ТЕХНИЧЕСКИЕ НАУКИ

STUDY OF LOW TEMPERATURE TECHNOLOGIES OF PROCESSING ZINC CAKES WITH THE METHOD OF THERMO-STEAMING

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ABSTRACT

The paper deals with efficient processing of zinc cakes wiht the method of thermo-steaming, which is intended to additional extraction of zinc and a number of non-ferrous metals, as a basis for increasing the complex using of raw materials.

Keywords: cake, thermo-steaming , leaching, roasting, decomposition, oxidation, extraction.

Zinc cake is insoluble residue after leaching of zinc calcine, and it has a complex composition, it contains more than 20 chemical elements. Mineralogical analysis of tested cake showed that it contained 23 % Zn (in the forms of ZnO (0,8%), $ZnSO_4$ (1,2%), $2ZnO \cdot SiO_2$ (3,9%), $ZnO \cdot Fe_2O_3$ (5,6%), ZnS (11,5%)), 17,3% Fe (as - FeS (2,5%), FeO (4,3%), Fe_2O_3 (8,7%)) , 6,43% P- (as - PbO (4,4%), PbS (1,9%)), 3,72% Cu - (in the form of CuS (1,6%), CuSO4 (1.9%)). Au and Ag are mainly in the metallic form.

Currently, pyrometallurgical and hydrometallurgical methods of processing zinc cakes are mainly applied in the world practice. Pyrometallurgical methods for processing zinc cakes differ the big variety and are mainly based on reducing reactions of zinc oxide and ferrites using carbonaceous reductants at relatively high temperatures, as a result gaining sublimated zinc and rare metals, and oxidizing fumes in the gas phase [1].

Waelz process is most prevalent among the pyrometallurgical methods for processing zinc cakes (reducing-sublimation firing) at a temperature of 1000 to 1200 0 C with the addition of coke in the amount of 35 ÷ 45% of the mass of material to be processed. This zinc fumes and clinker is the remainder of the Waelz process, which in turn contains many valuable components. Zinc fumes are returned back to the sulfuric acid leaching process.

The disadvantages of Waelz process are:

- High consumption of expensive and scarce coke;
- The need of high temperatures for the process flow;
- Unsolved issues of extracting other valuable components, such as - Au, Ag, Pb, Cu, Fe, etc. due to the lack of rational technology of methods of processing copper clinker.

Hydrometallurgical methods for processing zinc cakes are developed relatively recently and are based on dissolution of zinc ferrites and sulphides using sulfuric acid at atmospheric or elevated pressure transfering zinc, copper, cadmium, iron and rare metals into solution followed by separation of iron from solution as different compounds. At the present time there are three schemes of hydrometallurgical processing zinc cakes [2]:

- Leaching the cakes under pressure with separation of iron from solution as hematite (Fe2O3) - hematite process;
- Leaching the cakes under atmospheric pressure with separation iron from solution as goethite (FeOON) - goethite process;
- Leaching the cakes under atmospheric pressure with the release of iron from solution as jarosite ($MeFe_3(SO_4)_2(OH)_6$) - jarosite process.

The disadvantage of hematite technology is the necessity using of complex and expensive equipments- the autoclaves. The disadvantage of goethite technology is significantly more loss of zinc with iron cakes and the difficulty of filtering geothite cakes. The disadvantage of jarosite technology is the deterioration of solution purification from impurities, as well as solutions must be further purified from residual iron

Therefore we have been conducted investigations on the feasibility of processing zinc cakes with the method of thermo-steaming followed by sulfuric acid leaching of the calcine. Thermo-steaming contributes the transition of insoluble compunds of metals into water-soluble forms [3].

Series of chemical reactions occur during the thermo-steaming of zinc cake, which we divide into the following groups:

1. The oxidation of sulfur-containing minerals: sphalerite, pyrite, copper (I) sulfide, galena and others.
2. Decomposition of silicates and ferrites with steam in the presence of oxygen and sulfur dioxide.

It was defined that the beginning of sublimation of elemental sulfur occurs at 150-200^{0}C, arsenopyrite and pyrite begin to decompose at 450-500^{0}C. Complete decomposition of pyrite, arsenopyrite and chalcopyrite is completed at ~ 700^{0}C. Volatile oxides such as sulfur dioxide (sulfur dioxide) and other volatile components get into the gas phase.

