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RECOVERY OF COPPER AND SILVER FROM WAELZ CLINKER WASTED FROM ZINC PRODUCTION

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ABSTRACT

Waelz clinker is a waste material from the processing of zinc-lead cake into Waelz furnace in Bulgarian metallurgical plant KCM Ltd, Plovdiv, which contains valuable components such as copper silver, iron and carbon.

Previously the clinker was treated by sulfuric acid solution in order to remove iron. The residue which contains 3,8 % copper, 250 g t^{-1} Ag and 26 % C is an object of this experimental work. The purpose of the work is to investigate the silver and copper recovery from this residue using H_2SO_4-HNO_3 solutions. The influence of dissolution time, temperature and concentration of nitric acid at constant sulfuric acid concentration on the silver and copper recovery degree were investigated. The maximum silver recovery degree - 95 % is achieved at the following conditions: process duration - 1 h; temperature - 90°C; sulfuric acid concentration - 1M; nitric acid concentration - 1M; pulp density - 10 %. At these conditions the copper is practically completely recovered. The remaining insoluble residue contains 0,02 % Cu and 22 g t^{-1}Ag.

A technological scheme for two stage processing of Waelz clinker is developed.

Keywords: Waelz clinker, recovery, copper, silver, leaching.

INTRODUCTION

The applied method for processing of lead-zinc cake in Bulgarian metallurgical plant KCM Ltd. is Waelz process. The wasted clinker from this process contains 1-3 % copper, 15-20 % carbon and about 200 g t^{-1}silver that converts it into a valuable source. Waelz clinker contains the following main minerals - magnetite, hematite, troilite, jarosite, siderite, metallic iron, pyrite, bornite, chalcocite, arsenopyrite, pyrrhotite, galena, sphalerite (10 - 15 %), oxides, sulphates and carbonates of calcium, iron, lead, zinc and copper (5 %), aluminosilicates of potassium, sodium, magnesium, iron, lead and copper (20 – 25 %) and carbon. The metallic iron is connected with the iron and copper minerals. The common iron mineral in the clinker is troilite (FeS). Magnetite (Fe_3O_4) is finely mixed with triolite and chalcocite (Cu_2S). The main part of copper in the clinker is represented by chalcocite, finely mixed with triolite, partially with chalcopyrite and magnetite. Chalcopyrite ($CuFeS_2$) is sprout with troilite, chalcocite and magnetite [1].

The phase analysis of the iron, copper, zinc and lead in clinker showed that ~ 28 % of the iron is a metal, ~ 58 % exists as FeO and the rest is in the form of Fe_2O_3 and Fe_3O_4. Copper is mainly in the sulphide form (~ 80 %). The rest of copper is distributed between copper oxide (~ 15 %) and metal (~ 5 %) form. Over 37 % of the zinc is found in sulphide form, the rest is distributed between the oxide and silicate phases. Lead in the clinker presents mainly as jarosite.

Many methods for Waelz clinker processing are presented in recent years, but up to this moment effective technology allowing complete recovery of valuable metals is not developed [2-6]. Thus the problem for development of clinker processing technology is actual.

Previously clinker is leached in different environments - ammonia and acid solutions under atmospheric pressure and at elevated pressures. The results of these our experiments show unsatisfactory silver and copper recovery degree. This requires the demand for new methods for the treatment of clinker for the purpose of a higher silver and copper recovery degree.

Carbon contained in the clinker is mechanical (as a result of grinding) and chemical (as a result of acid treatment) activated which increases its adsorption capacity. This is may be the reason for low silver and copper recovery degree in solution.

The aim of this experimental work is to investigate silver and copper recovery from precipitates, generated from sulphuric acid leaching of Waelz clinker.

EXPERIMENTAL RESULTS

Chemical analysis of Waelz clinker

The chemical composition of the main Waeltz clinker components is determined by AAA and ICP analysis and is represented in Table 1.

