



DOI: 10.31643/2019/6445.29
UDC 669.85/.86: 553.3/.4(574)
IRSTI 53.37.35



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Silver, gold and palladium leaching from pre-prepared electronic scrap using bromine-bromide solution

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Received: 31 July 2019 / Peer reviewed: 14 August 2019 / Accepted: 04 September 2019

Abstract. The leaching of silver, gold, and palladium from printed circuit boards in the bromine - bromide system after preliminary removal of the associated metals and copper has been investigated. It was established experimentally that the dissolution of gold with a turnover of leaching solution from a previously prepared PCB concentrate in comparison with the leaching of the original electronic scrap proceeds at a higher rate and much more completely, so the average degree of gold extraction rose from 87.2 to 89.39%. The consumption of bromine decreased from 20-32 to 12 kg Br₂ per ton of scrap. So by seven leaching stages, it was possible to obtain a productive solution with the content, g · dm⁻³: 0.0652 Au, 0.015 Pb, 0.00052 Cu. Pretreatment PCB concentrate also increases the rate and completeness of silver and palladium leaching. At the same time, preliminary removal of the main part of copper allows reducing its content in the productive solution by almost 10 times. Under the conditions of collective leaching of silver, gold and palladium with a slightly acidic (pH = 1.98) bromine-bromide solution, with a content of 100.8 g · dm⁻³ of bromide ions, it is possible to convert 98.64% Au, 97.23% Ag and 98.33% Pd to the solution. The kinetics of precipitation of gold, silver and palladium from productive solutions using zinc dust, copper powder and hydrazine solution has been studied. As a results it was to precipitate gold on zinc dust in the form of cement powder with a purity of 99.4% and collective (Ag-Pd) and (Au-Ag-Pd) products using a 10% solution of hydrazine with content, mass. %: 1.18 Cu, 90.6 Ag, 7.2Pd and 1.2 Cu, 83.31Ag, 7.15 Pd, 7.95 Au, respectively.

Key words: hydrometallurgy of gold, silver, gold and palladium leaching in the bromine-bromide system, cementation of noble metals from bromide solutions.

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Introduction

Previously [1], we have studied in detail the thermodynamics and kinetics of leaching silver, gold, palladium and platinum from the initial electronic scrap represented by printed circuit boards in the bromine-bromide system in the presence of a phosphate buffer solution. The effect of pH noble metals, concentration of active bromine, content of bromide ions and concentration of buffer solution on the speed and entirety of leaching was studied. It was found that gold dissolves in the studied system practically in an alkaline environment quite selectively, fully and with a high speed. However, silver and palladium can be converted into a solution

only using a slightly acid bromine - bromide solution, which causes the dissolution of the accompanying metals, especially copper and leads to an increased consumption of bromine. In this regard, it was of interest to study the behavior of silver, gold, and palladium in the process of their bromine-bromide leaching from PCB concentrate after preliminary removal of accompanying metals and copper from it. As the initial sample, a PCB ordinary concentrate (Printed Circuit Boards) was used obtained as a result of physical and mechanical processing of dismantled electronic equipment by means of an industrial application of the Israeli company All Recycling Ltd (www.AllRecycling.co.il), of

composition, wt.%: 26.15 Cu, 4.7 Al, 3.6 Sn, 2.92 Pb, 2.1 Fe, 1.8 Zn, 1.32Ni, 0.65 Cr, 0.163 Ag, 0.0150 Au, 0.0136 Pd, 0.007 Pt. This concentrate is characterized by a complex composition, and, along with copper, both ferrous (Fe, Cr) and non-ferrous (Al, Sn, Pb, Zn, Ni) metals with different chemical resistance are present as accompanying metals. Speaking by their position in a number of electrochemical tension of metals: $Al < Zn < Fe < Ni < Sn < Pb < H_2 < Cu < Ag < Pd < Au$, most of the present metals can be removed chemically under non-oxidizing conditions [2-5]. Speaking by the literature and our data, copper can be selectively separated by treating the concentrate with a solution of sulfuric acid in the presence of hydrogen peroxide as an oxidizing agent [6-11]. In this regard, the study of the optimal conditions for the leaching of gold, silver and palladium from a partially unmetallized PCB concentrate in the bromine - bromide system and the subsequent isolation of noble metals from the bromide solution is of theoretical and practical interest.

Thus, the present paper is devoted to:

- the study of the conditions of selective leaching of related metals and copper from the provided PCB concentrate;
- the study of the kinetics of leaching of silver, gold and palladium from pre-processed concentrate of printed circuit boards in the bromine-bromide system depending on pH, the concentration of active bromine, the concentration of bromide ions and the content of phosphate buffer solution;
- the study of the kinetics of the deposition of precious metals from bromide productive solution using cement dust, copper powder and a solution of hydrazine.

