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Studying the Cake of Zinc Production Jsc "Almalyk Mmc", Thermodynamic Analysis of the Reactions Protecting At Thermal Processing

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ABSTRACT: The paper presents the results of studying the chemical, mineralogical and particle size distribution of zinc cake. Thermodynamics has been studied for all possible reactions occurring during thermo processing. The method of zinc cake roasting in the presence of steam has been determined, facilitating the extraction of valuable components from the cake.

KEY WORDS: concentrate, cake, zinc, roasting, gas, candle-end, steam, composition.

I. INTRODUCTION

The strategy for further development of the Republic of Uzbekistan defines the tasks for the timely implementation of measures for the deep processing of mineral resources in the implementation of investment projects and the continuation of policies to stimulate the localization of production, with particular attention being paid to the processing of technogenic formations of the mining and metallurgical industries.
The problem of rational and integrated use of raw materials occupies an important place in the work of non-ferrous metallurgy enterprises. One of the main trends in the production of zinc at the joint-stock company Almalyk Mining and Metallurgical Complex (JSC «Almalyk MMC») is to increase the complexity of using raw materials, determined by the presence of useful components in the raw materials and the degree of their extraction in all types of commercial products.

II. SIGNIFICANCE OF THE SYSTEM

The object of the research is zinc cake of zinc production of JSC «Almalyk MMC».
Currently, in the JSC «Almalyk MMC» for prior to extracting zinc, cake are subjected to valance (reduction-sublimation roasting) - at a temperature of 1373-1573 K with the addition of coke and petroleum coke in the amount of 30-40% of the mass of the processed material. At the same time, receive zinc sublimates and clinker (blade) - the residue from valance. The disadvantages of the valance-process are: high consumption of expensive and scarce coke; high temperature process; the unresolved issue of the extraction of other valuable components - gold, silver, lead, copper, iron, etc., due to the lack of rational technology of clinker processing. Therefore, the development of an improved technology for processing zinc cakes, which ensures high extraction of zinc and other valuable metals into marketable products, is an urgent task [1]. The authors of the work carried out studies on the study of the chemical, mineralogical and grading composition composition of zinc cake, with the aim of obtaining initial data for choosing the direction of further technological research for processing.

The developed technology allows:
- to increase the extraction of zinc at the plant due to the increased transition of zinc into the solution;
- reduce energy costs;
- stop the use of expensive and scarce coke in the processing of zinc cakes;
- extract copper and other valuable metals from zinc concentrate.

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The scientific and technical solution of the problem posed by this problem is to create a technology for extracting valuable components from the zinc production cake.

III. LITERATURE SURVEY

Analysis of the reviewed literature and practice of existing enterprises on the problem of processing zinc cakes allows conducting research in the following direction:

- the study of chemical, mineralogical and grading composition of zinc cake of zinc production;
- study of the behavior of compounds of metals in zinc cakes during firing in the presence of water vapor;
- development of a technological scheme for processing zinc production by an unconventional method.

In addition, in the work it is necessary to study: the real and phase composition of the solution, the nature of the relationship of the reactants with the surface of the minerals.

IV. METHODOLOGY

The study of the chemical, mineralogical and grading composition of zinc cake. A sample of the cake was used to study the material and chemical composition, as well as a mineralogical description of the minerals.
For the analysis of the sample, the "Spectrometer X-ray energy dispersive BRA-135F" certificate No. 05.9163-2015 dated 05.07.2015 was used. The X-ray energy dispersive spectrometer BRA-135F is a stationary instrument designed to perform X-ray spectral analysis of chemical elements of solid, liquid and powder samples in the range from fluorine (Z = 9) to uranium (Z = 92) (fig. 1-2).