As seen from the table the valuable metals content in Waelz clinker is a relatively high. Furthermore, the clinker is characterized by a high iron, silicon and aluminium content.

The main valuable components of the clinker are copper and silver. The value of the clinker is estimated based on copper and silver percentage in it and their quotations of the London Metal Exchange. The results of calculations for 2011 are presented in Fig. 1. As seen from the figure the value of the silver in the clinker exceeds that of copper. This indicates that the economic advantage in its processing should be searched only by technological option, which together with copper recovery (over 90 %) will provide an adequate degree of leaching of silver (over 75 %).

First technological stage - direct sulphuric acid leaching of Waelz clinker

Previously the clinker was treated by sulphuric acid solution in order to remove iron. The residue from this process is the object of this experimental work. This material contains 3,8 % Cu, 250 g/t Ag and 26 % C.

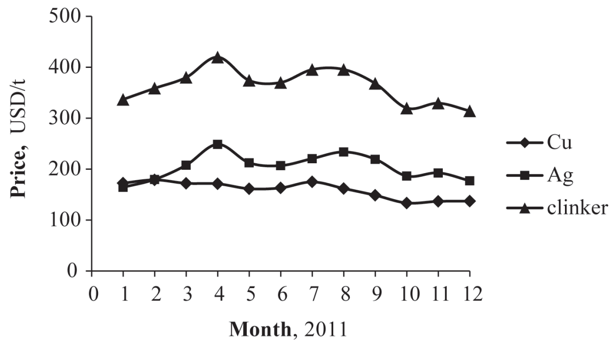

Fig. 1. Estimated value of the Waelz clinker for 2011.

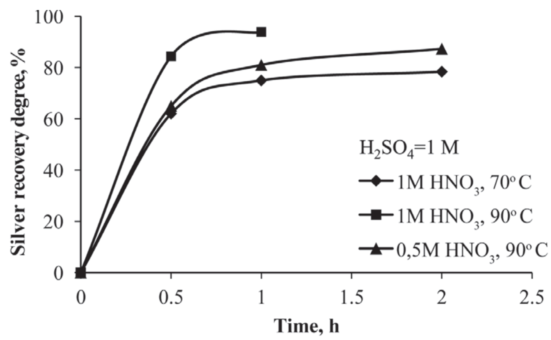

Fig. 2. Influence of leaching time on silver recovery degree.

Second technological stage - H_2SO_4-HNO_3 leaching of residue from Ist stage

The influence of time, temperature and concentration of nitric acid on the silver recovery degree is investigated.

Influence of the leaching time on the silver recovery degree

The highest degree of silver leaching - 93.8 % was reached by using a solution containing 1 M H_2SO_4 and 1 M HNO_3, temperature 90°C for 1 hour. By decreasing the temperature at a given concentration of the nitric

Table 1. Chemical composition of Waelz clinker, %.

Cu	Fe	Ag, g/t	C	Mn	Zn	Pb	As	Si	Al	Na	K	Ca	Mg	S
1.92	36.87	128	13.55	1.53	0.33	0.19	0.06	12.55	7.27	0.75	0.40	4.74	1.25	4.33

Table 2. Chemical composition of the solid residue, %.

Cu	Pb	Zn	Fe	Mn	Mg	Ca	Na	K	Ag, g/t
0.02	0.52	0.15	1.13	0.14	0.44	4.22	3.68	0.04	22

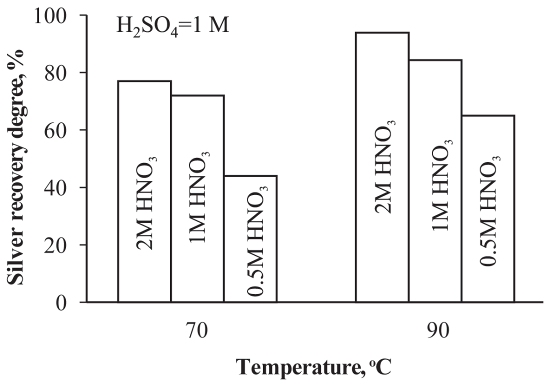

Fig. 3. Influence of leaching temperature on silver recovery degree.

