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# RECOVERY OF GOLD FROM ELECTRONIC WASTE BY IODINE-IODIDE LEACHING

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## ABSTRACT

*Gold recovery by iodine-iodide solution is an effective and environment-friendly method.*

*The aim of this research is to investigate the possibility of iodine-iodide gold recovery from gold-plated metal, which is a waste product of the electronic industry.*

*Leaching experiments were carried out in solutions, containing 25 g $l^{-1}$ iodine and 100 g $l^{-1}$ KI, under room temperature, rotating speed of 500 rpm and mass ratio of 1:10. The degree of gold recovery for 1 minute leaching was 97,55 %. The concentrations of copper and nickel in the solution were about 0.05 g $l^{-1}$, while the iron concentration was equal to that of the gold. It had been found that when gold concentration in the solution reached 1 g $l^{-1}$, the iodine concentration decreased with 20 %.*

*The optimal parameters of reducing dissolved gold iodide salts to gold metal are determined as 20 g KOH and 4 ml 10 % $N_2H_4.H_2O$ per one liter of the solution. Simultaneously with gold, iron and nickel almost completely precipitated (90 %), while the copper precipitation degree was around 25 %, because a large part of it precipitated as CuI during the leaching. The gold was separated from the precipitate by $HNO_3$ treatment.The overall gold recovery is 94,56 %.*

*Experiments were conducted to regenerate the solution by decreasing pH with $H_2SO_4$ and by adding of $H_2O_2$, as an oxidizing agent. The achieved regeneration degree was 80 %.*

*The main disadvantage of iodine-iodide leaching is the great consumption of reagents and the need for a significant number of filtrations.*

*Keywords: gold, iodine-iodide lixiviantsolution, leaching, precipitation.*

## INTRODUCTION

Cyanide leaching has been the most applied technique in the world for recovering gold for over a century. However, recovery of gold by cyanide leaching has serious environmental risks. Nowadays, much attention is paid to the study of new hydrometallurgical non-cyanide methods [1, 2], including thiourea leaching [3 - 5], thiosulfate leaching [6 - 8] and halide leaching [9], which appear to be less toxic and much safer for people and the environment than the cyanide usage.

The leaching of gold by iodine has been investigated in depth by various authors [10 - 13].

Gold metal is oxidized in the presence of $I^-$ and $I_3^-$ to $AuI_2^-$ and $AuI_4^-$ complexes according to the following oxidation-reduction reactions:

$$Au + 2I^- \rightarrow AuI_2^- + e^- \quad (1)$$

$$Au + 4I^- \rightarrow AuI_4^- + 3e^- \quad (2)$$

$$I_3^- + 2e^- \rightarrow 3I^- \quad (3)$$

Thus, iodine-iodide leaching of gold can be described by the overall reactions:

$$2Au + I_3^- + I^- \rightarrow 2AuI_2^- \quad (4)$$

$$2Au + 3I_3^- \rightarrow 2AuI_4^- + I^- \quad (5)$$

The anode reaction of gold complex formation is provided by the iodide ions in the aqueous solution. Since elemental iodine is slightly soluble in water, the oxidation process is limited by the activity of $I_2$. In the presence of free iodide ions, water-soluble complexes $AuI_2^-$ and $AuI_4^-$ are formed.

The Eh-pH diagram of the system Au-I-$H_2O$ (Fig. 1) is built at gold concentration of $10^{-3}$ M and iodine concentration of 0,1 M in a wide range of pH (from 2 to 16), using the software program HSC Chemistry 5.11. This diagram illustrates that the gold - iodide system has the largest stability region for both Au(I) and Au(III) complexes, and the stability area for $AuI_2^-$ extends up to about pH 12. In this figure the shaded area shows the region of the water domain, occupied by dissolved gold species.

The aim of this research is to investigate the possibility of iodine-iodide gold recovery from gold-plated metal, which is a waste product of the electronic industry.

## EXPERIMENTAL

The subject of this research is gold-plated metal waste from the electronic industry (Fig. 2). The sample used to conduct the experiments consists of four different materials with the chemical compositions, presented in Table 1.

