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RECOVERY OF PRECIOUS METALS FROM WASTE MATERIALS BY THE METHOD OF FLOTATION PROCESS

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The article presents the investigation results upon recovery of precious metals from electronics waste and used ceramic catalytic converters. Various frothing agents which generate stable and abundant foam as well as collectors and pH regulators have been used in the investigations . The tests were conducted with the use of laboratory flotation device

Key words: flotation, flotation reagents, waste, silver, recycled.

INTRODUCTION

Flotation is the method of separation commonly applied to the enrichment process of carbon and metal ores. It is an effect related to various interfacial phenomena present in solid/liquid/gas system. If the grain shows the hydrophilic properties under certain defined conditions then in the flotation process it can be separated from those that do not feature such properties [1-4]. The intensity of flotation process is determined by numerous factors the most important of which are: properties of flotation foam (type of frothing agent) and grain size. The flotation method can be used for separation of metal from grain fraction of some oxides and carbides. This was confirmed by test results obtained during recovery of native gold from polymetallic copper ores performed at CSIRO Minerals in Australia [5].

The authors of the presented article conducted a number of tests on the recovery of silver from jewellery wastes and silver semi-products with the application of flotation process [6-7]. They made some attempts at the recovery of precious metals from waste printed circuits boards of mobile phones, PC computers and used ceramic catalytic convertors. The results obtained are presented in the article.

In majority of PCBs cases, precious metals are coated upon ceramic or plastic elements. The content of precious metals in such products greatly depends on the age of the waste material. In the 80 s of the last century, the thickness of the layer upon contacts in electronic devices was 1-2,5 μm whereas now it is 300 – 600 nm. It is estimated that there is ca.1kg of silver and 0,3 kg of gold in only 1Mg of used mobile phones while 1 Mg of used computers contains 3 kg of silver and 0,3 kg of gold.

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End-of life catalytic reactors constitute another group of waste materials and have been used in vehicles since 2001. There are two types of catalytic convertors: ceramic and metal. In case of ceramic catalytic convertors the basic material is the mass which contains MgO, Al_2O_3 i SiO_2 as well as ZrO and which is coated with precious metals from the platinum family: platinum, palladium, rhodium and occasionally ruthenium. The average platinum content in a catalyst is ca. 2 kg. The platinum content in a catalytic reactor is relatively high thus ca. 0,5 kg of platinum can be recovered from 1 Mg of reactors. In the view of the fact that this type of waste material is systematically growing, the process of its treatment seems to be vital.

FLOTATION TEST STAND AND REAGENTS USED IN THE FLOTATION PROCESS

Flotation test stand constructed as part of the presented paper was designated for some laboratory attempts at selective separation of components in scrap materials. It consists of a flotation chamber made of

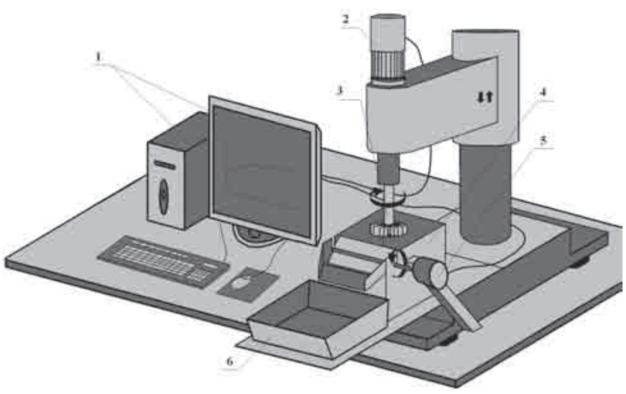

Figure 1 The diagram of the device used in tests of flotation process: 1 - the computer, 2 -the motor, 3 - the rotor, 4 – the flotation cell, 5 - the drift fender, 6 - the flotation concentrate cell

acid resistant steel and an engine-propelled rotor with height control device. The liquid is mixed by the rotor and air which is introduced by a compressor connected with the rotor. The rotor speed is set within the range from 100 – 1 500 rev/min whereas air flow is controlled by a rotometer. The scum is collected from the chamber surface with a mechanical rake as the process continues. Figure 1 presents a diagram of the device used in tests of flotation process.

Various types of frothing agents, collectors and pH regulators have been used for investigations. Table 1 presents the agents applied.

Table 1 **The agents applied**

Foaming agent	Collecting agent	pH regulator
α-terpineol	Acrylonitrile	$CuSO_4$
corflot	Sodium amyl xanthogenate	
Pine oil	Potassium etyl xanthogenate	
	X-23	

PREPARATION OF THE MATERIAL FOR FLOTATION PROCESS

In the first stage of the carried out research, the printed circuit boards from PC computers and mobile phones have been subjected to crushing and grinding process.