Testing. Devices and reagents

A series of experiments was prepared using the PCB concentrate sample presented above, previously grinded using a Retch GmbH laboratory hammer mill to a particle size of 0.5-2 mm. As reagents used: $MgCl_2$ (Fluka Israel), HCl (Fluka Israel), HNO_3 (Fluka Israel), $10.6 \text{ mol} \cdot \text{dm}^{-3}$ hydrogen peroxide solution (Negev Peroxide, Israel), $NaBr$ (Fluka Israel), HBr (Fluka Israel), NaH_2PO_4 (Fluka Israel) and concentrated ($434 \text{ g} \cdot \text{dm}^{-3} Br_2$) solution of elemental bromine (Bromine Compound Israel). Reagent solutions were prepared using bidistilled water. Preliminary leaching of the accompanying metals was carried out at 368 K, the ratio of the contacting phases S:L = 1:3 with a hydrochloric acid

solution containing additional magnesium chloride in a liter flask with a mechanical stirrer ($300 \text{ rpm} \cdot \text{min} \cdot \text{g} \cdot \text{dm}^{-3}$) and reflux condenser which was placed in a thermostat, which allowed to control the temperature of the liquid coolant within $\gamma 0.5-1,0^0 \text{ C}$. Copper was leached at 348 K. For this purpose, 0.5 dm^3 of sulfate leach solution of the desired composition was poured into a liter flask installed with nozzles installed under a tin electrode for monitoring the redox potential (Eh), a mechanical stirrer ($600 \text{ rpm} \cdot \text{min} \cdot \text{g} \cdot \text{dm}^{-3}$), for supplying an oxidizing agent (H_2O_2 solution), loading solid material and sampling the solution. Bromine-bromide leaching was carried out at 298.5 K, the ratio of the contacting phases S:L = 1:5 and the speed of rotation of the stirrer $300 \text{ rpm} \cdot \text{g} \cdot \text{dm}^{-3}$. The required amount of leaching solution containing $20 \text{ g} \cdot \text{dm}^{-3} NaBr$ and $70 \text{ g} \cdot \text{dm}^{-3} NaH_2PO_4 \cdot H_2O$ was poured into a reaction vessel equipped with a mechanical stirrer and electrodes for measuring pH and redox potential (Eh), after which the required amount was poured chopped scrap, then the vessel was placed in a Huber GmbH Unistat thermostat and the temperature in the reactor was adjusted to the desired value, after which the stirrer, measuring instruments were turned on and the pre-calculated amount of concentrated elemental bromine solution ($434 \text{ g} \cdot \text{dm}^{-3}$) was supplied reading recorded original redox - potential, hereinafter in the course of the reaction, if necessary adjusting the pH injected $20 \text{ g} \cdot \text{dm}^{-3} NaOH$ solution. The metal content in the solution was analyzed on an ISP-OES set up. Each leach residue was washed, dried, weighed, and the whole sample was decomposed sequentially: first with $6 \text{ mol} \cdot \text{dm}^{-3}$ with HNO_3 solution and then in aqua regia solution at 303.5 K, the resulting solution was analyzed by ISP-OES. Thus, the degree of extraction of associated metals, copper, silver, gold and palladium was determined by the material balance.

Results and discussion

Leaching of associated metals

Non-oxidative leaching of the accompanying metals was carried out with a solution of $2.5 \text{ mol} \cdot \text{dm}^{-3} HCl$ in the presence of $2.6 \text{ mol} \cdot \text{dm}^{-3} MgCl_2$. The leaching results are shown in Fig. 1. As can be seen from the presented results, after 200 min of processing the concentrate, it was possible to transfer the main part of the initial aluminum, zinc and tin to the solution, %: 94.4 Al, 92.3 Sn, 89.2 Zn. Along the way, a substantial part of iron, nickel and lead is extracted into the solution, %: 75.8 Fe, 72.4 Ni, 44.8 Pb, with the degree of dissolution of copper 1.2%, and silver 0.56%. Gold and palladium pretreatment are not affected.

The resulting hydrochloric acid solution contained $11.6 \text{ g} \cdot \text{dm}^{-3}$ Sn. Due to the increased demand for tin in the modern electronic industry and a reduction in the raw materials of this metal, its value on the London Metal Exchange has noticeably increased. The conditions for the extraction of tin from chloride productive solutions were examined in detail by us earlier [12].

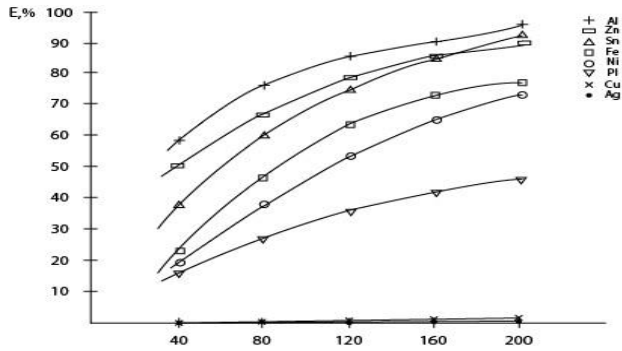


Figure 1 Results of preliminary leaching of the accompanying metals with hydrochloric acid solution: 368 K is temperature, the ratio of the contacting phases is S:L = 1:3, the rotation speed of the stirrer is 300 rpm

Copper leaching

The PCB concentrate (chemical concentrate 1) thus prepared was washed, dried to constant weight, and was used to study the kinetics of oxidative leaching of copper with a dilute solution of sulfuric acid in the presence of hydrogen peroxide as an oxidizing agent with scrap particle sizes ranging from 10-20 to 0.5-1 mm. As shown in the experiments, the fineness of the grinding of the material plays an important role, since electronic circuits containing copper and copper alloys are located inside the organic polymer material of the printed circuit board and are often additionally insulated with a protective varnish coating. Grinding scrap, especially in a ball mill, allows solvent to access the surface of the copper parts of the circuit. The experimental results are given in Table 1.

