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SELECTIVE REDUCTION OF TRIVALENT IRON IN ZINC FERRITE USING ELEMENTAL SULPHUR

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Abstract: *In this article, the process laws and technological aspects of the process of sintering the zinc-containing waste of a zinc plant with technical sulfur are considered. Zinc cake is obtained during the sulfuric acid leaching of calcined zinc ores and contains about 20% zinc and additional metals such as indium, cadmium, lead and copper. Copper cakes are somewhat difficult to work with because they contain ferrites and silicates belonging to acid-resistant spinels. Since the chemical and mineralogical composition of zinc production cakes consists of complex oxides, finding ways to process them is one of the actual topics of zinc metallurgy. For example, the majority of zinc and iron in zinc cake is in the form of zinc ferrite ($ZnO{\cdot}Fe_2O_3$), a compound insoluble in mineral acids and is not attracted to magnets. Therefore, finding a way to process zinc cakes so that zinc ferrite separates into zinc and iron compounds is one of the important tasks for metallurgical scientists. When the composition of zinc factory cakes was chemically analyzed, the amount of iron in it was 19.4%. In this study, based on the chemical composition of zinc and iron, quantitative analysis revealed that zinc and iron in raw materials are in the form of zinc ferrite compound. Based on this material composition, a method of converting iron into a magnetic form by recovering trivalent iron oxide from zinc ferrite in the presence of technical sulfur was proposed, and the conditions of the process flow were studied. The mechanism of chemical phenomena occurring in the interaction regions of zinc ferrite and technical sulfur has been developed.*

Keywords: *zinc metallurgy, zinc cakes, zinc ferrite, technical sulphur, reduction, sintering, optimal temperature, magnetic separation, degree of separation.*

INTRODUCTION. World practice shows that today many metallurgical plants have started processing secondary raw materials. It can be said that the reason for this is the lack of ore reserves and the waste from metallurgical enterprises causing environmental problems [1-2]. Uzbekistan also needs to review its resource potential utilization strategy. The most effective way to rationally use underground resources and save it is to intensify the use of mine-metal waste [3-5]. “Almalyk Mining and Metallurgical Complex” JSC (“Almalyk MMC” JSC) is one of the largest industrial enterprises of the Republic of Uzbekistan, which has been producing precious metals for many years.

Depending on the properties of the zinc concentrates and the operating conditions in the hydrometallurgical process, approximately 15-20% of zinc per ton of zinc production is lost to the hydrometallurgical waste – cake [6-10].

Today, zinc production in the world has a strong growth trend. At the same time, due to the decrease in the amount of zinc in the ore to 1-3% and up to 3.5-5% until the seventies of the last century, the increased requirements for environmental protection, the use of man-made waste raw materials of production special attention is being paid to increasing its complexity, using it, resource- and energy-saving technologies using man-made waste of production are being introduced. Therefore, special attention is paid to the processing and impoverishment of zinc production cakes [11-15].

"Almalyk MMC" JSC collected industrial waste in the form of zinc cakes in a large amount; their involvement in production allows the combination to significantly increase metal production without using the main raw material enrichment, fluxes and energy costs [16-17]. This research work is aimed at solving the same problems, in which trivalent iron oxide is selectively recovered by heating hydrometallurgical waste containing 15-20% zinc with sulphur in the temperature range of 500-700 ^{o}C. A method for obtaining iron-rich magnetic fraction and the zinc-rich calcined concentrate is proposed. A waste-free technology has been developed by diverting the resulting iron enrichment to steel production, and diverting the resulting zinc-rich carbon black to hydrometallurgical processing [18-19]. The purpose of the research is to develop a complex processing technology of waste cakes generated from the zinc plant of "Almalyk MMC" JSC.

The tasks of the research are as follows:

- to study the technological processes of extracting zinc from the waste cake, which is usually formed during zinc production;
- to study the interaction of the cake with local reducing substances in order to develop an effective technology for the processing of waste cakes containing zinc;
- to determine the optimal amount of local reducing substance used in the restoration of zinc cakes.

MATERIAL AND METHODS. The scientific and practical significance of the research results is to convert the iron contained in zinc cake to a magnetic form through the method of selective reduction, to find the optimal consumption of sulphur in the addition of elemental sulfur to the cake, to involve in the processing of man-made waste in the metallurgical production of the developed technology, from them It is explained by increasing the utilization level of the complex and selectively melting the product consisting of zinc-rich soot remaining after the re-magnetic enrichment after the initial enrichment, and directing it to additionally extract the precious metals contained in it [20].