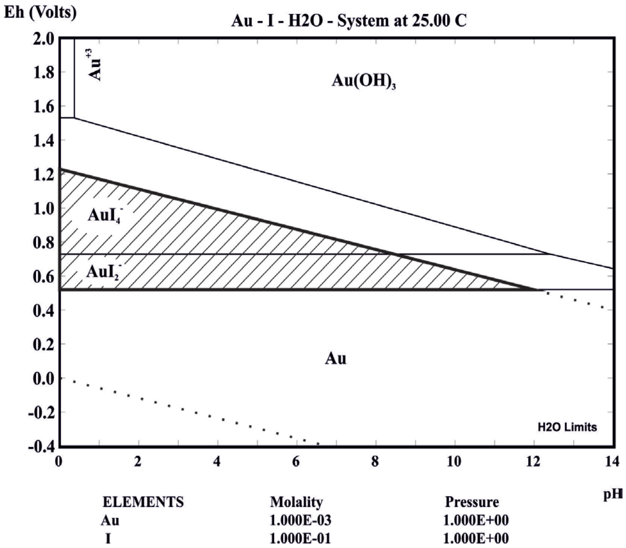

Fig. 1. Eh-pH equilibrium diagram for the gold - iodide system for [Au] = 10-3M and [I] = $10^{-1}$.

Besides gold, copper, iron and nickel, this material contains also tungsten, zinc, etc., the concentrations of which have not been determined.

One of the most important points for developing a hydrometallurgical process for the extraction of metal from a certain material, is the choice of the leaching solution and its concentration. Different concentrations of iodine and potassium iodide for extraction of gold can be used, depending on the type of the raw mate-

Table 1. Chemical composition of golded materials, %.

| Material | Proportion, % | Cu | Au | Fe | Ni |
|---|---|---|---|---|---|
| 1 | 4.50 | 50.11 | 0.95 | 46.68 | 0.61 |
| 2 | 6.10 | 61.59 | 0.51 | 11.49 | 8.29 |
| 3 | 75.36 | 33.23 | 0.15 | 43.04 | 9.99 |
| 4 | 14.04 | 65.52 | 0.34 | 10.17 | 7.72 |
| Average | 100.00 | 40.25 | 0.23 | 36.66 | 9.15 |

Table 2. Chemical composition of the iodine-iodide solution, g $l^{-1}$.

| After processing of | μ, $g.ml^{-1}$ | Cu | Ni | Au | Fe |
|---|---|---|---|---|---|
| 50 g | 0.5 | 0.09 | 0.23 | 1.00 | 1.80 |
| 100 g | 1 | 0.11 | 0.30 | 2.49 | 2.52 |

rial, subjected to processing. For the purpose of this research, the selected ratio between the reactants has been $I_2$:KI:$H_2O$ =1:4:40

The gold extraction experiments were carried out on a magnetic stirrer at room temperature. The material was fed in portions to the lixiviant solution, so as to maintain the ratio solid: liquid = 1: 10. After a certain period of time the processed material was separated from the solution and washed with water. Then new portion of material was added to the leaching solution and this continued until a certain amount of material was processed by the same solution volume.

Since various experiments had been conducted with different mass of material or with different volume of solution, a value- specific mass, μ was introduced in order to analyze the obtained results.

$$\mu = \frac{M}{V}, \text{g.ml}^{-1}, \qquad (6)$$

where:
M – mass of golded material, g
V – volume of iodine-iodide solutions, ml.

The concentrations of gold and other base metals in the leaching solution, as well as in the wash water, were determined by atomic absorption analysis. The concentrations of the iodine solutions were measured by a PHS-38W pH/mV Meter (Bante Instruments).

## RESULTS AND DISCUSSION

The experiments were conducted at room temperature by placing the material in contact with a leaching solution for a period of 1 min. The changes of the metal concentrations in the solution in dependence on the specific mass are shown in Fig. 3.

The concentrations of gold and iron in the solution linearly increases by increasing the mass of processed material (μ), while the concentration of nickel and copper remains constant – at around 50 mg $l^{-1}$.The obtained results are different from those published in [14], according to which the average rate of nickel extraction is 3 - 4 times higher than the rate of dissolution of gold, while iron partially passes in the iodine-iodide solvent.

Fig. 2. Golden plated material.