Table 1 The results of copper leaching with $1 \text{ mol} \cdot \text{dm}^{-3}$ sulfuric acid solution at a controlled redox potential of 520-680 mV, depending on the size of the scrap particles. The conditions of the experiments: temperature 348 K, the ratio of the contacting phases L:S = 3 and the rotation speed of the mechanical stirrer $600 \text{ rpm} \cdot \text{min}^{-1}$.

Time, min	Cu extraction into solution, %		
	10-20 mm	2-10 mm	0.5-1 mm
40	26.45	32.16	38.35
120	34.52	42.32	49.34
180	48.93	56.74	67.32
240	58.72	68.92	78.68
300	67.56	78.83	92.67

As a result of oxidative leaching, the results of which are presented in Table 1, it is possible to finely grind scrap to selectively transfer into solution up to 92.67% of the initial copper. At the same time, the remainder of the iron and nickel pass into the solution. Due to the reduction of material as a result of preliminary leaching, the concentration of precious metals increased by almost 1.4 times.

The resulting sulfate solution with a content of $68.5 \text{ g} \cdot \text{dm}^{-3}$ of copper can be electrochemically processed to obtain cathode copper suitable for subsequent refining.

Bromine-bromide leaching of precious metals

Chemical concentrate (2) obtained after sulfuric acid leaching, which contained, mass. %: 4.08 Cu, 0.55 Sn, 0.34 Al, 0.125 Fe, 0.136 Zn, 0.43 Pb, 0.324 Ag, 0.0297Au, 0.027 Pd and 0.0012 Pt were used for further experiments on the kinetics of gold leaching in the bromine-bromide system at pH 6 and subsequent leaching of silver and palladium from the residue at pH 1.98. The experimental results are provided in Tables 2 and 3. In the first case, experiments with the circulation of the productive solution were carried out on chemical concentrate 2.

Table 2 The results of the gold leaching in the bromine - bromide system at an initial pH of 6.1, the ratio of phases S:L = 3:1 with a revolution of the productive solution

Stage	[Br ₂] initial	[Br ₂] terminal	Br, ml	NaOH, ml	Buffer solution, ml	Eh, mV	pH	[Au], Ppm	[Au], Ppm terminal	E _{Au} , %
I	34.26	26.5	-	-	-	923	5.1	97	198	98.34
II	23.84	28.7	1.6	1.0	9.2	932	5.2	176	266	96.56
III	26.8	22.5	1.8	1.2	12.4	919	5.3	257	346	92.30
IV	20.4	18.6	1.8	1.2	18.6	917	5.2	342	428	90.65
V	17.6	14.3	1.8	1.2	28.9	908	5.1	389	472	86.58
VI	13.2	10.6	1.8	1.2	28.6	900	5.4	478	568	82.67
VII	9.6	6.8	1.8	1.2	28.6	882	5.3	572	652	78.63

Gold leaching with the circulation of the productive solution from the previously prepared scrap proceeds more fully, the average degree of gold recovery rose from 87.2 to 89.39%. Moreover, as a result of reducing the consumption of active bromine, it was possible to increase the number of stages to 7. The consumption of bromine per ton of scrap was reduced, thanks to these factors, from 20-32 to 12 kg

of Br_2 per ton of scrap. As a result of leaching, a productive solution (1) was obtained with a content of $0.0652 \text{ g} \cdot \text{dm}^{-3} \text{ Au}$, 0.0015 Pb , 0.00052 Cu .

Table 3 The results of the leaching of palladium and silver from the residue from the leaching of gold in the bromine - bromide system at an initial pH of 1.98, a bromine solution volume of 16 ml, a phase ratio of S:L = 1:5 and a concentration of bromide ions of $100.5 \text{ g} \cdot \text{dm}^{-3}$

Time, min	$[\text{Br}_2]$, $\text{g} \cdot \text{dm}^{-3}$	Eh, mV	pH	$[\text{Ag}]$, ppm	E_{Ag} , %	$[\text{Pd}]$, ppm	E_{Pd} , %
0	29.86	922	1.98				
60	24.10	918	1.50	300	46.34	15.46	28.63
240	21.54	908	1.40	404	62.34	24.64	45.26
300	20.43	912	1.50	567	87.45	37.86	68.82
360	19.78	900	1.30	612	94.32	48.64	89.15
420	19.13	899	1.50	625	96.20	53.08	97.20

The experimental results provided in Table 3 show that as a result of preliminary treatment of scrap, the speed and completeness of leaching of palladium increases. It should be noted that, probably, due to the easier conversion of the passivating AgBr film to the well-soluble AgBr_2^- anion complex, silver dissolves much faster than palladium. The resulting productive solution (2) contained, $\text{g} \cdot \text{dm}^{-3}$: 0.0053 Pd , 0.0625 Ag , 1.4 Cu , 0.00032 Fe , 0.0067 Pb . Thus, as a result of preliminary dissolution of the bulk of the initial copper, its content in the productive solution decreased by almost 10 times.

Table 4 presents the results of experiments on the kinetics of co-leaching of gold, palladium and silver at pH 1.98.

