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THE OBTAINED OF CONCENTRATES CONTAINING PRECIOUS METALS FOR PYROMETALLURGICAL PROCESSING

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In the presented study the flotation process has been proposed as a method of enrichment of silver-bearing jewellery waste. This method, traditionally used for the enrichment of non-ferrous metal ores, is based on differences in wettability between individual minerals. Flotation concentrate, enriched with Ag, was subjected to further processing by the pyrometallurgical method in order to produce silver from these wastes.

Key words: flotation concentrate, silver, jewellery wastes, pyrometallurgical method

INTRODUCTION

Flotation is a well-known method of separation, which is most commonly used for the beneficiation processes of non-ferrous metal ores and coal. In Poland it is used for enrichment of sulphide copper ores, sulphide zinc-lead ores as well as in hard coal preparation processes.

Flotation can also be used to separate metal from some grain size oxides and carbides. This is confirmed through research on recovery of native gold from polymetallic copper ores, presented by Allan and Woodcock [1]. Promising results were obtained by the application of xanthogenates (e.g. NaC_2H_5OCSS), dithiophosphates (DTP) and monothiophosphates (MTP) as collectors, with coaction of activators (Na_2CO_3, $CuSO_4$) and depressors (sodium sulphide). Pine oil and cresol acid were used as frothers and H_2SO_4 was used as a regulator.

The results of research performed by Łuszczkiewicz [2] also indicate the potential application of flotation for enrichment of fractions in gold. He subjected landfilled waste from the area of the decommissioned mine Złoty Stok to flotation. Having used sodium isobutyl xanthogenate as a collector, α-terpineol as a frother and H_2SO_4 as a regulator, he obtained yields of gold at a maximum level of 40 %.

Soto and Toguri [3] conducted research on the application of flotation for the recovery of Al from waste slag from aluminium works; the concentration of this metal being too low for profitable pyro-metallurgical path processing. Milling the slag and introducing it to a water solution of sulphuric acid and $CuSO_4$, as well as the application of collectors in the form of diisobutyl dithiophosphate or amyl xanthogenate, yielded concentrate with aluminium contents reaching 80 % by weight.

G. Siwiec, B. Oleksiak, J. Wieczorek - Silesian University of Technology, Katowice, Poland
A. Blacha-Grzechnik - Silesian University of Technology, Gliwice, Poland

Until now flotation's most important application has been in the processing of waste materials in copper production. Slags from suspension-based processes for the production of copper matte with the application of technology Inco and Outokumpu with copper content over 0,5 % by weight are commonly processed by this method. After slow cooling and size reduction these are subjected to a flotation process with the use of flotation reagents, which are traditionally used for producing copper concentrates from sulphide ores [4, 5].

TEST RESULTS

A wide cycle of tests was conducted using synthetic mixtures in order to determine whether or not flotation in systems like ceramics - metallic fraction, polymer - metallic fraction, ceramics-polymer-metallic fraction can be used to process jewellery waste containing precious metals. The composition of these mixtures is collated in Table 1.

Table 1 **Types of synthetic mixtures used in the research**

Mixture type	Percentages of individual constituents / wt. %			
	Ag	SiO_2	Al_2O_3	Epoxy resin
Al_2O_3-Ag	10	------	90	-------
SiO_2-Ag	10	90	-----	-----
epoxy resin-Ag	1	-----	-----	99
SiO_2- epoxy resin-Ag	5	50	-----	45

The purpose of the tests was to determine the correct conditions in which to conduct the flotation of materials present in actual wastes.

The following factors, which were held to influence the outcome of the flotation process, were subjected to analysis:

- rotational speed of rotor,
- flow rate of gas (air),
- duration of the process,

- type and quantity of flotation reagents.

Tests on synthetic systems were conducted with rotor speeds of 300, 500, 700 and 900 rpm and a gas flow rate from 2 to 8 dm^3/min.

An analysis of test results from synthetic mixtures, indicates that maximum concentrations of silver in flotation concentrate for individual systems are appreciably higher from initial ones and amount to:

- Al_2O_3-Ag - 60 wt. %,
- SiO_2-Ag - 53 wt. %,
- epoxy resin-Ag – 7,5 wt. %,
- SiO_2-epoxy resin-Ag - 26 wt. %.

This significant degree of beneficiation of flotation concentrate was achieved while using Corflot (2 cm^3), amyl sodium xanthogenate (0,25 cm^3) and $CuSO_4$ as flotation reagents. The best results of silver recovery were obtained at pH=6 for epoxy resin - Ag and at pH=8 for the remaining systems. Too low or too high pH correlated with a significant reduction of silver content in flotation concentrate.

The following reagents also offered promising results during the course of flotation process:

- frothers: pine oil, sodium sulphide(II) (water solution), α-terpineol,
- collectors: polyacrylonitryle, naphtha, oleinic acid, ethyl sodium xanthogenate and X-23.