The following installation has been used in the investigations of the crushing process of waste materials which contain precious metals: screw mill, sharp mill, ball mill and buhr stone mill.

In the course of the carried out investigations it was found that grinding of big size printed boards in a ball grinder does not bring satisfactory results. Although a significant part of the charge sustains fine grinding, part of the post-process fraction retains the size which is not suitable for the process of flotation. This problem had been eliminated by the application of preliminary crushing with screw mill, before ball mill was used.

Two-step grinding of printed circuit boards helps obtain the fraction with granularity proper for flotation process. Similarly satisfactory effect is obtained at additional grinding of the fraction initially refined with screw mill and with the assistance of buhr stone mill or sharp mill.

In all cases, classification of the materials obtained as the consequence of grinding was performed with LPzE-2e vibrating screen. Sieve analysis shows that in case of two-step crushing (screw mill - buhr stone mill, screw mill – sharp mill) the average 90 % of output fraction from mills shows the crushing which is appropriate for flotation process. The remaining part (around 10 %) has to be subjected to additional grinding since it shows granularity above 0.2 mm. In case of the device system screw mill - ball mill, the proportions are slightly less favorable and their average value amounts from 80 % to 20 %.

Apparent improvement of grinding efficiency of such materials as printed circuit boards can be obtained by cooling them before they are introduced into crushing devices. An attempt was made with the application of liquid nitrogen. Crushing of ceramic catalytic convertors has to be a two stage procedure. The use of screw mill and then a ball mill, buhr stone mill or sharp mill assures positive effects. Sieve analysis shows that over 95 % of the output fractions (for three layouts of devices) presents granularity below 0.2 mm and thus is appropriate for flotation process.

The material obtained after grinding process has been subjected to X-ray analysis and the analysis on atomic adsorption spectrometer. Three samples were taken from each type of waste material.

Chemical analysis of used printed circuit boards performed upon atomic adsorption spectrometer is presented in Tables 2 and 3.

Table 2 **Chemical composition of printed circuit boards from PC computers / % wt**

Sample number	Ag	Cu	Pb
1	0,044	23,6	4,76
2	0,0017	26,8	5,24
3	0,011	27,8	6,01

Table 3 **Chemical composition of printed circuit boards from mobile phones / % wt**

Sample number	Ag	Cu	Pb
1	0,044	23,6	4,76
2	0,0017	26,8	5,24
3	0,011	27,8	6,01

Chemical analysis performed upon atomic adsorption spectrometer proved that the platinum content in crushed fraction of ceramic catalytic convertors is 0,026 %.

THE INVESTIGATIONS RESULTS OF FLOTATION PROCESS

In order to learn more about flotation kinetics in combinations ceramics-metallic fraction, polymer-metallic fraction, ceramics-polymer-metallic fraction which are quite essential when wastes containing precious metals are dealt with, the authors performed a series of tests with the use of synthetic mixtures. Silver powder and ceramic materials from the wastes containing precious metals i.e. aluminum oxide, silicon oxide and epoxy resin (typical representative of polymers) have also been used for tests.

The carried out research were to determine the conditions of flotation process of materials included in waste materials which occur in a real world. The obtained results were satisfactory therefore further tests were performed on real materials. Tables 4 and 6 present exemplary test results of flotation process performed upon crushed printed circuits from PC boards.

Table 4 **Results of the flotation tests for printed circuit boards from PC computers using pine oil as frothing agent and oleic acid as collector**

Rotation frequency equal / rot/min	pH	Content in flotate / % wt.			Ag content in chamber residues /% wt.
		Ag	Cu	Pb	
Air flow rate 2 /dm³/min					
500	6	0,055	8,6	4,2	0,001
	7	0,032	5,6	1,2	0,004
	8	0,029	8,8	2,2	0,003
	10	0,020	6,3	1,6	0,004
Air flow rate 4 /dm³/min					
700	6	0,074	9,7	1,6	0,002
	7	0,060	9,8	1,1	0,003
	8	0,026	8,0	2,1	0,002
	10	0,018	7,7	1,8	0,004

Table 5 **Results of the flotation tests for printed circuit boards from PC computers using Corflot as frothing agent and X-23 as collector**

Rotation frequency equal /rot/min	pH	Content in flotate / % wt.			Ag content in chamber residues /% wt.
		Ag	Cu	Pb	
Air flow rate 2 /dm³/min					
500	6	0,099	6,0	0,92	0,001
	7	0,097	6,0	0,91	0,001
	8	0,090	6,3	0,99	0,002
	10	0,072	7,8	1,01	0,003
Air flow rate 4 /dm³/min					
700	6	0,096	7,8	0,93	0,001
	7	0,061	6,8	0,97	0,005
	8	0,059	5,7	1,04	0,006
	10	0,023	5,2	1,82	0,007