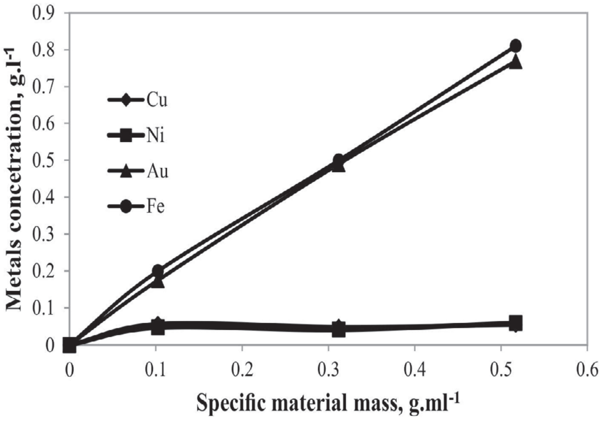

Fig. 3. Metal concentration in leaching solution dependence on the specific material mass.

Copper is also dissolved vigorously, forming $CuI_2$, which is not stable and is reduced to CuI, according to the reaction:

$$2CuI_2 \rightarrow 2CuI\downarrow + I_2\downarrow \qquad (7)$$

For this reason the pregnant solution should be filtered before the precipitation of gold, in order to remove the insoluble CuI.

The degree of gold extraction in this method of treatment is insufficient, either due to the way in which the experiment was conducted, or due to insufficient duration of contact between the material and the solvent. Next, experiments with different process duration, which involved vigorous stirring of the material to increase the degree of gold extraction, were carried out. The obtained results are shown on Fig. 4. It is observed that the extraction of the gold coating at room temperature for a period of one minute is 97.55 %. The concentrations of copper and nickel in the solution are again low, respectively 0.048 g $l^{-1}$, and 0.055 g $l^{-1}$, while the iron concentration in iodide solution is comparable to that of gold.

Experiments at specific mass (μ) of 0.5 and 1.0 g $ml^{-1}$ (50 g and 100 g of material, processed with 100 ml solution) were performed. The metal concentrations in the solution after 50 g and 100 g material processing are presented in Table 2.

As noted in the table above, the concentration of gold as well as that of iron in the solution rises to 2,5 g $l^{-1}$ at a value of μ = 1.0. It is established, that with the increase of the mass of processed material (μ), the time for complete dissolution of the gold coating increases to about 3 min. The change in the concentration of iodine depending on the specific material's mass is presented in the Fig. 5. The increase of the processed material mass leads to reduction of the iodine concentration. Upon reaching gold concentration of 1 g $l^{-1}$, the concentration of iodine in the leachate is reduced by 20 %.

The advantages of the iodine-iodide extraction of gold from golded materials are: the high rate of the leaching process, the ability to carry it at room temperature and not least - the visual control for determining the end of the extraction. The main disadvantage is the higher concentration of iron in solution, comparable to that of gold. According to the constructed Eh-pH diagram (Fig. 1), gold from the iodine-iodide solution will precipitate from the solution at high value of pH (> 12) and at lower potential of the system. For this reason in order to increase the pH of the solution and to create reduction conditions, 20 % KOH and 10 % hydrazine have been used.

Experiments for determination of the base consumption, necessaryto precipitate the gold, have been carried out at a constant amount of reducing agent (4 ml 10 % $N_2H_4.H_2O$ per 1 liter gilded solution) and the results are presented in Fig. 6. The chemical composition of the starting solution for gold precipitation, g $l^{-1}$, is: 0,081 Cu; 1,2 Au; 0,179 Ni; 1,795 Fe and has pH of 3,44. The highest degree of gold precipitation is obtained at base consumption of 20 g KOH per liter golded solution. In this case, the pH of the solution increases up to 12,74. Quantitative gold precipitation is achieved by addition of hydrazine solution.

The degree of gold precipitation using 100 ml 20 % KOH and 4 ml 10 % $N_2H_4.H_2O$ is 95 %. Iron and nickel,

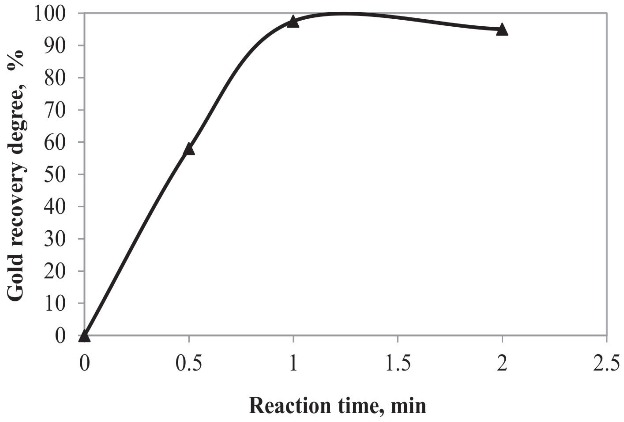

Fig. 4. Gold recovery degree dependence on the reaction time.