Similarly to Corflot, the optimum amount of frother was 2 cm^3. This amount in all cases ensured the formation of durable and stable foam during the whole process. 0,25 cm^3 of collector was used as for amyl xanthogenate. Too low an amount of collecting reagents resulted in the reduction of silver content in flotation concentrate, whilst an excess did not increase the efficiency of the process.

In order to perform a more complete analysis of the test results, yield values for useful constituent in concentrate (ε_{Ag}) and non-useful constituent in tailing (ε_N) were determined on the basis of the results of silver concentration in flotation concentrate [6 - 8].

Graphical interpretation of changes of silver yield in the flotation process under analysis is also presented in form of enrichment curves of ε_{Ag} - ε_N relation in exemplary Figure 1. Enrichment curves are described with the relation (1) [9]:

$$\varepsilon_N = a \cdot \frac{(100 - \varepsilon_{Ag})}{(a - \varepsilon_{Ag})} \quad (1)$$

Values of coefficient *a* in equation (1) are between the 100,18 to 136 range indicate good floatability of silver from the synthetic mixtures being analysed [9].

An analysis of test results for synthetic mixtures indicates a regular increase of flotation concentrate mass over time. In the first minutes of the process, the mass of flotate sludge increases significantly and then stabilizes.

Flotation process research results and the evolution of silver enrichment curves indicate that the best results from the flotation process were achieved with rotor speeds of 500 rpm and 700 rpm and an air flow rate in the range of 2 - 6 dm^3/min.

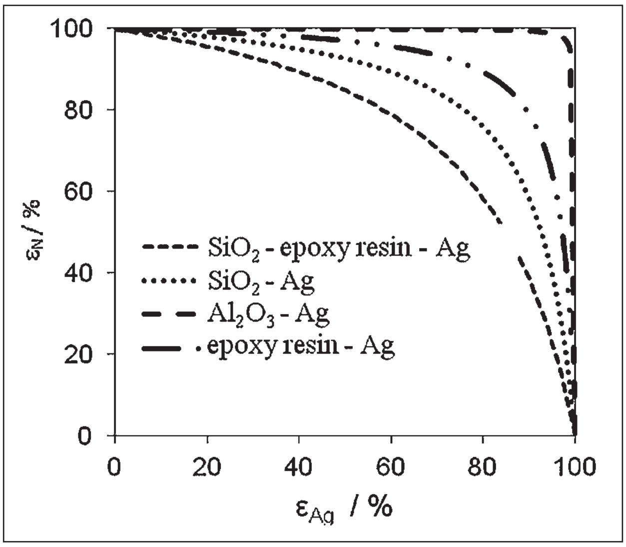

Figure 1 Silver beneficiation curves for synthetic materials (flow rate 4 dm^3/min, rotor speed 700 rpm)

Optimum parameters for the flotation process were determined through research using synthetic systems and used in the enrichment process of materials originating from the surface treatment of silver semi-products and jewellery.

PROCESSING OF FLOTATION CONCENTRATES WITH PYROMETALLURGICAL METHOD

Silver sludges originating from the process of surface treatment of silver semi-products and jewellery in wet conditions, after prior drying, were subjected to further pyrometallurgical processing in order to obtain semi-product for the production of silver or its alloys. The average composition of flotation concentrate subjected to further treatment is collated in Table 2.

Table 2 **Average composition of flotation concentrates subjected to pyrometallurgical treatment**

Type of concentrate	Content of main components of concentrate / wt. %			
	Ag	Cu	SiO_2	Al_2O_3
Concentrate after sludge flotation (jewellery processing)	41,8	2,7	49,6	4,9
Concentrate after sludge flotation (silver semi –products processing)	39,2	3,2	50,4	6,2

Below 4 wt. % copper content in the concentrates allows the direct processing of these materials in order to obtain Dore metal without additional decoppering.

The whole cycle of tests had three main objectives:

- to determine the optimum smelting temperature (range 1 273 K – 1 373 K),
- to determine the optimum smelting duration (range 30 – 150 minutes),
- to select the composition of the charging mix that yielded the maximum amount of silver.

Borax, as a slag-forming addition (sodium tetraborate decahydrate), was used mainly to form liquid slag with a low viscosity, absorbing impurities contained in the concentrate being smelted. With this type of slag silver, being heavier, accumulated on the bottom of melting pot after smelting. In the course of each experiment the weighed quantities of charging materials were placed in magnesite melting pots and mixed thoroughly. Flotation concentrate and borax were introduced in various weight ratios. Then the melting pots were heated to the required temperatures, after which they were soaked over a period of 30 to 150 minutes. Liquid charge was continually purged with air at a flow rate of 2 dm^3/min. The lance supplying air was made of Al_2O_3. Metallic phase, separated from slag after the process, was weighed and subjected to chemical analysis. Test results (with addition of borax 2:1 as compared to mass of the concentrate) are presented in Table 3 and in Figures 2- 3.

