

Technology of high-temperature sulfidizing roasting of oxidized lead-zinc ore in a fluidized bed furnace

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Zinc and lead are one of the most used metals in the world. The average annual growth rate of the zinc market is about 3.5%. Half of the zinc consumed in the world is used as electroplating, more than 30% is spent on the production of zinc alloys, including for the production of brass and bronze. At present, polymetallic ores are the main raw material for the production of lead and zinc. The production technology includes flotation enrichment of the initial ore raw material with subsequent pyrometallurgical or hydrometallurgical processing of the resulting concentrates. Unfortunately, the reserves of well-enriched sulfide ores are declining, which leads to the need to involve mixed and oxidized ores in the production. Obtaining zinc is also a relatively expensive process, one of the stages of which is the roasting of zinc sulfide concentrates in a fluidized bed furnace using oxygen-enriched air blast. In this regard, technologies aimed at processing hard-to-cut oxidized lead-zinc ores, as well as improving the process of roasting in a fluidized bed, are topical and in demand today. The article presents the technology and method for processing oxidized lead-zinc ore, including high-temperature sulfidizing roasting of oxidized compounds of lead and zinc, the results of roasting carried out in the presence of a high-sulfur sulfidizing agent in the form of pyrite (sulfur content is 45.15%), at molar ratios of metal oxide to pyrite $NZnO/NFeS_2$ and $NPbO/NFeS_2$ equal to 0.1–0.14 for sulfidizing in an air-blown fluidized bed furnace at a flow rate of 10 to 20 l/min, at a temperature of 750–800 °C, with a roasting time of 30–45 minutes. As a result of sulfidizing roasting, the degree of sulfidization reaches 88%, and the subsequent extraction of zinc from the non-magnetic fraction into a froth product in an open flotation cycle is 90% with a content of 23.4% zinc.

Key words: high-temperature sulfidizing roasting, fluidized bed furnace, fluidization, air blast, oxidized lead-zinc ore, sulfidizer.

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1. Introduction

The problem of increasing the rational and integrated use of mineral raw materials becomes most relevant when refractory polymetallic ores are involved in the production, which is due to significant industrial volumes of deposits. These types of ores include a number of deposits in Kazakhstan — this is the Zhairem deposit, as well as deposits in the Ural and Siberia [1–3].

A characteristic feature of refractory ores is the complex mineralization of valuable components, significant oxidation and intergrowth of minerals, the presence of ore metals in the form of refractory minerals such as plumboyarosite, calamine, bendatite, zinc oligonite, monheimite, and others [4].

The practice of concentrating plants has shown that the direct processing of such ores by enrichment methods,

even with the selection of the reagent regime and the improvement of enrichment schemes, does not give satisfactory results. An analysis of existing technologies for the enrichment of oxidized and mixed ores of heavy non-ferrous metals shows that more than half of the metal losses in the tailings are due to their presence in the form of oxidized compounds [3–4]. The practice of using new flotation reagents and combined schemes does not allow increasing the extraction of metals by more than 2–3%. The new reagents-collectors proposed in recent years are expensive, and their effectiveness largely depends on the observance of special conditions, which is rather difficult to implement in practice, since oxidized ores that are hard to be enriched are characterized by composition variability.

For the processing of oxidized lead-zinc ores, it is possible to use direct hydrometallurgical technological schemes. There are methods of underground leaching, percolation (as an analogue of underground) leaching of

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sulfide lead-zinc ore, using ferric chloride, acid sodium hypochlorite as a solvent [5], there are methods of underground bacterial leaching of residual sulfide Cu – Zn ores in depleted deposits [6]. In the presence of oxidized ores with a high content of carbonates in the form of cerussite PbCO_3 and smithsonite ZnCO_3 , it is advisable to use leaching with hydrochloric and sulfuric acids when sodium chloride is added to the solution. More difficult is the leaching of oxidized ores, in which zinc is in the form of silicate — calamine, and lead in the form of plumbrosite or crocoite, due to the complexity of the composition.

Hydrochloric acid is a stronger solvent than sulfuric acid. But the high cost, the difficulty of transportation, environmental requirements hinder the use of this reagent. It is recommended to use solutions of chlorides of alkali and alkaline earth metals, acidified with sulfuric acid, for leaching lost and substandard ores [7].

Alkalis can be an effective solvent for polymetallic raw materials. Studies conducted in the CIS and abroad on the autoclave alkaline leaching of various concentrates and middlings have shown their promise [8]. However, the use of alkalis in geotechnological processes is hampered by the reversibility and extremely low rate of interaction of alkalis with sulfides under normal conditions. It is proposed to use ammonia for leaching polymetallic sulfide concentrates.

The Institute of Metallurgy and Beneficiation of the National Academy of Sciences of the Republic of Kazakhstan has developed a method for underground leaching of sulfide lead-zinc ores with low-concentration solutions of ferric chloride [9]. The disadvantages of this solvent are: maintaining a fairly high acidity to ensure the stability of ferric chloride, the presence of Fe (II) and Fe (III) ions interfere with the isolation of valuable components (Pb and Zn) in the form of selective or collective products; regeneration of expensive ferric chloride complicates the process.