Table 4 The results of gold leaching, palladium and silver in a bromine - bromide system at a controlled pH of 1.98 and a redox potential of 920-908 mV, a bromine solution volume of 20 ml, a phase ratio of S:L = 1:5 and $100.5 \text{ g} \cdot \text{dm}^{-3} \text{ Br}^-$

Time, min	$[\text{Br}_2]$, $\text{g} \cdot \text{dm}^{-3}$	$[\text{Au}]$, ppm	E_{Au} , %	$[\text{Ag}]$, ppm	E_{Ag} , %	$[\text{Pd}]$, ppm	E_{Pd} , %
0	29.86						
60	23.72	34.95	58.84	321	49.62	15.30	28.32
240	20.18	57.51	96.82	430	66.34	25.10	46.48
300	19.64	58.41	98.34	599	92.40	39.10	72.34
360	19.18	58.43	98.45	626	96.62	47.88	88.67
420	18.44	58.56	98.64	628	97.23	53.10	94.33

The results of collective leaching of precious metals are presented in table. 4 show that under the presented conditions, silver and gold leach at close rates and after 6 hours of contact of the phases pass into the solution almost completely. Palladium also exhibits a high degree of recovery, however, as a result of passivation of the reaction surface, it dissolves relatively more slowly. The resulting solution (3) obtained by co-leaching contained, $\text{g} \cdot \text{dm}^{-3}$: 0.0059 Au , 0.0053 Pd , 0.0628 Ag , 1.8 Cu , 0.00032 Fe , 0.0067 Pb , 16.23 Br_2 and 110 Br^- .

Next, the conditions for the separation of gold, palladium and silver from productive solutions (1), (2) and (3) were studied.

Isolation of precious metals from bromine-bromide solutions by cementation

The separation of precious metals from productive solutions by cementation is complicated by the presence in the final solutions of a residual concentration of active bromine. In order to reduce the Br_2 content and its regeneration, the final solutions were evacuated before cementation. In this case, the outgoing gaseous bromine was passed through a solution with $100 \text{ g} \cdot \text{dm}^{-3} \text{ NaBr}$, which absorbed up to 80% bromine, the rest was hydrolyzed in an alkaline solution trap.

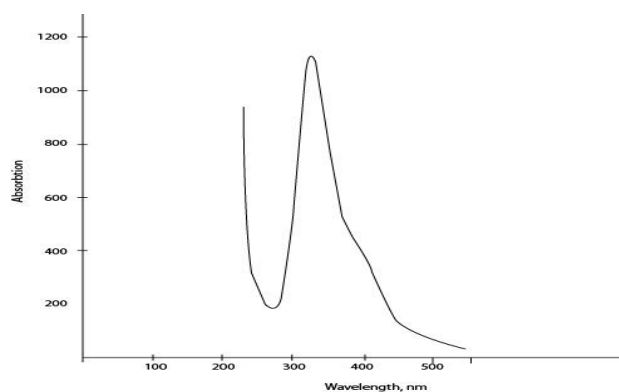


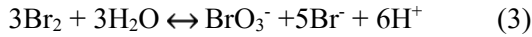
Figure 2 UV spectrum of a gold-containing bromine-bromide solution

Regenerated bromine-bromide solution can be used in the leaching stage.

In order to determine the composition of gold anionic bromide complexes present in the productive solution, the solution was analyzed using a UV spectrophotometer. The resulting spectrum shown in Fig. 2, it is characterized by a pronounced peak at 379 nm, which is usually associated with the presence of the most stable tetrabromaurate (III) AuBr_4^- in the solution under the studied conditions.

Figure 3 and table 5 show the results of studying the kinetics of gold deposition on zinc dust from solution (1) after its preliminary evacuation and adjustment of the corresponding pH value.

Cementation of gold on zinc dust in an alkaline medium can be described by reaction (2):



In this case, hydrolysis of active bromine by reaction (3) with the release of an H⁺-ion neutralizes the formation of sodium hydroxide, which stabilizes the pH of the medium.

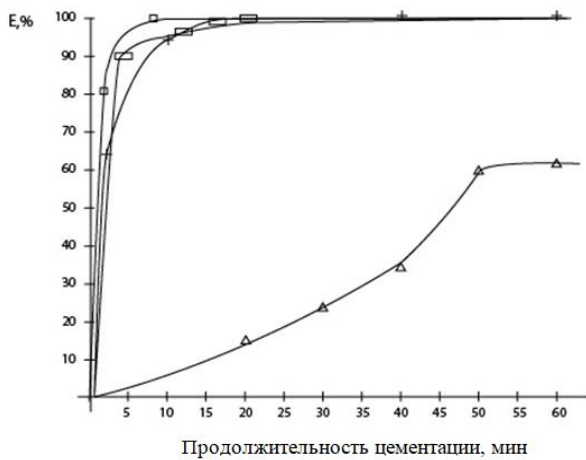


Figure 3 The results of the cementation of gold on zinc dust, depending on the initial pH of the productive solution

As can be seen from the data presented (Figure 3 and Table 5), gold cementation at zinc dust from

Table 5 Gold cementation results using zinc dust (-230 mesh) from bromine-bromide solution at pH 6 and a temperature of 290 K

Time, min	[Br ₂], g · dm ⁻³	pH	Eh	[Au], ppm	E _{Au} , %	Solution color
0	1.20	4.30	701	572	0	Brilliant orange
Start	0.86	8.11	697	567	0	Brilliant orange
2	0.82	8.19	650	121	78.66	Brilliant orange
15	0.80	8.40	465	30.3	94.66	Light-yellow
20	0.76	8.23	305	28.4	94.99	colorless
30	0.72	8.21	286	23.3	95.89	colorless
60	0.65	8.50	272	1.2	99.79	colorless

a pre-evacuated bromide solution in a relatively alkaline medium at pH 8, proceeds slowly and practically does not end, since the hydrolysis of dissolved zinc complicates the formation of cement gold. In slightly alkaline solutions, gold cementation occurs quickly and the bulk of the metal precipitates during the first 15 minutes.