Elemental sulfur is always present in the zinc product in free or bound forms of organic compounds. In addition, it can be formed during the flow of the various reactions, including through the expansion of sphalerite, pyrite, chalcopyrite, arsenopyrite and copper (I) sulfide . In terms with the method of thermo-steaming it may be in solid, liquid and vapor states. Therefore, the chemical interaction between the elemental sulfur and water vapor can be described by reactions:

$$3S_{(solid)} + 2H_2O_{(gas)} = 2H_2S + SO_2$$

$$3S_{(solid)} + 2H_2O_{(liquid)} = 2H_2S + SO_2$$

$$1{,}5S_2 + 2H_2O_{(r)} = 2H_2S + SO_2$$

During the thermo steaming zinc ferrite with steam and sulfur dioxide decomposes forming zinc sulfate.

$$ZnO{\cdot}Fe_2O_3+SO_2+H_2O_{steam}=ZnSO_4+Fe_2O_3+H_2$$

Sphalerite reacts with water vapor involving oxygen according to the following reaction:

$$: ZnS + O_2 + 2H_2O_{steam} = ZnSO_4 + 2H_2$$

During the thermo-steaming with the presence of steam and oxygen copper sulfides are oxidized according to the reaction:

$$2CuS+H_2O+1{,}5O_2=2CuO+H_2S+SO_2$$

We studied chemical compunds of the cake using spectral, chemical, and mineralogical analysis techniques, and its results are given in the table 1

Table 1

The chemical composition of the initial zinc cake

Elements	Zn	Cu	Cd	Fe	S_{total}	S_s	Pb	SiO_2	Al_2O_3	Au	Ag	H_2O
Content, %	23,3	3,72	0,11	17,3	8,72	6,45	6,43	11,2	4,1	0,9g/ton	211,5 g/ton	2,1

On the stream of investigation there were studied influence of temperature of thermo-steaming on the rate of extracting different metals into solution. Experiments were conducted in the temperature range 400^{0}C – 800^{0}C. The results are given in fig.1.

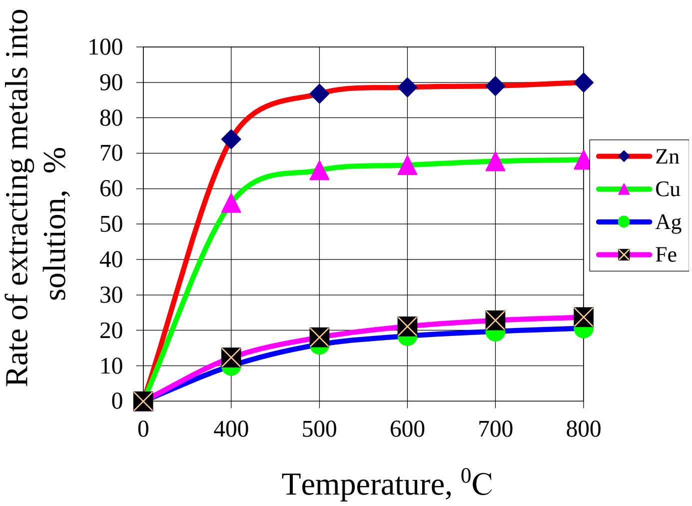

Fig.1. Dependence of extracting metals into solution on the temperature of thermosteaming.

Conditions of experiments: thermo-steaming (water steam feed rate 15-20 ml/min, τthermo-steam – 1hour), leaching (C_{H2SO4} -100 g/l, L:S=5:1, $\tau_{leaching}$ – 1 hour, t=60^{0}C).

According to fig.1 thermo-steaming in the temperature of 600^{0}C has a positive influence on the extraction rate of zinc in sulfuric solution. In the temperature of over 600^{0}C, extraction of Zn and Cu from thermo-steamed product into solution increases to a very little degree. There fore the optimal temperature for thermo-steaming of zinc cake is considered to be 600^{0}C.

By studying influence of thermo-steaming duration on the level of extracting metals into the solution, the experiments were conducted with duration of 0,5; 1; 2; 2,5; 3 hours. The results are given in fig.2.