Table 1

Chemical and material composition of "Almalyk MMC" JSC zinc plant cakes selected for the experiment, %

Compounds	Quantity, %	Compounds	Quantity, %
Zn	19.4	Cu	1.57
ZnO	1.72	CuO	0.144
$ZnSO_4$	0.74	$CuSO_4$ _	0.052
ZnS	1.66	CuS	0.12
$ZnO·Fe_2O_3$	15.3	$CuO·Fe_2O_3$	1.25
Pb	5.8	S	7.7
also**:**		Fe	23.2
PbO	0.54	CaO	2.7
$PbSO_4$	0.21	MgO	1.0
PBS	0.45	Al_2O_3	2.2
$PbO·Fe_2O_3$	4.52		
Cd	0.20		
CdO	0.019		
$CdSO_4$ _	0.007		
CdS	0.015		
$CdO·Fe_2O_3$	0.154		

The waste cakes from the hydrometallurgical leaching process of JSC “Almalyk MMC” Zinc Plant were selected as objects of research. The chemical composition of the waste cake from “Almalyk MMC” JSC Zinc plant is presented in Table 1 below. The values presented in Table 1 show that the chemical composition of zinc plant cake contains significantly more iron and zinc. The main part of zinc in the cake is in the form of ferrite, this compound belongs to the spinel type of the class of oxides and differs from other types of oxides by its insolubility in acids and alkalis. Technical sulphur was used as a reducing and sulphiding agent in the research. Technical sulphur and technical modified sulphur are produced in accordance with technological regulations approved in accordance with standard requirements.

Technical sulphur, depending on the production method, is produced in liquid, lumpy, granular and ground form. It was precisely ground sulphur that was required to carry out the research. In terms of physical and chemical parameters, crushed technical sulphur must meet the requirements and standards specified in Table 2.

Table 2

Physical and chemical parameters of ground technical sulphur

Indicator name	Signs		Analysis method
	High variety	Type 1	
1. External appearance	Yellow powder, Mechanic mixtures (paper, wood, sand and others) to existence the way is not placed.		Visual
2. Sulfur mass share , from % less it’s not	99.94	98.00	7.2 according to
3. Of water mass share , %, more it’s not	0.2	Not standardized	7.6 according to
4. Arsenic mass share , %, more it’s not	0.000	0.000	GOST 127.2 according to
5. Mesh in a sieve residue 014N, %, more it’s not	3.0	3.5	GOST 127.2 according to
Note - The 4th indicator of the table is the consumer or control doer of the organization at your request according to is determined.			

Tire, rubber industry, metallurgy and village economy for crushed technical in sulphur of additions to existence permission is given. In order to study the chemical and material composition of zinc production cakes, technical sulphur and products obtained as a result of research, samples were taken and analysed at the State Enterprise “Central Laboratory” of the State Committee for Geology. Minerals were analysed using a mass spectrometric analyser (ICP-MS) and a high-performance energy-dispersive X-ray fluorescence spectrometer NEX CG RIGAKU at the Institute of Chemical Technology [21].

RESULTS AND DISCUSSION. After it was determined that zinc in the waste cake from the hydrometallurgical shop of Almalyk Mining and Metallurgical Combine (AMMC) was in the form of oxide and ferrite minerals, this waste was first analysed in a mill under laboratory conditions. A total of 8 zinc cake samples of 10 g each were weighed on an electronic scale for the research work. Then technical sulphur was crushed dry in a porcelain mortar, and the obtained raw materials were subjected to preliminary granulometric analysis. The results of granulometric analysis are shown in Figure 1. The results of granulometric analysis showed that the particle size in samples of zinc cake and commercial sulphur obtained by milling was less than 0.1 mm. Then, when analysing the magnetizing properties of zinc cake, it was found that the main iron-containing component of zinc in the cake, zinc ferrite ($ZnFe_2O_4$), has a very low magnetic attraction, so it is practically inseparable from the magnetic method. It cannot bind to flotation reagents due to its high hydrophilicity in flotation.

Fig.1. Granulometric analysis of a sample of zinc cake (right) and crushed industrial sulfur (left)

Accordingly, the research was faced with the task of converting iron and zinc oxides from minerals in the form of zinc ferrite ($ZnFe_2O_4$) into separate compounds. As a result, iron is transformed from a non-magnetic ferrite into a magnetic oxide. To do this, in the scientific laboratory of the Department of Metallurgy of the Tashkent State Technical University, the practice of converting ferric oxide into a divalent form was carried out under the influence of crushed industrial sulphur on zinc cake. A weighing of 10 g of zinc cake was prepared by mixing different amounts of crushed technical sulphur samples (Fig.2).