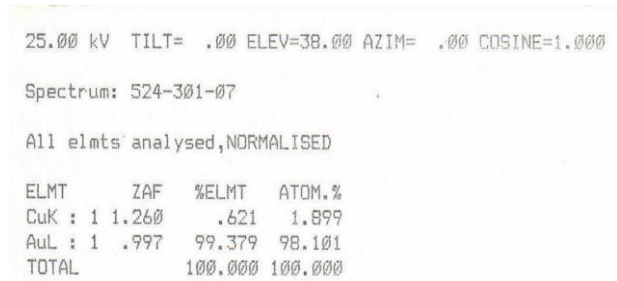


Figure 4 Results of SEM analysis of cement gold extracted from bromine-bromide solution on zinc dust

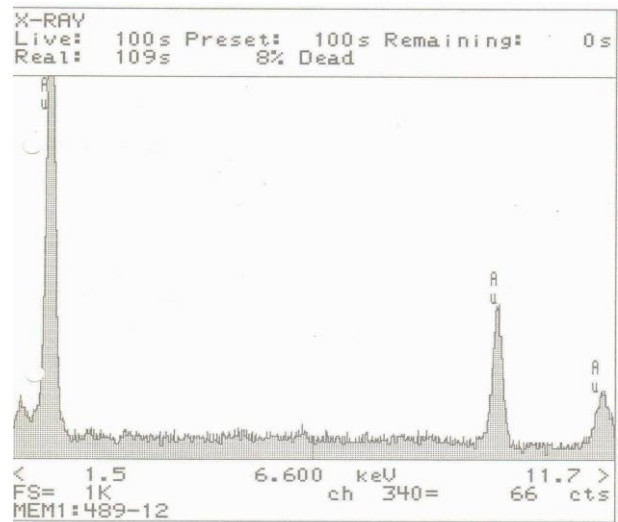


Figure 5 X-ray of cement gold isolated from bromine bromide on zinc dust

The cement slurry obtained from the bromine - bromide solution was analyzed using an X-ray phase analyzer (see Fig. 4) and an electron microscope (see Table 6). As can be seen from the results of the analysis, by zinc cementation, gold can be isolated in the form of a metal powder with a purity of 99.4%. The main impurity (0.6%) is copper.

Tables 6 and 7 show the kinetics of the deposition of precious metals from solutions (2) and (3) after their preliminary evacuation. Given the high content of copper ions in these solutions, preliminary experiments were carried out on the cementation of gold, palladium and silver on a copper powder, but no positive results were obtained because active bromine passivated the reaction surface of the copper powder.

Table 6 The results of the recovery of palladium and silver from a bromide solution (2) 1 ml of 10% solution of $N_2H_4 \cdot H_2O$ at pH 6, temperature is 278 K

Time, min	[Br ₂], g · dm ⁻³	pH	Eh	[Ag], ppm	E _{Ag} , %	[Pd], ppm	EPd, %
0	6.32	1.9	734	625	0	53.0	0
Start	5.86	8.10	697	574	0	50.5	0
2	3.23	8.23	650	141	77.4	8.9	82.3
15	1.86	8.40	465	43.3	93.1	2.7	94.6
20	1.23	8.67	305	32.4	94.8	1.9	96.2
30	1.20	8.72	286	28.3	95.5	0.7	98.6
60	1.18	8.78	272	8.2	98.7	0.6	98.8

Table 7 The results of the recovery of gold, palladium and silver from solution (3) 1.3 ml of 10 solution of hydrazine at pH 6 and temperature

Time, min	[Br ₂], g · dm ⁻³	Eh	[Ag], ppm	E _{Ag} , %	[Pd], ppm	EPd, %	[Au], ppm	E _{Au} , %
0	16.23	908	628.0	0	53.0	0	59.0	0
Start	7.23	762	616.0	0	52.0	0	57.8	0
2	6.12	332	197.7	67.8	9.0	82.6	11.4	80.3
15	4.34	282	69.6	88.7	2.5	95.2	4.3	92.6
20	3.56	223	47.2	92.4	2.1	96.0	2.2	96.2
30	3.18	234	22.3	96.4	0.8	98.5	0.75	98.7
60	2.76	216	7.4	98.8	0.4	99.2	0.81	98.6

For precipitation of noble metals from a bromide solution containing copper, a hydrazine solution was chosen as a reducing agent. The data on the separation of gold, palladium and silver from the productive solutions (2) and (3), presented in tables 7 and 8, showed that noble metals can be extracted by reduction with a 10% solution of $N_2H_4 \cdot H_2O$ with high speed and almost completely. It was found that the copper present in the solution is also reduced with the successive formation of oxides Cu_2O , CuO and metallic copper. The resulting precipitates were purified from copper by treating them at a temperature of 313 K with a dilute sulfuric acid solution containing $2.5 \text{ mol} \cdot \text{dm}^{-3} H_2SO_4$ and $0.9 \text{ mol} \cdot \text{dm}^{-3} H_2O_2$. Chemical analysis of the obtained collective products found that the final collective products isolated from solutions (2) and (3) contained, mass. %: 1.18 Cu, 90.6 Ag, 7.2 Pd, the rest is moisture, lead; 1.20 Cu, 83.31 Ag, 7.15 Pd, 7.95 Au, the rest is moisture, lead.

