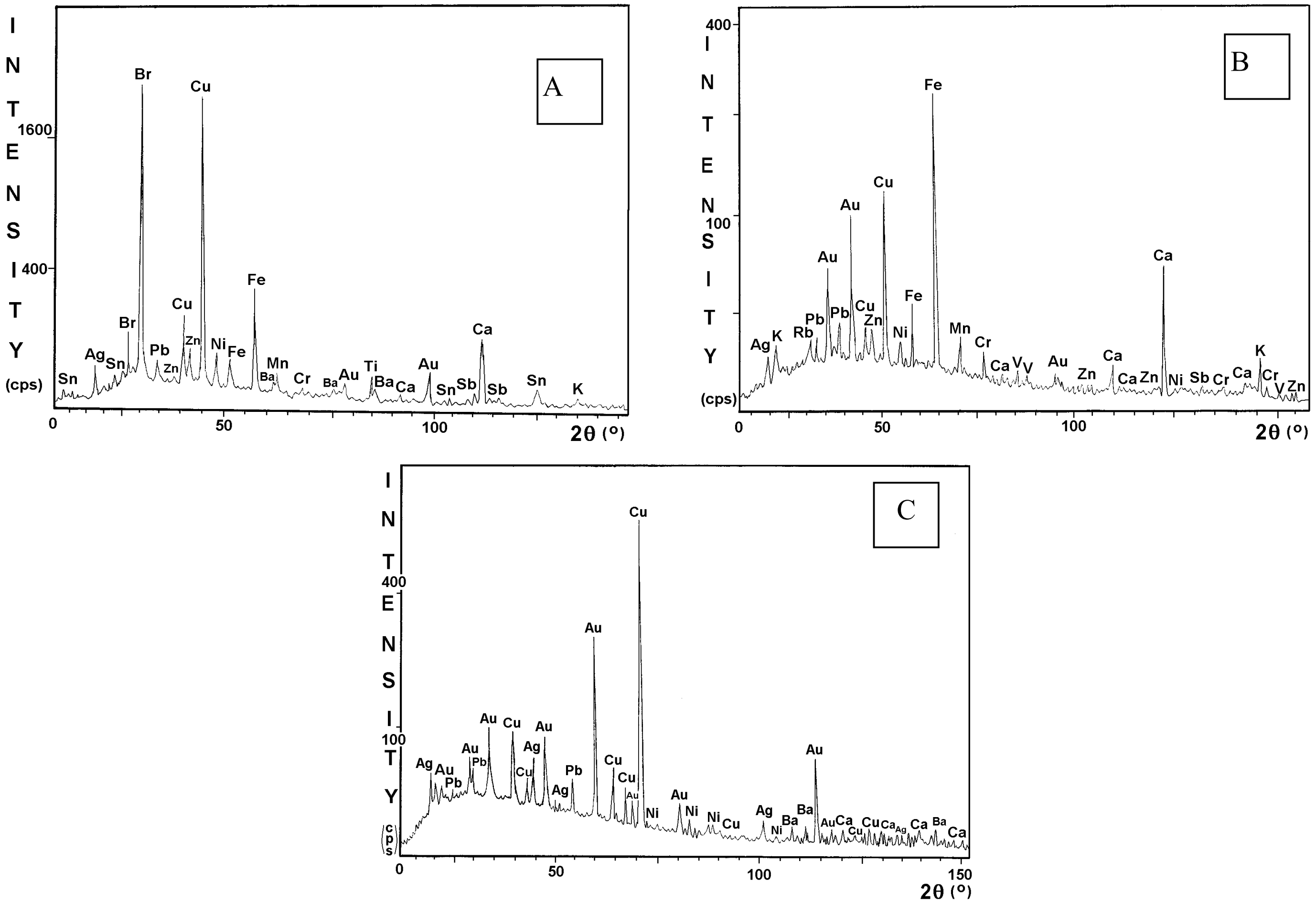

Fig. (1). X-ray fluorescence spectrum of electronic waste (**A**), goldsmith's waste (**B**) and ceramic waste (**C**).

of crushed electronic, goldsmith's and ceramic wastes were added. The leaching was performed at pH 1 for up to 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 and silver by AAS method.

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

$$-\ln\left(1-\varepsilon_x\right)=k_X t_L \qquad (1)$$

where ε_x is recovery of gold/silver into the leach solution, k_X is the rate constant (s^{-1}) and t_L is the leaching time (s).