Table 6 **Results of the flotation tests for printed circuit boards from PC computers using Corflot as frothing agent and X-23 as collector**

Rotation frequency equal /rot/min	pH	Content in flotate / % wt.			Ag content in chamber residues /% wt.
		Ag	Cu	Pb	
Air flow rate 2 /dm³/min					
500	6	0,012	10,60	1,65	0,11
	7	0,011	8,34	1,45	0,16
	8	0,007	6,28	1,22	0,26
	10	0,003	6,12	1,05	0,45
Air flow rate 4 /dm³/min					
700	6	0,014	10,16	1,64	0,09
	7	0,009	8,12	1,32	0,10
	8	0,001	6,13	1,13	1,17
	10	0,000	6,04	1,00	0,33

Tables 7-8 depict exemplary tests results of flotation process performed upon crushed printed circuits from mobile phones.

Table 7 **Results of the flotation tests for printed circuit boards from mobile phone using Corflot as frothing agent and sodium amyl xanthogenate as collector**

Rotation frequency equal /rot/min	*pH*	Content in flotate / % wt.			Ag content in chamber residues /% wt.
		Ag	Au	Cu	
Air flow rate 2 /dm³/min					
500	6	0,16	0,04	17,2	0,12
	7	0,11	0,02	10,1	0,24
	8	0,13	0,06	12,1	0,17
	10	0,15	0,05	17,9	0,13
Air flow rate 4 /dm³/min					
700	6	0,17	0,03	16,9	0,13
	7	0,15	0,02	16,0	0,20
	8	0,13	0,05	14,1	0,17
	10	0,14	0,04	13,6	0,14

Table 8 **Results of the flotation tests for printed circuit boards from mobile phone using Corflot as frothing agent and sodium etyl xanthogenate as collector**

Rotation frequency equal /rot/min	*pH*	Content in flotate / % wt.			Ag content in chamber residues /% wt.
		Ag	Au	Cu	
Air flow rate 2 /dm³/min					
500	6	0,2	0,05	15,7	0,13
	7	0,2	0,06	14,1	0,28
	8	0,4	0,04	11,1	0,27
	10	0,2	0,05	16,3	0,23
Air flow rate 4 /dm³/min					
700	6	0,2	0,03	16,9	0,14
	7	0,2	0,04	16,0	0,19
	8	0,1	0,04	14,0	0,18
	10	0,1	0,03	13,5	0,14

The application of different flotation parameters i.e. the change of gas flow, rotor speed and flotation reagents did not affect the scum enrichment.

The tests results of flotation process carried out upon ground ceramic catalytic convertors are presented in Table 9.

The application of different flotation parameters i.e. gas flow above 2 dm^3, rotor speed 700 and different reagents than those presented in Table 9 did not bring satisfactory flotation results (slight platinum enrichment in the scum as compared with the initial content).

Table 9 **The results of the flotation tests carried out upon ground ceramic catalysts with the use of Corflot as a frothing agent, selected collecting reagents and CuSO4 as pH regulator (gas flow rate 2 dm³/min, rotation speed – 500 rot/min.)**

Collector reagent	pH	Content in flotate / % wt.	Pt content in chamber residues / % wt.
----------	7,01	0,19	0,012
Ksantog amylowy	10,03	0,32	0,001
Ksantog amylowy	8,00	0,34	0,001
Ksantog etylowy	10,01	0,14	0,018
Ksantog -etylowy	8,00	0,38	0,001
X-23	10,03	0,33	0,001
X-23	8,03	0,30	0,003
Akrylonitryl	10,01	0,12	0,015
Akrylonitryl	8,04	0,32	0,001

CONCLUSIONS

The parameters of flotation process and flotation re agents applied and presented in the paper, in case of waste printed circuit boards from mobile phones and PC boards, did not bring satisfactory results (though the results obtained with synthetic materials were promising). The obtained scum did not exhibit high content of precious metals. However, the increase of silver concentration in the flotation chamber (Table 6) was observed.

Promising results, on the other hand, were obtained from the tests on end-of-life ceramic catalytic convertors used in vehicles. The best results were obtained for rotor speed of 500 rev/min and gas flow of 2 dm^3/min. In case of these wastes the best results were obtained for the following reagents:

- Frothing agents: corflot,
- Collecting: sodium amyl xanthogenate, X-23, ethyl xanthogenate.

The application of such reagents helped obtain platinum concentration in a final product up to 0,38 % which is close to its concentration in anode slime obtained in the process of copper electrorefining. The application of slightly different flotation conditions (the same as in case of wastes from final treatment of silver semi-products and jewellery) i.e. gas flow above 2 dm^3 rotor speed 700 and different foaming reagents, did not bring satisfactory flotation results (slight platinum enrichment in the scum as compared with its initial content).

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Note: Nowak P is responsible for English language, Katowice, Poland