Collective products obtained may be sent to a refinery. Considering that from each ton of PCB concentrate, usually sent to the refinery, using bromine - bromide technology it is possible to obtain only 10-15 kg of the collective product, the advantages of hydrometallurgical processing associated only with lowering the cost of refining and reducing technological losses are obvious.

Findings

Within 180 minutes of treating the initial PCB concentrate with a hydrochloric acid solution containing $2.5 \text{ mol} \cdot \text{dm}^{-3} HCl$ in the presence of $2.6 \text{ mol} \cdot \text{dm}^{-3} MgCl_2$, it is possible to transfer to the solution, %: 94.4 Al, 92.3 Sn, 89.2 Zn, 75.8 Fe, 72.4 Ni, 44.8 Pb, while the degree of dissolution of copper is 1.2%, and silver 0.56%. Gold and palladium pretreatment are not affected.

As a result of oxidative leaching of the residue from hydrochloric acid treatment, it is possible to finely grind scrap of 0.5-1 mm scrap into the solution to 92.67% of the initial copper.

The dissolution of gold with the circulation of the leaching solution from a pre-prepared concentrate of printed circuit boards in comparison with the leaching of the initial electronic scrap proceeds with a higher speed and much more complete, as the average degree of gold recovery increased from 87.2 to 89.39%. Bromine consumption decreased from 20-32 to 12 kg of Br_2 per tonne of scrap. Moreover, for 7 stages of leaching, it was possible to obtain a productive solution with a content of, $g \cdot \text{dm}^{-3}$: 0.0652 Au, 0.015 Pb, 0.00052 Cu.

Pretreatment of scrap also increases the speed and completeness of leaching of silver and palladium.

Under conditions of collective leaching of silver, gold and palladium with a weakly acid (pH = 1.98) bromine-bromide solution containing $100.8 \text{ g} \cdot \text{dm}^{-3}$ bromide ions can be converted into a solution of 98.64% Au, 97.23% Ag and 98.33% Pd.

Gold cementation on zinc dust from a pre-evacuated bromide solution proceeds quickly and the bulk of the gold precipitates at pH 6 during the first 15 minutes. In this case, gold is released in the form of a metal powder with a purity of 99.4%. The main impurity (0.6%) is copper.

The deposition of gold, palladium and silver from collective productive solutions by reducing precious metals with a 10% solution of $N_2H_4 \cdot H_2O$ proceeds with high speed and almost completely. In this case, the copper present in the solution is also reduced with the successive formation of oxides Cu_2O , CuO and metallic copper. The resulting precipitates can be purified from copper by treating them at a temperature of 313 K with a dilute sulfuric

acid solution containing $2.5 \text{ mol} \cdot \text{dm}^{-3} \text{H}_2\text{SO}_4$ and $0.9 \text{ mol} \cdot \text{dm}^{-3} \text{H}_2\text{O}_2$. Final collective products contain, mass. %:
- 1.18 Cu, 90.6 Ag, 7.2 Pd, the rest is moisture, lead;
- 1.20 Cu, 83.31 Ag, 7.15 Pd, 7.95 Au, the rest is moisture, lead and suitable for refining.

The obtained experimental results made it possible to recommend the proposed technological methods for the design of a pilot plant for semi-

industrial optimization of bromine-bromide technology.

Acknowledgement. Authors of the work are grateful to the Chief Scientific Secretary of the Ministry of Industry and Trade of the State of Israel for sponsoring the studies described in this article.

Cite this article as: Kogan V.S., Berkovich I.V. Silver, gold and palladium leaching from pre-prepared electronic scrap using bromine-bromide solution // Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a (Complex Use of Mineral Resources). – 2019. – №3 (310). – P. 55-63.
<https://doi.org/10.31643/2019/6445.29>

Бром-бромид ерітіндісін пайдалана отырып алдын ала дайындалған электрондық жиындыдан (скраптан) күмісті, алтынды және палладийді ерітінділеу

Коган В. С., Беркович И. В.