Thermo-steaming Zinc cakes in optimal temperature mode and time leads to the decrease of product mass, and the increase of zinc and other metals concentration in the cinder. Based on the results of experiments and according to economic considerations it can be stated that the optimal temperature for thermo-steaming is 600^{0}C, and the duration is 1 hour.

Chemical composition of the cinder was analyzed using chemical method of analysis. The results are given in the table 2

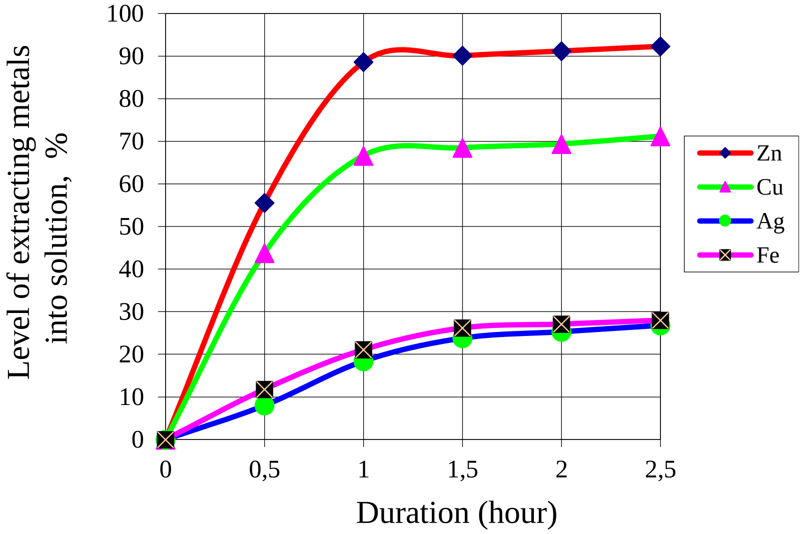

Fig.2. Dependence of the level of extracting metals into solution on thermo-steaming duration

Condition of experiments: thermo-steaming (water steam feed rate 15-20 ml/min, t=600^{0}C), leaching (C_{H2SO4} -100g/l, L:S=5:1, $\tau_{leaching}$ – 1 h, t=60^{0}C).

Table 2

Chemical composition of the cinder

Elements	Zn	Cu	Cd	Fe	S_s	Pb	SiO_2	Al_2O_3	Au	Ag
C, %	25,2	4,02	0,11	18,8	0,2	6,98	12,1	4,6	0,92g/ton	224,3 g/ton

In the choice of solvent for leaching thermo-steamed product many factors are taken into account. The most important factors are:

1) Chemical and physical character of thermo-steamed product;

2) Price of the solvent;

3) Corrosive action of the solvent on the equipment;

4) Selectivity of the solvent for the being leached product;

5) Possibility of solvent regeneration.

As it is seen from the facts above, sulfuric acid is quite appropriate for leaching the product of thermo-steaming. Sulfuric acid is considered to be a good solvent for oxidized zinc minerals (ZnO), in this connection the solubility of Ag is insignificant, and Au does not dissolves at all. Use of sulfuric acid is considered to be technologically and economically justified, because using it we get zinc sulfate which can be loaded into the main operation of the electrolytic department of zinc producing plant. Besides sulfuric acid is distinguished by the low price, and it exerts comparatively weak corrosive effect on the equipments for hydrometallurgical processes.

The calcine after thermo-steaming was leached with solution of sulfuric acid. Well solubility of zinc oxides in sulfuric acid solutions served as a base to study the process of leaching calcine of thermo-steamed zinc cakes depending on the duration, temperature, density of the pulp, and the concentration of the solvent. In addition, with a glance of complex character of source material it was important to investigate features of the behaviour of accompanying components(Cu, Ag and etc.) in sulfuric acid solutions.