The results of research into the possibility of using the pyrometallurgical method to process beneficiated sludges from the surface treatment of silver jewellery and semi-products indicate that if appropriate conditions are maintained during the process, it is possible to obtain silver with purity near to that of Dore metal (produced using traditional metallurgical technologies such

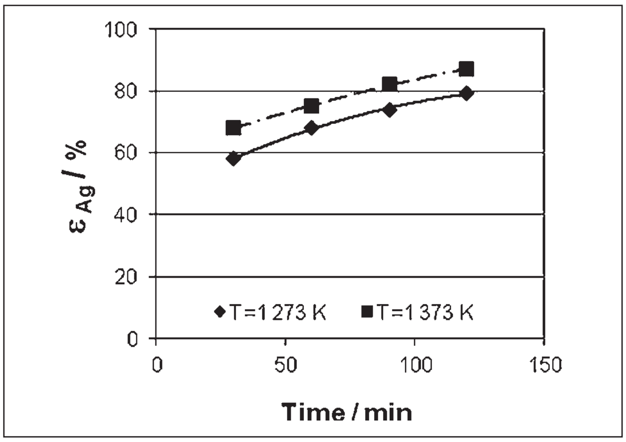

Figure 2 Impact of smelting parameters of flotation concentrates on yield of silver (the concentrate after sludge flotation from jewellery processing)

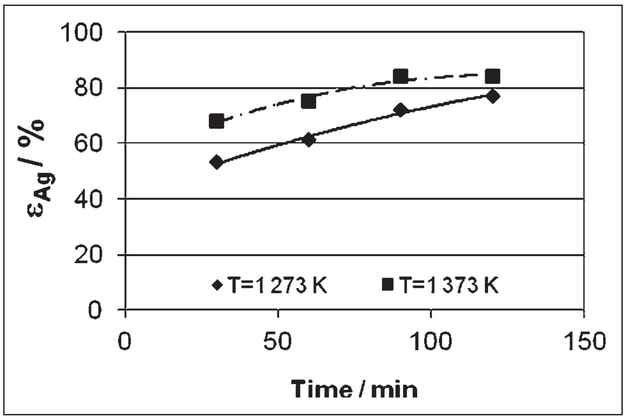

Figure 3 Impact of smelting parameters of flotation concentrates on yield of silver (the concentrate after sludge flotation from silver semi-products processing)

Table 3 **Test results for silver smelting from flotation concentrates**

Type of concentrate being smelted	Process parameters		Ag /wt. %	ε Ag / %
	Temp / K	Time / min		
Concentrate after sludge flotation from jewellery processing	1 273	30	62,12	58
Concentrate after sludge flotation from jewellery processing	1 273	60	79,30	68
Concentrate after sludge flotation from jewellery processing	1 273	90	83,77	74
Concentrate after sludge flotation from jewellery processing	1 273	120	94,64	79
Concentrate after sludge flotation from jewellery processing	1 373	30	67,12	68
Concentrate after sludge flotation from jewellery processing	1 373	60	82,35	75
Concentrate after sludge flotation from jewellery processing	1 373	90	96,09	82
Concentrate after sludge flotation from jewellery processing	1 373	120	98,96	87
Concentrate after sludge flotation from silver semi-products processing	1 273	30	56,59	53
Concentrate after sludge flotation from silver semi-products processing	1 273	60	77,45	61
Concentrate after sludge flotation from silver semi-products processing	1 273	90	79,54	72
Concentrate after sludge flotation from silver semi-products processing	1 273	120	81,60	77
Concentrate after sludge flotation from silver semi-products processing	1 373	30	65,89	68
Concentrate after sludge flotation from silver semi-products processing	1 373	60	83,23	75
Concentrate after sludge flotation from silver semi-products processing	1 373	90	97,11	84
Concentrate after sludge flotation from silver semi-products processing	1 373	120	97,94	84

as smelting silver from sludges that originate from copper electrorefining), The optimum smelting conditions are:

- temperature of the process – 1 373 K,
- time of heat – 120 minutes,
- addition of borax – 2:1 in relation to the mass of concentrate.

SUMMARY

- The flotation process can be applied successfully for the beneficiation of silver-bearing jewellery wastes (sludges from surface treatment) prior to their further pyrometallurgical processing.
- Research on flotation in synthetic systems – Al_2O_3 –Ag, SiO_2 – Ag, SiO_2-epoxy resin-Ag, epoxy resin-Ag – indicates a possibility for the beneficiation of concentrates with silver to concentration

as high as 60 wt. % with initial concentration not exceeding 10 wt. %. In some systems a silver yield ε_{Ag} of over 90 % was obtained from the concentrate.

- Silver concentrate obtained from the flotation process can be an excellent raw material for the production of both silver and its alloys. This was confirmed by smelting this material with *sodium tetraborate decahydrate* (borax). The final product of smelting contained between 87 - 98 wt. % Ag.

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