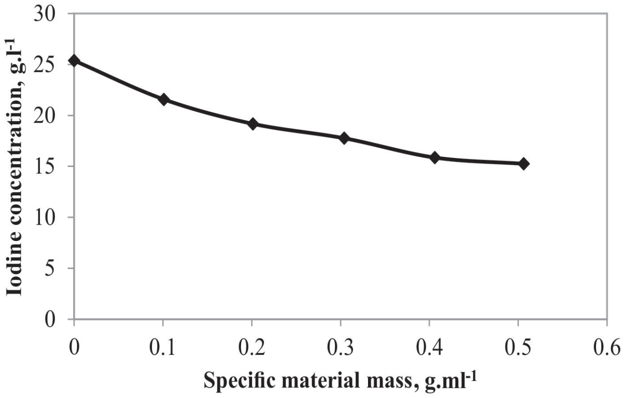

Fig. 5. Iodine concentration dependence on the specific material mass.

Table 3. Degree of regeneration of leaching solutions, %.

| Starting solution, ml | 1M $H_2SO_4$, ml | 1M $H_2O_2$, ml | Degree of regeneration, % |
|---|---|---|---|
| 10 | 2 | 2 | 0 |
| 10 | 5 | 5 | 32 |
| 10 | 8 | 8 | 85 |
| 10 | 10 | 10 | 86 |
| 10 | 20 | 20 | 92 |

together with gold, almost completely precipitate (90 %), while the degree of copper precipitation is about 25 %. This can be explained by the fact that at iodine-iodide leaching, nickel goes into solution as nickel iodide, and iron as iron (II) iodide. In an alkaline environment the following reactions of precipitation take place:

$$NiI_2 + 2KOH \rightarrow Ni(OH)_2 + 2KI \qquad (8)$$

$$FeI_2 + 2KOH \rightarrow Fe(OH)_2 + 2KI \qquad (9)$$

Under the action of hydrazine, $Ni(OH)_2$ can be reduced to metallic nickel, while $Fe(OH)_2$ is oxidized to $Fe(OH)_3$:

$$2Ni(OH)_2 + N_2H_4 \rightarrow 2Ni + N_2 + 4H_2O \qquad (10)$$

$$2Fe(OH)_2 + N_2H_4 + 4H_2O \rightarrow 2Fe(OH)_3 + 2NH_4OH \qquad (11)$$

As a result of the conducted experiments of gold precipitation from the iodine-iodide solution, obtained upon leaching at value of $\mu = 0.5$ g ml$^{-1}$, the following reagents consumptions for high degree of gold, nickel and iron precipitation have been determined:

- 20 g KOH per 1l solution;
- 4 ml 10 % $N_2H_4.H_2O$ per 1 l solution.

The base should be added in a solid form, in order to prevent a solution volume increase.

The above reactions indicate that the obtained gold-containing residue should be processed to purify the gold from impurities before melting. Therefore, the gold precipitate has been washed with hot water and alcohol for separation of iodide solution and then has been treated with diluted (1:1) $HNO_3$.

The solution regeneration could be achieved in an acid medium, in the presence of an oxidizer (hydrogen peroxide). The iodide $I^-$ and iodate $IO_3^-$ ions predominate in the highly alkaline solution. Hydrogen peroxide reduces the iodate to iodine and is oxidized to oxygen:

$$5\,H_2O_2 + 2\,IO_3^- + 2\,H^+ \rightarrow I_2 + 5\,O_2 + 6\,H_2O \qquad (12)$$

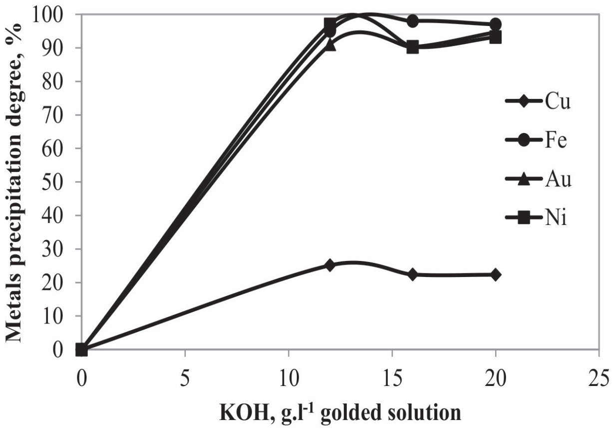

Fig. 6. Metals precipitation degree dependence on consumption of KOH (at constant reducer amount of 4 ml 10 % $N_2H_4.H_2O$ for 1 l gold containing solution).