Thiourea, $CS(NH_2)_2$ forms a stable soluble complex with gold and silver ions. Bruckard [14] suggested the equations for gold and silver dissolution in the presence of Fe^{3+} ions as:

$$Au+2\,CS\left(NH_2\right)_2+Fe^{3+}\rightarrow Au\left[CS\left(NH_2\right)_2\right]_2^{+}+Fe^{2+} \qquad (2)$$

$$Ag+3\,CS\left(NH_2\right)_2+Fe^{3+}\rightarrow Ag\left[CS\left(NH_2\right)_2\right]_3^{+}+Fe^{2+} \qquad (3)$$

3. RESULTS AND DISCUSSION

3.1. Thiourea Leaching of Gold and Silver from Crushed Au-Ag Wastes

The X-ray fluorescence spectral records of the Au-Ag wastes under study, are shown in Fig. (**1**). The results confirm the presence of gold/silver and following metallic and non-metallic elements.

The dependence of gold and silver recovery on the leaching time from electronic waste is shown in Fig. (**2**). 120 min leaching of "as-received" sample with thiourea yielded only a 76 % Au and 71 % Ag leachate (Fig. **3**). The treatment using crushing makes it possible to achieve a more than 90 % recovery of gold and silver in the leachate even after 60-90 minutes. Here, the recovery of accompanying metals was 68 % Cu, 45 % Fe, 43 % Pb and 28 % Zn. The results for crushed waste show increased recoveries of noble metals.

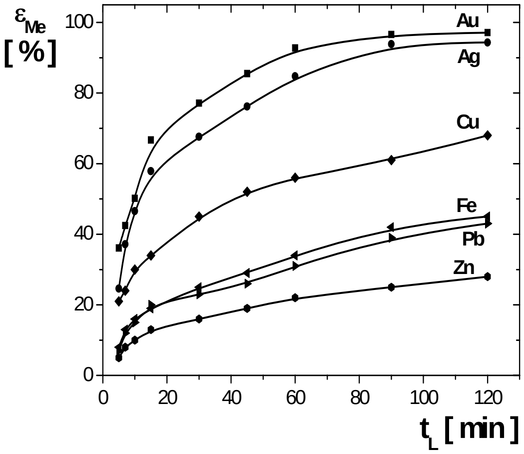

Fig. (2). Recovery of Au, Ag, Cu, Fe, Pb and Zn, ε_{Me} *vs.* leaching time, t_L for electronic waste (Germany) pretreated by Omniplex-hammer crusher, 40/20 Ha (Alpine, Germany).

Fig. (**4**) shows the effect of leaching time on gold and silver recovery for crushed goldsmith's waste. In the "as-received" sample 87 % of gold and 83 % of silver was recovered after 120 min of leaching in thiourea (Fig. **5**). The results for the treated waste indicated that the comminution of the Au-Ag waste brought about an acceleration of the leaching process. In this case, it was possible to achieve 99 % gold recovery and about 96 % silver recovery after less than 60 min of leaching. Here, the recovery of accompanying metals was 87 % for Cu, 55 % for Fe and 28 % for Zn.

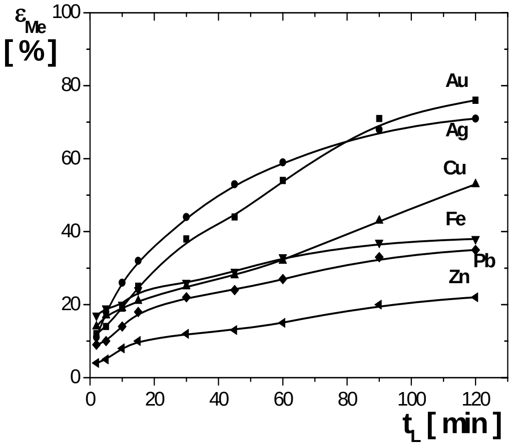

Fig. (3). Recovery of Au, Ag, Cu, Fe, Pb and Zn, ε_{Me} *vs.* leaching time, t_L for "as- received" sample of electronic waste (Germany).

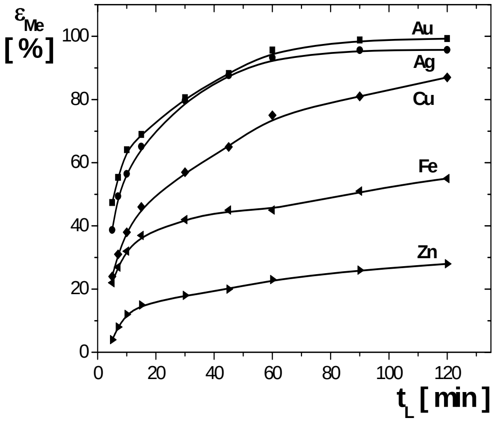

Fig. (4). Recovery of Au, Ag, Cu, Fe and Zn, ε_{Me} *vs.* leaching time, t_L for goldsmith's waste (Slovakia) pretreated by Rotoplex-shredder crusher, A20/12 Ro (Alpine, Germany).