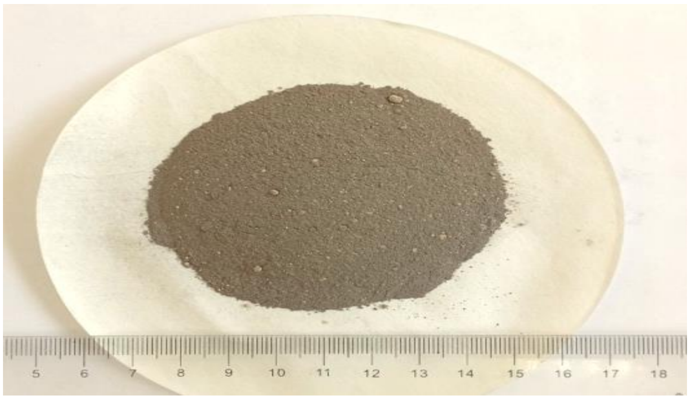

Fig.2. A sample of a charge made from a mixture of samples of zinc cake and technical sulphur

A sample of the mixture obtained was placed in a crucible made of refractory materials and heated in a SNOL-2.5x2.5x2.5/3I muffle furnace at a temperature of 500-700 ^oC for 1 hour. When zinc cake and industrial sulphur mine are heated in the Muffle Furnace at 500-700 ^oC during the process, the following chemical reactions occur:

$$2(ZnO \cdot Fe_2O_3) + S = 2ZnO + 4FeO + SO_2 \qquad 1$$

$$ZnO \cdot Fe_2O_3 + 5S = ZnS + 2FeS + 2SO_2 \qquad 2$$

Samples obtained after high-temperature heating were subjected to magnetic separation. Bivalent iron oxide (FeO), released as a result of chemical reactions (1) and (2), was also isolated by magnetic separation (Fig.3).

Fig.3. The magnetic fraction of the product formed after the sintering of zinc cake with crushed technical sulphur

For sintering zinc cakes with technical sulphur at various temperatures and time units, several studies of sulphur consumption in the process were carried out. Accordingly, the consumption of sulphur was 5-40% by weight of the original zinc cake. The temperature range was from 500 to 700 ^{o}C. Studies were also carried out on the course of the reduction reaction in terms of the difference in time and concentration. The first 4 batch samples were heated for 30 minutes and the next 4 samples were heated for 60 minutes at various temperature ranges in a muffle furnace. The performance of each experimental sample in the study is presented in Table 3.

Table 3

Experimental indicators of the consumption of technical sulphur in the processing of zinc cake

№	Zinc cake mass, g	Consumption of technical sulphur, %	Temperature, ^{o}C	Time, min
1	10	5	500	30
2	10	10	525	30
3	10	15	550	30
4	10	20	575	30
5	10	25	600	60
6	10	30	625	60
7	10	35	650	60
8	10	40	700	60

With the indicators given in Table 3, 8 experiments were carried out and the interaction of technical sulphur with zinc cake was studied. The results obtained are presented in Table 4.

Table 4

The degree of release of iron oxide in the product obtained after heating

№	Consumption of technical sulphur, %	Temperature, °C	The amount of magnetic fraction released after firing, g	The degree of separation of the magnetic fraction, %
1	5	500	0,68	5,0
2	10	525	1,78	13,08
3	15	550	2,11	15,51
4	20	575	2,56	18,82
5	25	600	3,07	22,57
6	30	625	3,84	28,23
7	35	650	4,95	36,39
8	40	700	5,87	43,16
9	50	700	4,73	34,77
10	60	700	4,05	29,77
11	70	700	3,98	29,26

The degree of separation of the magnetic fraction, the indicative results of the experiment, presented in Table 4, were calculated according to the following formula, depending on the mass of the initial cake obtained for the study:

$$\eta = \frac{m_{mag.frac}}{m_{kek}} \cdot 100 \quad (3)$$

The dependence of the amount of reducing agent during sintering on the degree of separation of the magnetic fraction is shown graphically in Fig.4.