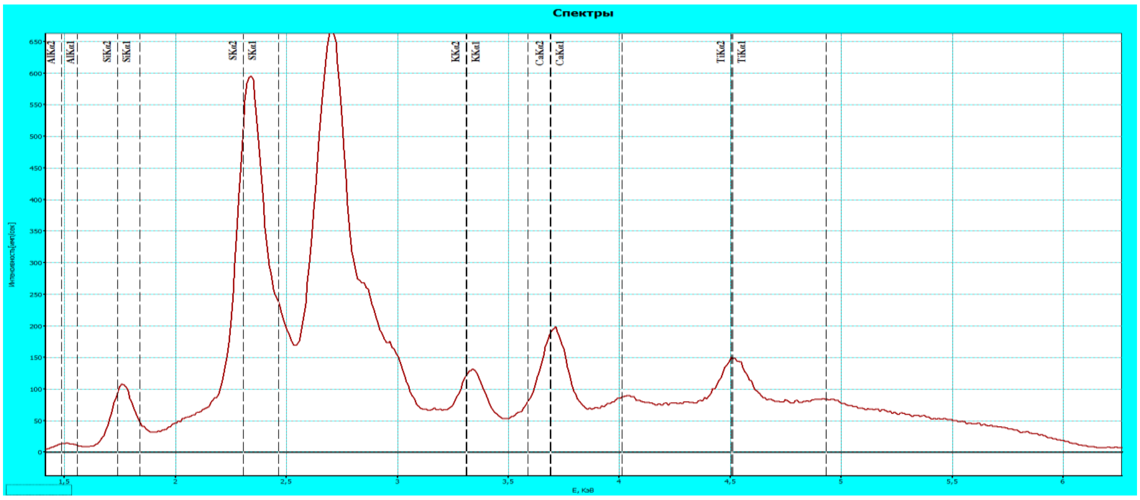

Fig.1. The results of analyzes of light elements of zinc cake on X-ray fluorescence analyzer BRA-135F.

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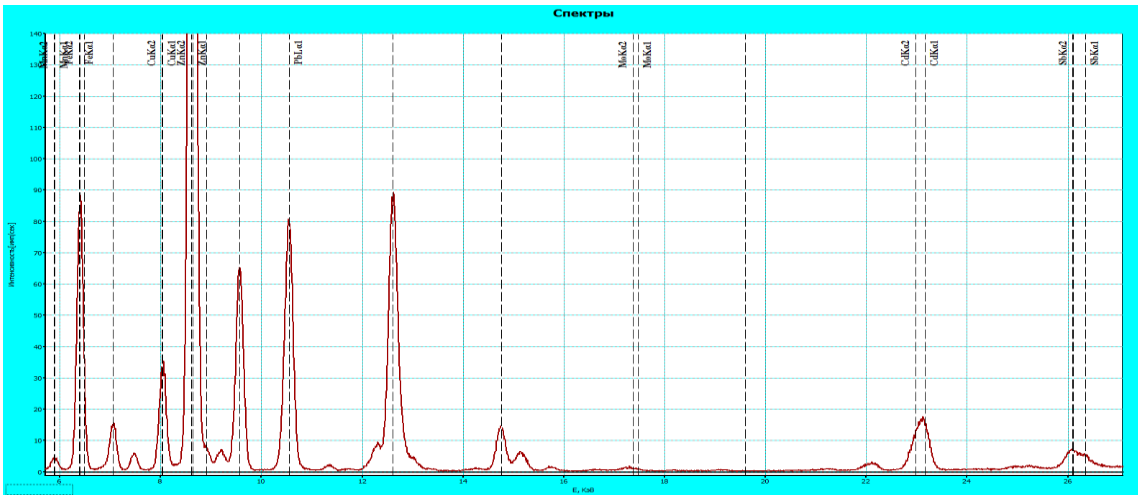

Fig.2. Results of the analysis of heavy cake elements on X-ray fluorescent analyzer BRA-135F.

The results of the chemical and mineralogical composition of zinc cake using spectral, chemical and mineralogical methods of analysis are shown in Table 1-2.