It also oxidizes iodine to iodate:

$$5\ H_2O_2 + I_2 \rightarrow 2\ IO_3^- + 2\ H^+ + 4\ H_2O$$

Hydrogen peroxide in an acidic medium also reduces the iodide ions to iodine:

$$2KI + H_2SO_4 + H_2O_2 \rightarrow I_2 + K_2SO_4 + 2H_2O \qquad (13)$$

To determine the consumption of sulfuric acid and hydrogen peroxide, the synthetic solutions of iodine (28,55 g $l^{-1}$) and KI (100 g $l^{-1}$) have been treated with potassium hydroxide until pH reaches a value of 13. Equal amounts of solutions of 1M $H_2SO_4$ and 1M $H_2O_2$ have been added to the same volume of the synthetic iodine-iodide solution (10 ml). The resulting degrees of regeneration are presented in Table 3.

The sulfuric acid and hydrogen peroxide should be added in a more concentrated form to prevent excessive volume increasing. For example, regeneration of a real iodine-iodide solution of 100 ml, obtained by processing of 50 g gold-plated material, requires 6 ml conc. $H_2SO_4$ and 20 ml 30 % $H_2O_2$. The conducted test showed that the degree of regeneration of such real solution is lower (80 %).

The experiment to extract gold from the studied material has been conducted, by using the same iodine-iodide solution, three times. The initial solution, with a volume of 100 ml, containing 25 g $l^{-1}I_2$, 100 g $l^{-1}$KI, has been used for leaching of 50 g material. The concentration of gold in the pregnant solution has been 1,1 g $l^{-1}$. After precipitation of the metals by 2 g KOH and 0,4 ml $N_2H_4.H_2O$ and regeneration of the leachate solution by 5 ml $H_2SO_4$ and 20 ml $H_2O_2$, the concentration of the iodine was reduced to 19,67 g $l^{-1}$. Then the solution was adjusted to the initial values by 0,5 g $I_2$ and 2 g KI.

The adjusted solution has been used for leaching of another 50 g of golded material. In this case, the processing time was increased to 2,5 min. Precipitation of the metals was carried out with the same amount of hydrazine (0,4 ml), but with a much higher consumption of base (6 g KOH), since the second leaching was performed in an acid medium (pH = 3). The second regeneration of the solution was conducted with the same reagent amounts, as the first one. The concentration of gold was 0,90 g $l^{-1}$. The concentration of iodine in this case was reduced to 12,05 g $l^{-1}$. The solution was adjusted with 2 g $I_2$ and 8 g KI. However, the reagent costs are so high that they make the solution regeneration meaningless.

Table 4. Chemical composition of the final solution after precipitation, g $l^{-1}$.

| Cu | Au | Ni | Fe |
|---|---|---|---|
| 0.1 | 0,018 | 0.013 | 0.011 |

With the resulting adjusted solution from the second extraction a new batch of 50 g material has been processed. Leaching time has been increased to 3 min. The concentration of gold in the pregnant solution was 1,3 g $l^{-1}$. The precipitation of the metals was realized with 10,2 g KOH and 1 ml $N_2H_4.H_2O$. The solution, after precipitation has the chemical composition, given in Table 4.

As can be seen from the table, the metals in the solution are precipitated, but due to the transition from alkaline to acidic media and back, potassium sulfate is accumulated in the solution. Its solubility is not high - 11,1 g in 100 g $H_2O$ at 20°C. Therefore, presence of white crystals of $K_2SO_4$ in the final solution is observed.

The residues from these three operations of precipitation have been treated with hot water, alcohol and $HNO_3$, to dissolve the base metals, and melted under a layer of borax. The resulting gold mass was 0,3258 g with 99.985 % purity. The chemical composition of the gold is determined by X-ray fluorescence analysis. The overall gold recovery was 94,56 %.

## CONCLUSIONS

Leaching of gold by iodine-iodide lixiviant solutions is a very attractive method, because it is very quick and takes place at room temperature. Nevertheless, the use of the present research method for gold recovery from the solution is unsuitable, since other metals present in the solution simultaneously with the gold are reduced, leading to the need for further purification operations. Furthermore, the reagent costs for the iodine solution regeneration are so high that they make it meaningless.

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