The metals in the calcine are mainly in the form of oxides. During the process of leaching thermo-steamed product using sulfuric acid the following reactions take part with a participation of main minerals and impurities. (ZnO, CuO, FeO, Fe2O3 and etc.):

$$ZnO + H2SO4 = ZnSO4 + H2O, (1)$$

$$CuO + H2SO4 = CuSO4 + H2O. (2)$$

Impurities such as iron oxide also dissolve:

$$Fe2O3 + 3H2SO4 \rightarrow Fe2(SO4)3 + 3H2O, (3)$$

Forming Fe2(SO4)3 and interacts with zinc compounds:

$$3ZnO + Fe2(SO4)3 + 3H2O \rightarrow 3ZnSO4 + 2Fe(OH)3 (4)$$

Metallic zinc dissolves well in the presence of sulfate of trivalent iron in acidified solutions.:

$$Zn + Fe2(SO4)3 = ZnSO4 + 2FeSO4. (5)$$

Solution of iron(III) sulfate is a good solvent for many natural sulfides. However this solvent does not have any unassisted significance in hydrometallurgy of zinc. The reason for that is hydrolysis of Fe2(SO4)3 in aqueous solutions. The solvents need to be acidified with sulfuric acid in order to give steadiness to sulfate ions. In case of combined using the mentioned reagents for sulfide minerals Fe2(SO4)3 serves as oxidant of sulfides, although the sulfuric acid is the actual oxidant of the process.

Hence there is always certain amount of trivalent sulfuric iron (sulfide oxidant) in the pulp. But dissolution of sulfides flow more slowly than dissolution of oxides. It gives an opportunity of additional oxidizing minerals.

In laboratory conditions studies were conducted taking into account various influensing factors (temperature, concentration of the acid, duration of leaching, the pulp density, and etc.) on the level of extracting of metals into solution.

The degree of extraction of zinc and other metals in the leaching of calcine (S: L = 1: 5) at 60^0C has a certain dependace on the concentration of sulfuric acid (Figure 3)

As it is seen from the results of experiments with increasing the concentrations of sulfuric acid in the solution (to 150 g / l) solubility of components in calcine increased linearly. Increase of the sulfuric acid concentration over 150 g / l does not significantly increase the degree of transfer of zinc into the solution while the solution in the transition impurities (especially iron) begins to increase.

150 g/l is a recommended concentration of sulfuric acid leaching for themo-steamed calcines.

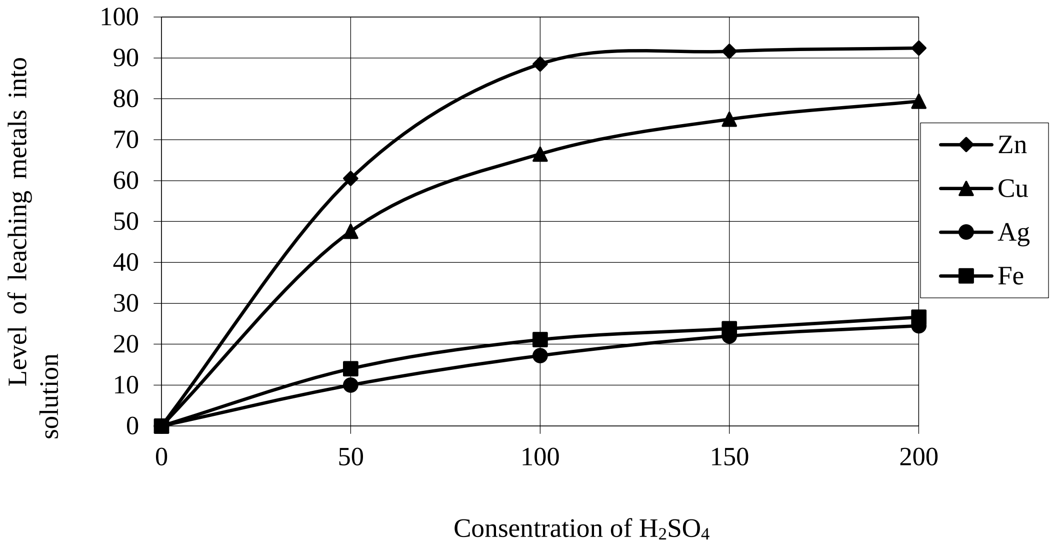

Fig.3. Dependence of the metals extraction degree from a solution on the acid concentration.

A study of the length effect on of zinc leaching from the product with sulfuric acid solution with a concentration of 150 g / l shows that in the initial period (60 min) of zinc into solution the process proceeds very rapidly, and after 120 minutes comes to a dynamic equilibrium of leaching process (Fig. 4) .