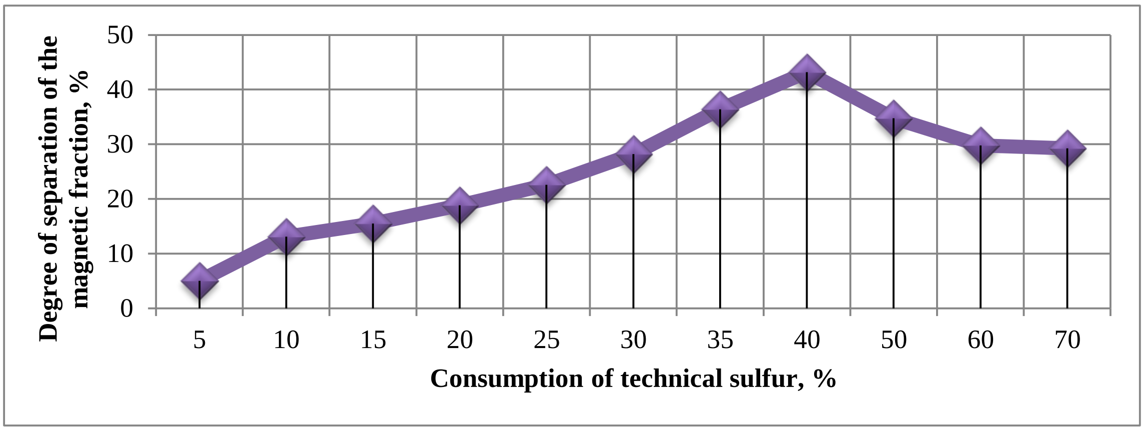

Fig.4. Dependence of technical sulphur consumption during sintering on the degree of separation of the magnetic fraction

From the graph presented in Fig.4, it can be seen that the chemical process initially accelerated as the consumption of technical sulphur increased, resulting in a relatively large magnetic fraction. At a consumption of technical sulphur of 40% of the mass of the original zinc cake, the degree of separation of the magnetic fraction as a whole turned out to be the maximum value equal to 43.16%. An increase in the consumption of technical sulphur had a positive effect on the chemical reaction. However, it has been determined that the degree of separation of the magnetic fraction has a negative effect. Hence it follows that the optimal consumption of technical sulphur in the process of reduction of zinc ferrite in a cake with sulphur to obtain low-iron oxide (FeO) was 40% of the mass of the original zinc cake. This required a temperature of 700 ^oC for optimal reaction.

An increase in the consumption of technical sulphur leads to an acceleration of the chemical reaction (2). Since the oxides of zinc and iron formed by the reaction (1) due to its susceptibility to sulphur, sulfidation occurs in zones with high sulphur concentrations. Due to the weak magnetization of the resulting sulphide mixture, the rate of extraction of the magnetic fraction decreases with increasing sulphur consumption.

Zinc oxide (ZnO) and iron (II) oxides (FeO) are formed as a result of the chemical reaction (1) at the initial stages of the zinc cake sulfidation reaction mechanism, i.e. in areas with low sulphur concentrations. The chemical reaction (1) itself is sufficient for the selective reduction of zinc ferrite in zinc cake. The main purpose of the study is the separation of zinc and iron oxides by magnetic separation due to the sintering of zinc cake, and is to reduce the consumption of a reducing-sulfiding substance – sulphur.

CONCLUSION. Based on the results of the study, the following conclusions were presented:

1. Hydrometallurgical leaching of calcined zinc concentrates from zinc production revealed the formation of a large amount of cake, consisting of insoluble oxidized compounds. Chemical analysis of the waste showed that they contain a large amount of oxidized zinc compounds. Quantitative analysis showed that the zinc in this material is mainly in the form of zinc ferrite ($ZnFe_2O_4$).

2. To facilitate the separation of zinc from the cake of a zinc plant, a technology was developed for sintering zinc ferrite with technical sulphur, since this required the conversion of zinc from ferrite to oxide or sulphide. The developed technology serves to develop a more efficient technology for processing zinc cake.

3. In the course of the research, the thermodynamic aspects of the process of sintering zinc-containing waste from zinc production with technical sulphur were studied. Accordingly, a mechanism has been developed for chemical phenomena occurring in the zones of interaction between zinc ferrite and technical sulphur. Based on the mechanism of the developed chemical reactions, each chemical reaction occurring in the process was analysed from a thermodynamic point of view.

4. After grinding the resulting sinter, it was subjected to magnetic separation to isolate iron oxide from its composition.

5. The non-magnetic zinc enriched fraction was sent to the hydrometallurgical leaching process, and the iron enriched coniron-enrichedsent to the steel production process. The degree of extraction of metallic zinc from the resulting product was 96%.

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