Researching on the study of particle size distribution. Wet sieve analysis. The study of particle size was performed by wet sieve analysis by mixing the sample with a particle size of 40 mm in a 15-liter cylindrical container for 15 minutes, with a ratio W: T = 4: 1, followed by sieving and washing each size class [2, 3]. The obtained size classes were subjected to cutting with sampling for chemical analysis, in which the content of metals was determined. Fractional composition of zinc cake are given in table 3.

By mineralogical analysis, it was found that zinc in concentrates is mainly found in the form of sphalerite, iron in the form of pyrite, chalcopyrite and arsenopyrite, copper in the form of chalcopyrite, lead in the form of galena, gold and silver are mostly in metallic form.

Zinc in cakes is contained in the amount of 21-23 %, including, in the form of ZnO (0,8-3%), $ZnSO_4$ (1-8 %), $2ZnOxSiO_2$ (3-4 %), $ZnOxFe_2O_3$ (5-6,5 %), ZnS (1-5 %). Iron in cakes is contained in the amount of 12-17 %, including in the form of FeS (2-5%), FeO (3-4%), Fe2O3 (5-8%). Lead in cakes is contained in the amount of 5-6%, including PbO (3-5 %), PbS (1-2 %). Copper in cakes is contained in the amount of 2-3 %, including in the form of CuS (1-2 %), $CuSO_4$ (1-2 %). Gold and silver are mostly in metallic form.

From fig. 1-2 and Table 1-3, it can be seen that, in addition to zinc, copper, lead, cadmium, iron and others are of industrial interest for the extraction of metals.

Table1. The chemical composition of zinc cake, %

name of ppгoduct	Composition , %												
	$Zn_{\text{общ}}$	$Zn_{\text{в}}$	$Zn_{\text{к}}$	C	$S_{\text{об}}$	S_{SO4}	Pb	Fe	SiO_2	Al_2O_3	Cu	Cd	CaO	MnO
Zinc cake	23,15	4,28	15,3	7,34	8,62	6,63	6,62	11,51	9,4	1,54	2,46	0,22	2,29	0,79

Table 2. Mineralogical composition of zinc cake, %

name of product	$Zn_{\text{общ}}$	$ZnSO_4$	ZnO	$ZnO \cdot Fe_2O_3$	ZnS	$ZnO{\cdot}SiO_2$
Zinc cake	21,42	7,79	3,05	6,11	1,07	3,4

Table 3. The chemical composition of zinc cake fractions

Class, mm	Class exit, %	composition %							
		Zn	Cu	Pb	Cd	Fe	Al_2O_3	SiO_2	S
+40	1,925	22,89	4,27	6,48	0,12	17,23	4,11	11,23	8,77
-40+20	11,35	22,60	4,38	6,57	0,12	17,34	4,13	11,18	8,75
-20+10	30,35	22,80	4,35	6,52	0,11	16,48	4,08	11,14	8,66
-10+5	32,25	22,72	4,34	6,49	0,11	16,50	4,15	11,36	8,69

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-5+2	20,8	22,66	4,23	6,37	0,10	16,66	4,12	11,29	8,71
-2+1	0,7	23,63	3,33	6,25	0,09	14,60	4,07	11,17	8,74
-1+0,315	0,75	23,95	3,37	6,32	0,09	13,75	4,08	11,19	8,65
-0,315+0,140	0,5	24,45	3,29	6,32	0,08	12,09	4,17	11,14	8,68
-0,140	1,375	24,66	3,08	6,39	0,08	12,07	4,18	11,16	8,73

Analysis of the results shown in Table 3 shows that in the class of -20 + 10 mm size the content was zinc 22,80 %, copper 4,35 %, lead 6,52 %, cadmium 0,11 %, iron 16,48 %, alumina 4,08 %, silica 11,14 %, sulfur 8,66 %. The output of this size class was 30,35 %. The overall yield of the size class -10 + 5 mm was 32,25 % with an average zinc content of 22,72 %, copper 4,34 %, lead 6,49 %, cadmium 0,11 %, iron 16,50 %, alumina 4,15 %, silica 11,36 %, sulfur 8,69 %. After washing the cake, there is an uneven distribution of zinc, copper, and iron by size class. In large classes there is an increase in the content of iron, in small classes there is an increase in the content of zinc and copper. The distribution of lead, cadmium, alumina, silica and sulfur by size class is almost uniform.