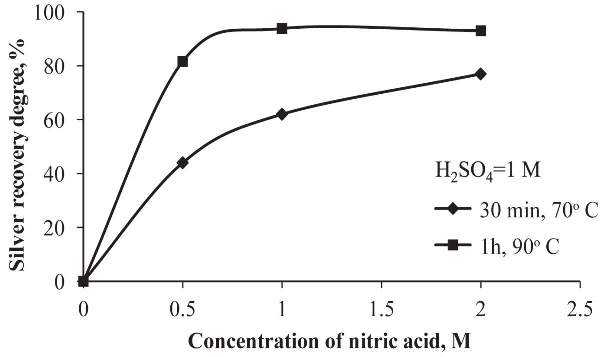

Fig. 4. Influence of the nitric acid concentration on silver recovery degree.

acid and the same process duration, the degree of silver recovery is decreased (Fig. 2).

Influence of the leaching temperature on silver recovery degree

The experiments were carried out at the same duration of the process - 30 min, temperature 70 and 90°C and concentration of nitric acid - 0.5, 1 and 2 M. The concentration of the sulphuric acid (100 g l^{-1}) remains constant. The results of experiments are presented in Fig. 3. By increasing the concentration of nitric acid at constant temperature, the silver recovery degree is increased. It turned out that the silver recovery degree using 1M H_2SO_4 + 2M HNO_3 leaching solution, for 30 min process duration and temperature 90°C is the same when using a solution containing 1M H_2SO_4 and 1M HNO_3 for a period of 1 hour at the same temperature.

Influence of the nitric acid concentration on silver recovery degree

The influence of nitric acid concentration on silver recovery degree is represented on Fig. 4. The silver recovery degree is increased by increasing the concentration of nitric acid at constant temperature and leaching duration. It is higher when the process is carried out at higher temperatures. At a concentration of nitric acid above 1M and temperature of 90°C the silver recovery degree does not increase.

Based on the conducted experiments the optimum conditions under which the rate of silver recovery is at a maximum are: duration - 1 hour; temperature - 90$^{oC;}$ H_2SO_4 concentration - 1M; HNO_3 concentration - 1M; pulp density - 10 %. At these conditions the copper is practically recovered completely.

The behaviour of the other essential metal is monitored and the results are shown in Fig. 5. As seen, copper has the highest recovery (practically 100 %) at 30 min leaching time, and lead has the lowest recovery degree.

The chemical composition of the solid residue obtained in the experiments with the highest silver recovery degree (1M HNO_3 + 1M H_2SO_4, 1 hour, temperature 90°C) is presented in Table 2.

As a result of 1M H_2SO_4- 1M HNO_3 leaching of the residue, obtained from the direct sulphuric acid dissolution of the clinker the original sample weight is reduced by 30 %. Thus, after the two-stage processing the clinker mass is reduced by 72 %.

The main drawback of the experiments in the second stage is that the nitric acid can not be regenerated. This may be achieved by introducing of an oxidizer - oxygen into the reaction space.

An autoclave experiment with regeneration of nitric acid was carried out in order to confirm the results. It was performed under the following conditions: material mass - 30 g; temperature - 100 °C; process duration - 1

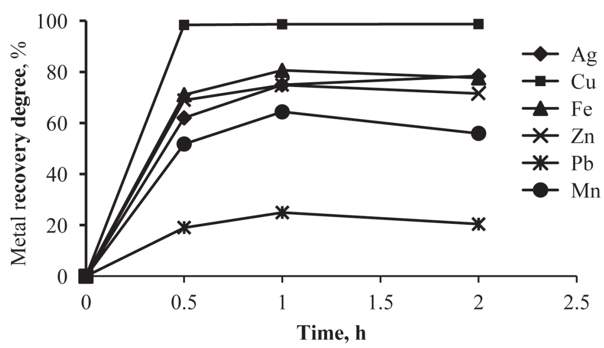

Fig. 5. Recovery degree of some metals in H_2SO_4-HNO_3 leaching 1M H_2SO_4; 1M HNO_3, temperature 70°C.