Түйіндеме. Бұл жұмыста ілеспе металдар мен мысты алдын ала алып тастағаннан кейін бром-бромид жүйесіндегі баспа платаларынан күмісті, алтынды және палладийді ерітінділеу зерттелді. Бастапқы электрондық жиындыны ерітінділеумен салыстырғанда алдын ала дайындалған баспа платаларының концентратынан ерітінділеу ерітіндісінің қайтарымымен алтынды еріту жоғары жылдамдықпен және айтарлықтай толық өтеді, сондықтан алтынды бөліп алудың орташа дәрежесі 87.2-ден 89.39% - ға дейін көтерілді. 1 тонна жиындыдағы бромның Br_2 шығыны 20-32 кг-нан 12 кг-ға дейін қысқарды. Сонымен қатар ерітінділеудің 7 кезеңінде құрамында $\text{г} \cdot \text{дм}^{-3}$: 0.0652 Au, 0.015 Pb, 0.00052 Cu бар өнімді ерітінді алынды. Жиындыны алдын ала өңдеу күміс пен палладийді ерітінділеудің жылдамдығы мен толық жүруін арттырады. Бұл ретте мыстың негізгі бөлігін алдын ала алып тастағанда оның өнімді ерітіндідегі құрамын 10 есеге төмендетуге мүмкіндік береді. Күміс, алтын және палладийді құрамында $100.8 \text{ г} \cdot \text{дм}^{-3}$ бромид ионы бар әлсіз қышқыл бром-бромид ерітіндісімен ($\text{pH}=1.98$) біріктіріп ерітінділегенде ерітіндіге 98.64% Au, 97.23% Ag және 98.33% Pd бөлуге болады. Мырыш шаңын, мыс ұнтағын және гидразин ерітіндісін пайдалана отырып, өнімді ерітінділерден алтынды, күмісті және палладийді тұндыру зерттелді. Нәтижесінде цемент ұнтағы түріндегі мырыш шаңында тазалығы 99.4% болатын алтын және 10% гидразин ерітіндісін пайдаланып құрамында массалық %: 1.18 Cu, 90.6 Ag, 7.2 Pd және 1.2 Cu, 83.31 Ag, 7.15 Pd, 7.95 Au болатын ұжымдық (Ag-Pd) және (Au-Ag-Pd) өнімдері алынды.

Түйін сөздер: алтын гидрометаллургиясы, бром-бромид жүйесіндегі күмісті, алтынды және палладийді ерітінділеу, бромид ерітінділерінен жасалған асыл металдарды цементациялау.

Выщелачивание серебра, золота и палладия из предварительно подготовленного электронного скрапа с использованием бром-бромидного раствора

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Реферат. Изучено выщелачивание серебра, золота и палладия из печатных плат в бром-бромидной системе после предварительного удаления сопутствующих металлов и меди. Экспериментально установлено, что растворение золота с оборотом выщелачивающего раствора из предварительно подготовленного концентрата печатных плат в сравнении с выщелачиванием исходного электронного скрапа протекает с более высокой скоростью и существенно полнее, так средняя степень извлечения золота поднялась с 87.2 до 89.39%. Расход брома сократился с 20-32 до 12 кг Br_2 на тонну скрапа. Причем за 7 стадий выщелачивания удалось получить продуктивный раствор с содержанием, $\text{г} \cdot \text{дм}^{-3}$: 0.0652 Au, 0.015 Pb, 0.00052 Cu. Предварительная обработка скрапа увеличивает также скорость и полноту выщелачивания серебра и палладия. При этом, предварительное удаление основной части меди, позволяет снизить её содержание в продуктивном растворе практически в 10 раз. В условиях коллективного выщелачивания серебра, золота и палладия слабокислым ($\text{pH}=1.98$) бром-бромидным раствором, с содержанием $100.8 \text{ г} \cdot \text{дм}^{-3}$ бромид-ионов удается перевести в раствор 98.64% Au, 97.23% Ag и 98.33% Pd. Изучено осаждение золота, серебра и палладия из продуктивных растворов с использованием цинковой пыли,

медного порошка и раствора гидразина. В результате удалось выделить золото на цинковой пыли в форме цементного порошка чистотой 99.4% и коллективные (Ag-Pd) и (Au-Ag-Pd) продукты с использованием 10% раствора гидразина с содержанием, масс. %: 1.18 Cu, 90.6 Ag, 7.2 Pd и 1.2 Cu, 83.31Ag, 7.15 Pd, 7.95 Au соответственно.

Ключевые слова: гидрометаллургия золота, выщелачивание серебра, золота и палладия в бром-бромидной системе, цементация благородных металлов из бромидных растворов.