V. EXPERIMENTAL RESULTS

Consider the specific and most important for the technology of transformation occurring during the firing of zinc cakes. Although technological regimes cover narrow intervals of operational parameters, we consider the chemistry of processes in a wider range of conditions in order to present the consequences of deviations from the modes accepted in practice. Zinc sulfide is found in the cake in two versions: distribution - sphalerite and ZnS and more rare - wurtzite β-ZnS. When heated, the α↔β transition occurs at 1293 K, at lower temperatures (β-ZnS exists as metastable). The oxidation chemistry of these modifications is the same.

It has been established that, from the onset temperature of noticeable oxidation of sphalerite to 1173 K, ZnO is the primary solid oxidation product. This is confirmed by the oxidation of thin films of ZnS and ZnS powder at t> 1173-1273 K. Therefore, at t> 1173-1273 K ZnS oxidation proceeds by reaction.

$$ZnS + 1{,}5O_2 = ZnO + SO_2. \qquad (1)$$

However, at high temperatures, sublimation of the material is observed during roasting of ZnS. This is due to the occurrence of oxidation by the reaction:

$$ZnS_{hard} + O_2 = Zn_{steam} + SO_2. \qquad (2)$$

Next, zinc fumes are oxidized. The reaction is likely to be total and involves the dissociation of ZnS into Zn^0 and S_2. Isomorphic iron in the oxidation of (Zn, Fe)S immediately forms $ZnFe_2O_4$. Studies have shown that isomorphic iron completely binds zinc to ferrite. Zinc ferrite obtained at a temperature of less than 1273 K is practically non-magnetic and poorly soluble in H_2SO_4 solutions. But at temperatures above 1273 K, $ZnFe_2O_4$ becomes ferromagnetic as a result of a change in the placement of Zn^{2+} and Fe^{2+} in the ferrite crystal lattice (the transition from "normal" spinel to "inverted"), but the solubility of $ZnFe_2O_4$ in H_2SO_4 remains almost unchanged. The observed increase in the solubility of zinc from calcine after high-temperature calcination is due to the binding of Fe^{2+} to silicates, which reduces the ferritization of zinc in the calcine.

In the scale on grains of sphalerite, sulfate sulfur is found in the outer part, remote from the surface of the sulfide core. This indicates the formation of zinc sulfate as a result of the interaction of ZnO with SO_3 (secondary sulfates). In this case, $ZnSO_4$ is formed stable up to 943 K, and ZnO $2ZnSO_4$ - up to 1033 K.

The authors propose roasting zinc cake in the presence of water vapor. For this it is necessary to study the thermodynamics of various reactions. The basis of thermodynamic research methods are calculations of the equilibrium of chemical reactions, stable ratios and the determination of the limiting conditions for the existence of phases. Exact calculations are very difficult, because require the search for a number of source data in reference publications, in which these data are described differently, and ultimately, the calculation of the equilibrium of just one reaction often takes many hours. The calculated data of ΔG^0_T at various temperatures for all possible reactions during the thermo pair processing of zinc cake supplied with standard values of isobaric-isothermal potentials borrowed from the literature [4-5] and calculated by the method of L.P. Vladimirova [6]. Calculations were made on a specially developed computer program.