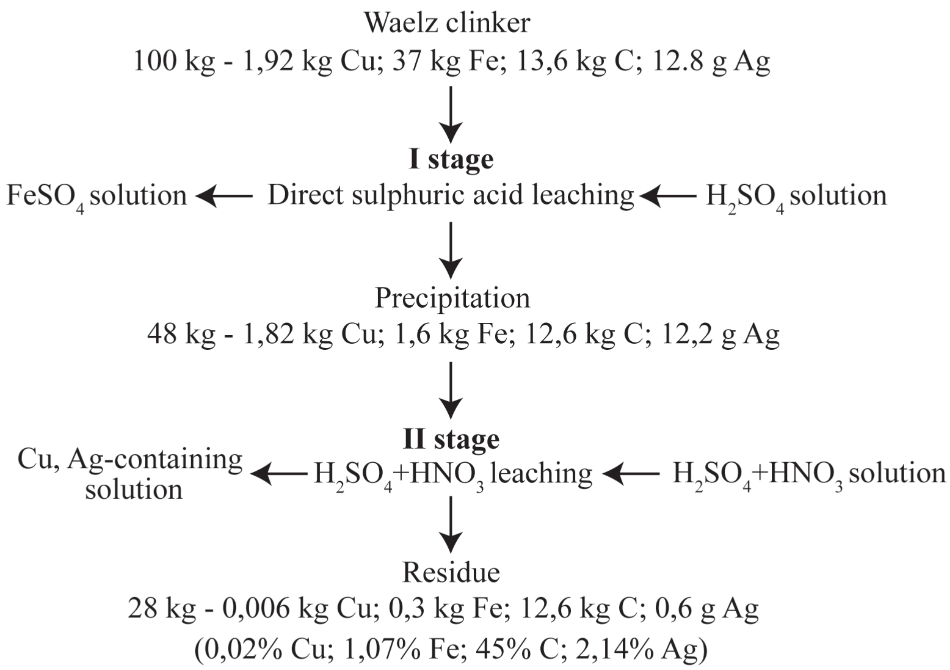

Fig. 6. Material balance of the solid residues in the two-stage flow chart.

hour; oxygen pressure - 4 atm; pulp density - 1:10; solution concentration - 0,5M HNO_3 + 1M H_2SO_4.

It turned out that the silver recovery degree in this experiment was 53 %. It is difficult to draw any conclusions on the basis of one experiment only. But it is likely that oxygen, which is introduced into the system "oxidizes" further the surface of an already activated carbon and increases its adsorptive capacity, which leads to a decrease in the silver recovery degree.

The material balance of the solid residues generated in the two-stage clinker processing regarding Cu, Ag, Fe and C is presented in Fig. 6. Distribution of Cu, Fe and Ag between the precipitate and solution in various stages of the processing of the clinker is presented in Table 3.

The final solid residue contains 0,002 % Ag, 1,07 % Fe and 0,02 % Cu as well as 45 % C. It is of interest the acidic treatment of the clinker after it has passed through the carbon flotation. This will be the goal of future experiments.

CONCLUSIONS

Copper and silver containing in Waelz clinker can be recovered by applying two-stage technological scheme - direct sulphuric acid leaching and H_2SO_4- HNO_3 leaching which achieves 95 % silver recovery degree and almost 100 % copper recovery degree. Most likely, the conditions of recovery of copper and silver from the clinker will be less "soft" if the clinker previously passed through carbon flotation.

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