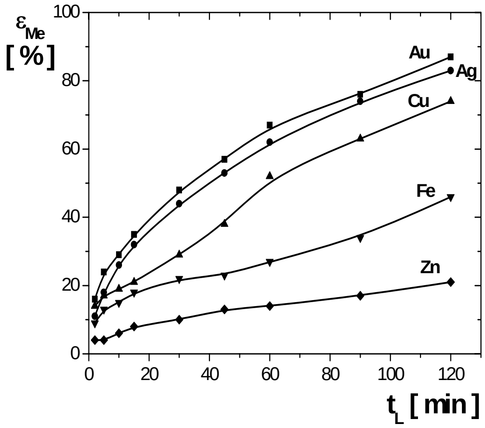

Fig. (5). Recovery of Au, Ag, Cu, Fe and Zn, ε_{Me} *vs.* leaching time, t_L for "as-received" sample of goldsmith's waste (Slovakia).

The dependence of gold and silver recovery as well as the recovery of accompanying metals (Cu and Pb) for the crushed ceramic waste is given in Fig. (**6**). It is possible to achieve a 98 % recovery of gold and 97 % recovery of silver into the leachate even after 45 minutes. After 120 min of leaching, 71 % of Cu and 18 % of Pb was recovered. A recovery of 90 % Au and Ag was achieved after 120 min of leaching of the “as-received“ sample (Fig. **7**).

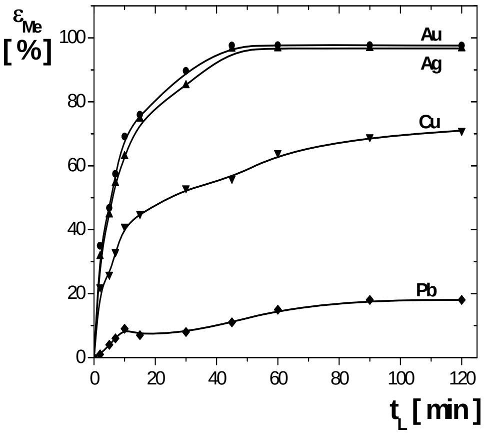

Fig. (6). Recovery of Au, Ag, Cu and Pb, ε_{Me} *vs.* leaching time, t_L for ceramic waste (Czech Republic) pretreated by Omniplex-hammer crusher, 40/20 Ha (Alpine, Germany).

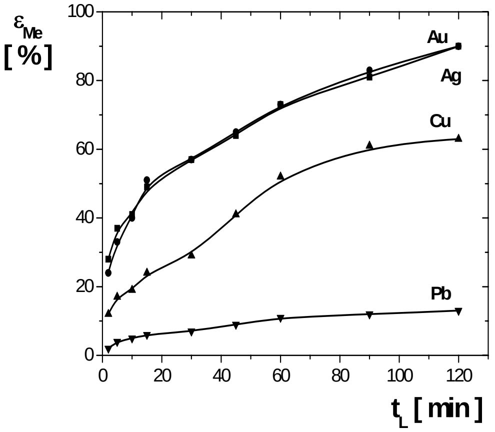

Fig. (7). Recovery of Au, Ag, Cu and Pb, ε_{Me} *vs.* leaching time, t_L for “as-received” sample of ceramic waste (Czech Republic).

The application of crushing proved to be an effective method of pretreatment of the Au-Ag wastes before extraction of gold and silver into thiourea leaching liquors.

4. CONCLUSIONS

Crushing of Au-Ag electronic, goldsmith’s and ceramic wastes from Germany (Clausthal-Zellerfeld), Slovakia (Košice) and Czech Republic (Praha) in a shredder crusher and hammer crusher influences the changes part sizes of the gold and silver-bearing wastes and this leads to an accelerated thiourea leaching. It increases the fraction of components and improves their contact with leaching reagents. Thiourea leaching is more suitable for rapid extraction of gold and silver from the given types of Au-Ag wastes than other alternatives. In this way, it is possible to achieve more then 90 % recovery of gold and silver.

The process of thiourea leaching is non-toxic and moreover brings kinetic advantage over classical cyanide leaching.

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