Under thermo processing conditions, sulfur can be in solid, liquid and vapor states. Therefore, the chemical interaction between elemental sulfur and water steam can be described by the following reactions:

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$3S_{hard} + 2H_2O_{steam} = 2H_2S + SO_2,$ (3)
$3S_{sublimation} + 2H_2O_{steam} = 2H_2S + SO_2,$ (4)
$3S_{steamed} + 2H_2O_{steam} = 2H_2S + SO_2,$ (5)
$3S_{hard} + 2H_2O = 2H_2S + SO_2,$ (6)
$3S_{sublimation} + 2H_2O = 2H_2S + SO_2,$ (7)
$3S_2+4H_2O_{steam} = 4H_2S + 2SO_2 .$ (8)

Displacement of the equilibrium of these reactions contributes to the flow of water steam over the solid phase. However, it is safe to say that the last two reactions are quite intensive, starting with a temperature of 573-623 K. Intensive course of these reactions is very important during thermo processing of the cake, since on the one hand, it makes it possible to selectively extract elemental sulfur from the cake and, on the other hand, ensures that the process complies with environmental requirements. When condensation of water steam in the heat exchanger sulfur is released in a finely dispersed solid phase. The incoming vapor from the steam generator reacts with sulfur to form hydrogen sulfide and sulfur dioxide, which are absorbed on the surface of another part of the water steam and carried to the cooling zone. Thus, the dissolved (in the vapor state) in water, the gases mutually react and re-form elemental sulfur in the subcolloidal state. In other words, during thermo pairing, water steam ultimately serves as a mass carrier.
Zinc sulphide is the main component of the cake, but its (ZnS) interaction with water steam has been little studied. Zinc sulfide with water steam interacts by the reaction:

$ZnS + H_2O_{steam} = ZnO + H_2S$ (9)
$ZnS + 4H_2O_{steam} = ZnSO_4 + 4H_2.$ (10)

As shown by the results of the experiment, zinc sulfide in an atmosphere of water vapor at certain temperatures turns into ZnO and $ZnSO_4$. However, as can be seen from thermodynamic calculations, the reaction 9, 10 is unlikely. We have established the oxidation of zinc sulfide in the presence of water vapor without oxygen and with its participation.
In an oxygen-free environment, the oxidation of zinc sulfide in the presence of water steam proceeds by the following mechanism: S_{hard}, $S_{sublimation}$ and $S_{2(gaseous)}$ interact with water steam according to the above principle. The product of these reactions - sulfur dioxide - reacts with zinc sulfide by the reaction:

$2ZnS + SO_2 = 2ZnO + 3S_{steamed},$ (11)
$ZnS + 3H_2O_{steam} + S_2 = ZnO + 3H_2S.$ (12)

The following reactions take place with the participation of oxygen:

$2ZnS + 1{,}5O_2 + H_2O = 2ZnO + H_2S + SO_2,$ (13)
$4CuS \rightarrow 2Cu_2S + S_2,$ (14)
$4CuS \rightarrow 2Cu_2S + 2S_{hard},$ (15)
$4CuS \rightarrow 2Cu_2S + S_{sublimation},$ (16)
$4CuS \rightarrow 2Cu_2S + S_{steamed},$ (17)
$2CuS + H_2O+1{,}5O_2=2CuO+H_2S+SO_2,$ (18)
$2CuS + H_2O + O_2 = Cu_2O + H_2S + SO_2,$ (19)
$Cu_2S + 0{,}5H_2O + 1{,}25O_2 = 2CuO + 0{,}5H_2S + 0{,}5SO_2,$ (20)
$Cu_2S + 0{,}5H_2O + 0{,}75O_2 = Cu_2O + 0{,}5H_2S + 0{,}5SO_2,$ (21)
$2CuS + H_2O + 2O_2 = Cu_2O + H_2 + 2SO_2,$ (22)
$CuS + H_2O + O_2 = CuO + H_2 + SO_2,$ (23)
$Cu_2S + H_2O + O_2 = Cu_2O + H_2 + SO_2,$ (24)
$Cu_2S+H_2O+1{,}5O_2 = 2CuO + H_2 + SO_2.$ (25)