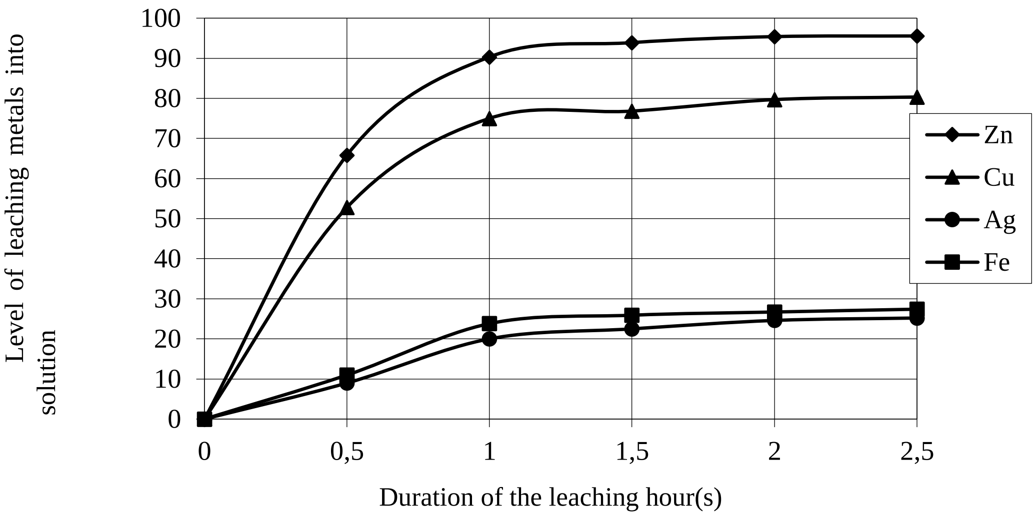

Fig.4. Dependence of the metals extraction degree from a solution on the leaching duration

Increased contact time of the sulfuric acid solution and calcine may increase impurities in the solution. When calcine leaching with sulfuric acid react primarily oxidized minerals zinc and copper. Minerals of iron and silver react with sulfuric acid slowly. Therefore, in order to achieve maximum extraction of zinc with minimal impurities moving in the solution, leaching time can be installed 2 hours

Speed of vast majority of chemical reactions, and also the diffusion increase with rise of temperature. With a rise of temperature there is a slow increase in the concentration of zinc in the solution. However, strarting from 40^0C with an increase in the duration of the process there is more intensive increase in the degree of extraction of zinc and copper. This is because at high temperatures $ZnSO_4$ is formed more rapidly. It is expected that with further increase in temperature will increase the rate of dissolution. At the same time it is necessary to consider that increasing the temperature significantly affects on the dissolution of the useful component (the concentration of zinc), while the transition of the impurity into the solution is greatly increasing . Increasing the temperature over 800C has little effect on leaching of the concentration of zinc, but highly increases the transfer of impurities into the solution. The required hydrodynamical mode to achieve a homogeneous slurry density provided with a mechanical stirring device.

Thus, the following optimal conditions for leaching zinc cake after thermo-steaming were set: the sulfuric acid concentration of 125-150 g / l, 75-800S temperature, duration 2 h. In these conditions the degree of extraction of zinc into into the solution is 85-95% and iron is 28.1%, and the yield of cake is 58-60% of the calcine weight . Results of the study indicate the possibility of efficient processing of zinc cakes using the method of thermo-steaming followed by sulfuric acid leaching.

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MODELLING OF A THREE-DIMENSIONAL PROBLEM OF DISTRIBUTION OF HARMFUL IMPURITY IN THE RIVER A RECURRENTLY-OPERATIONAL METHOD

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ABSTRACT

In this article the decision of a three-dimensional problem of diffusion is considered by a recurrently-operational method which describes process of distribution of harmful impurity along a watercourse.

The received numerical results on the COMPUTER where it is possible to define for what time are resulted there is a distribution and river clarification. The received results are illustrated in drawings.

Keyword: Modelling, process of distribution of harmful impurity, recurrent parity, the recurrent equation, diffusion factor, factor no conservation, the exact decision, Problem Kashi, concentration of emission.

Introduction

With the growth in the development of industrial enterprises, emissions of harmful substances into the atmosphere and the water environment increase, along with this, with an even increase in production, land is depleted, improper use of chemical fertilizers, various harmful emissions significantly affect water and land resources.