REFERENCES

- [1] Kogan V.S., Berkovich I.V. Vyshchelachivaniya zolota, serebra, palladiya i platiny iz elektronnoho skrapa v brom- bromidnoy sisteme // (In press, in Rus.).
- [2] Yang C., Tan Q., Liu L., et al. Recycling Tin from Electronic Waste: A Problem that needs more attention// ACS Sustainable Chem. Eng.-2017.-№ 5.-P.2292-2301 (In Eng). <https://doi.org/10.1021/acssuschemeng.7b02903>
- [3] Debnath B., Chowdhury R., Kumar S. Sustainability of metal recovery from E-Waste //Front. Environ. Sci. Eng. -2018.-№ 12(6).- P.2095-2201. 2301 (In Eng.). <https://doi.org/10.1007/s11783-018-1044-9>
- [4] Kim Y., Seo H., Roh Y. Metal Recovery from the Mobile Phone Waste by Chemical and Biological Treatments//Minerals.- 2018. -V. 8(1). -№8 (In Eng). <https://doi.org/10.3390/min8010008>
- [5] Yang T., Zhu P., Liu W. et al. Recovery of Tin from metal powders of waste printed circuit boards// Waste Manag.- 2017.- № 68.- P.449-457 (In Eng). <https://doi.org/10.1016/j.wasman.2017.06.019>
- [6] Seyed M., Seyed A., Azizi A., Hayati M. Copper leaching from waste printed circuit boards (PCBs) using sulfuric acid and hydrogen peroxide//Res. J. of Chem. and Eng.- 2019.-v.23(8)- P.1-9 (In Eng).
- [7] Fabio dos Santos et al. Copper extraction from electronic scrap by oxidative acid leaching process //HydroCopper2011. 6th International Seminar on Copper Hydrometallurgy. - 6-8 July 2011. - Vila Del Mar. Chile. - P. 1-8; (In Eng).
- [8] Sharma A., Sharma S., Badgi U., Gautman D. Copper Extraction from the discarded printed circuit boards by leaching// Inter. J. Appl. Res. -2017.v.3(3). - P. 634-637 (In Eng).
- [9] Isidar A. et al. Two-step Leaching of Valuable Metals from Discarded Printed Circuit Boards, and Process Optimization using Response Surface Methodology //Adv. Recycling Waste Manag.- 2017.- v. 2.- Iss. 2.- P. 2 -9. (In Eng). <https://doi.org/10.4172/2475-7675.1000132>
- [10] Kogan V.S., Raykhman G.O. Gidrometallurgicheskoye izvlecheniye medi, olova i serebra iz produkta fiziko-mekhanicheskoy pererabotki elektronnoho skrapa // Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a (Complex Use of Mineral Resources). -2016. -No.1. -P.88-98 (In Rus.). <https://doi.org/10.31643/2018/166445>
- [11] Jimenez Correa M. et al. Separation copper from a leaching solution of printed circuit boards by using solvent extraction with D2EHPA // Brazilian Journ. Of Chem. Eng. September - 2018.- v. 35 (03) .- P.919-930 (In Eng).
- [12] Kogan V.S., Raykhman G.O. Vydeleniye olova (IV) iz sul'fatno-khlordnykh rastvorov s pomoshch'yu Alamine 336 i Cyanex 923 // Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a (Complex Use of Mineral Resources). - 2014.- № 4. P.79-86. (In Rus.). <https://doi.org/10.31643/2018/166445>

ЛИТЕРАТУРА

- [1] Коган В.С., Беркович И.В. Выщелачивания золота, серебра, палладия и платины из электронного скрапа в бром- бромидной системе // (в печати)
- [2] Yang C., Tan Q., Liu L., et al. Recycling Tin from Electronic Waste: A Problem that needs more attention// ACS Sustainable Chem. Eng. -2017.-№5.- P. 2292-2301. <https://doi.org/10.1021/acssuschemeng.7b02903>
- [3] Debnath B., Chowdhury R., Kumar S. Sustainability of metal recovery from E-Waste //Front. Environ. Sci. Eng. -2018.-№ 12(6).- P. 2095-2201. <https://doi.org/10.1007/s11783-018-1044-9>
- [4] Kim Y., Seo H., Roh Y. Metal Recovery from the Mobile Phone Waste by Chemical and Biological Treatments//Minerals.- 2018. -V.8(1). -№8. <https://doi.org/10.3390/min8010008>
- [5] Yang T., Zhu P., Liu W. et al. Recovery of Tin from metal powders of waste printed circuit boards// Waste Manag.- 2017.- № 68.- P.449-457. <https://doi.org/10.1016/j.wasman.2017.06.019>
- [6] Seyed M., Seyed A., Azizi A., Hayati M. Copper leaching from waste printed circuit boards (PCBs) using sulfuric acid and hydrogen peroxide//Res. J. of Chem. and Eng.- 2019.-V.23(8)- P.1-9.
- [7] Fabio dos Santos et al. Copper extraction from electronic scrap by oxidative acid leaching process //HydroCopper2011. 6th International Seminar on Copper Hydrometallurgy. - 6-8 July 2011. - Vila Del Mar. Chile.- P. 1-8;
- [8] Sharma A., Sharma S., Badgi U., Gautman D. Copper Extraction from the discarded printed circuit boards by leaching// Inter. J. Appl. Res. -2017.v.3(3). - P. 634-637.
- [9] Isidar A. et al. Two-step Leaching of Valuable Metals from Discarded Printed Circuit Boards, and Process Optimization using Response Surface Methodology //Adv. Recycling Waste Manag.- 2017.- V. 2.- Iss. 2.- P. 2-9. <https://doi.org/10.4172/2475-7675.1000132>

[10] Коган В.С., Райхман Г.О. Гидрометаллургическое извлечение меди, олова и серебра из продукта физико-механической переработки электронного скрапа// Комплексное использование минерального сырья. - 2016.- №1.- С.88-98 <https://doi.org/10.31643/2018/166445>

[11] Jimenez Correa M. et al. Separation copper from a leaching solution of printed circuit boards by using solvent extraction with D2EHPA// Brazilian Journ. Of Chem. Eng. September. - 2018.- V.35(03).- P.919-930. <https://doi.org/10.1590/0104-6632.20180353s20170144>

[12] Коган В.С., Райхман Г.О. Выделение олова (IV) из сульфатно-хлоридных растворов с помощью Alamine 336 и Суанех 923// Комплексное использование минерального сырья. -2014.- №4.- С.79-86; <https://doi.org/10.31643/2018/166445>