By studying the change in the Gibbs energy of the reactions forming ZnO at different temperatures, we can conclude that ZnO is mainly formed during the oxidation of ZnS in the presence of water vapor (with little air access). Since copper sulfides are one of the main components of zinc cake, they studied the behavior of copper sulfides during thermal processing in the presence of water steam and oxygen.
When water steam interacts with copper sulfides, the following reactions occur:

$1{,}5Cu_2S + H_2O = 3Cu +H_2S + 0{,}5SO_2,$ (26)
$0{,}5Cu_2S + H_2O = Cu + 0{,}5SO_2 + H_2,$ (27)
$Cu_2S + H_2O = Cu_2O + H_2S.$ (28)

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Thermodynamic calculations show a low probability of reactions. It was established from calculations that copper sulfides in the presence of water steam at 1223 K are oxidized by the reactions:

$2CuS + SO_2 = 2CuO + 3S_{steamed}$, (29)
$4CuS + SO_2 = 2Cu_2O + 5S_{steamed}$, (30)
$2Cu_2S + SO_2 = 2Cu_2O + 3S_{steamed}$, (31)
$Cu_2S + SO_2 = 2CuO + 2S_{steamed}$, (32)
$3CuS + 7H_2O = Cu + Cu_2O + 7H_2 + 3SO_2$, (33)
$Cu_2S + 5H_2O + 0{,}5S_2 = Cu_2O + 5H_2 + 2SO_2$, (34)
$Cu_2S + 5H_2O + S_{sublimation} = Cu_2O + 5H_2 + 2SO_2$, (35)
$Cu_2S + 5H_2O + S_{hard} = Cu_2O + 5H_2 + 2SO_2$. (36)

Copper sulfides with the participation of oxygen interact with water steam at 1223 K and are oxidized by the reactions:

$2CuS + H_2O + 1{,}5O_2 = 2CuO + H_2S + SO_2$, (37)
$2CuS + H_2O + O_2 = Cu_2O + H_2S + SO_2$, (38)
$Cu_2S + 0{,}5H_2O + 1{,}25O_2 = 2CuO + 0{,}5H_2S + 0{,}5SO_2$, (39)
$Cu_2S + 0{,}5H_2O + 0{,}75O_2 = Cu_2O + 0{,}5H_2S + 0{,}5SO_2$. (40)

Thus, thermo processing of zinc cake involves a complex process, the stages of which are the interaction of elemental sulfur with water steam and the interaction of the resulting product — sulfur dioxide — with sulfide minerals. The resulting elemental sulfur again reacts with water steam, etc. It follows that to start the reaction, elemental sulfur is needed in small quantities, and then vaporous sulfur, formed as a result of the reaction between sulfur dioxide and sulfides, again interacts with the sulfide mineral.
In this process, elemental sulfur serves as a carrier of oxygen through water, i.e. it is a catalyst for the reaction of zinc, copper, and iron sulfides with water steam. Under these conditions, water vapor is directly involved in the conversion of sulfur to the catalytically active form of SO_2.
Thus, the change in the phase composition of the zinc cake, depending on the duration of treatment at 1223 K: ZnS is oxidized mainly to ZnO, in addition, the following compounds are formed: $ZnFe_2O_4$, Zn_2SiO_4, $ZnSO_4$, $3ZnO \cdot 2SO_3$ [7].

VI. CONCLUSION AND FUTURE WORK

The main conclusions and recommendations from the research are as follows:
• determined the chemical, mineralogical composition of the zinc filter cake zinc production;
• oxidation of sulfides in the presence of water steam occurs without and with the participation of oxygen. Elemental sulfur and sulfur formed during the decomposition of sulfides interact with water steam to form sulfur dioxide, which interacts with sulfide minerals.
Found technological solutions can be applied in other industries related to the processing of metal-containing products.

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