All solvents described above can be used for both sulfide and mixed lead-zinc ores with various ratios of oxidized and sulfide minerals. However, when using the above solvents, with the exception of HCl and solvents with the addition of NaCl to bring lead sulfate into solution in the form of chloride complexes, all PbSO_4 remains in the ore. In addition, using collective solvents during leaching, solutions containing Pb^{2+} , Zn^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} and other impurities are obtained. There is a complex problem of processing such solutions in order to obtain commercial lead, zinc products. The extraction of metals from such solutions is associated with great technological difficulties and is not always economically justified. Thus, due to the increase in the activation ability of raw materials, it is advisable to use activating roasting before direct hydrometallurgical methods for processing oxidized ores.

There are hydrochemical methods of enrichment, which allow increasing the recovery of metals up to 90%. However, these processes are distinguished by significant specific costs due to their multi-stage nature, high

consumption of expensive and aggressive reagents, and also require the use of corrosion-resistant equipment [10–14].

The most promising processes are the directed transformation of non-ferrous metals minerals by their transfer from the oxidized form (sulfates, carbonates) to the easily floatable sulfide one.

The authors [15] use the technology of processing oxidized lead ore by sulfidizing roasting with a sulfidizer in an atmosphere of water vapor at low temperatures in a furnace of 500–600 °C, as a sulfidizer, an off-standard pyrite concentrate with a sulfur content of at least 40% is used. However, there are a number of difficulties — this is a multi-stage process, the need to control the concentration of hydrogen sulfide and hydrogen in the atmosphere of water vapor.

There is a known method of changing the mineralogical composition of valuable ore components according to flotation properties by deeper sulfidization of the surface of the oxidized mineral with sodium polysulfides during grinding [16–18].

However, the existing methods of mineral surface sulfidization do not provide the desired effect, since the formed sulfide film on the surface of the oxidized mineral is easily destroyed during flotation [19–22].

Processing of carbonate ores of the Zhairam deposit by the Waelz method does not produce an oxidized product of standard zinc with the use of one furnace, due to the low zinc content in the ore. The KIVCET-TSS method can process only lead-rich concentrates [9].

The economics of choosing a sulfidizer suggests that sulfidizing with sour petcoke with a sulfur content of at least 3% (weight %) is too costly a choice, due to the high production costs; sulfidizing with sulfur-containing additives requires additional hardware design and there is no data on their use for processing oxidized and mixed refractory ores; the use of elemental sulfur as a sulfidizing agent is expensive, since sulfur is a commercial product, the production of which requires the development of technology. Thus, pyrite is the most accessible sulfidizing agent for use in the technology of processing refractory oxidized mixed ores. The results of studies carried out in various countries [23] make it possible to consider the gases that form oxidized compounds of non-ferrous metals during pyrite roasting as a sulfidizing agent. In world practice, a number of methods for implementing the process of thermal dissociation of pyrite are known, which differ in the methods of heat supply and the nature of chemical interaction. The versatility of pyrite as a sulfidizing agent lies in the possibility of its thermal decomposition in a vacuum, in an atmosphere of dissociation products, in an atmosphere of fuel combustion products, in an air atmosphere, in various thermal units.

Thus, from the analysis of literary sources and the practice of operation of metallurgical plants in the CIS countries and far-abroad enterprises, it follows that the solution to the problem of efficient processing

of oxidized ores lies in the development of combined technologies [24–27].

The most promising combined method is the preliminary preparation of ores for enrichment by activating roasting, which affects non-ferrous minerals. Among them, the method of high-temperature sulfidizing activation of ore minerals has a significant effect [27].

The use of this method for the zinc-oligonite type of ores of the Zhairesky deposit showed the feasibility of working out the regime parameters of roasting and flotation to develop a technological scheme for processing zinc-oligonite ore.

The purpose of the research is to develop technology and practical development of sulfidizing roasting modes at an enlarged laboratory installation of a “fluidized bed” furnace with further processing of cinders of zinc-oligonite ore from the Zhairesky deposit of Kazzinc LLP to conditioned products.

2. Materials and experimental methods

2.1. Materials

Zinc-oligonite ore from the Zhairam deposit taken from the 2nd quarry of the Far-Western mine was used as the starting material for sulfidizing roasting. The content of zinc is 2.5%, lead is 0.1%, the degree of zinc oxidation exceeds 60%.

The Ridder pyrite concentrate with a sulfur content of 45.15% was used as a sulfidizing agent. The original ore was crushed before roasting, crushed to a particle size of –0.1 and –0.25 mm, mixed with pyrite of the 0.074 mm class.

Samples of the original ore and pyrite concentrate accepted for research were subjected to chemical, X-ray diffraction and mineralogical studies. The results of chemical analysis for the average content of the components are presented in **Table 1**.

2.2. Experimental Methods

X-ray phase analysis was carried out on a BRUKER D2 analyzer, Cu/Ni radiation, $A = 1.54184$ Å, 30 kV, 10 mA, 2θ –5–70, time 1720 s) and SEM – EDS (JEOL – JSM–6010PLLI/LA). The results of the spectral analysis

agree with the data of the chemical analysis. X-ray diffraction analysis of the original ore and pyrite concentrate showed that in the ore zinc is represented by carbonates and sulfide, and in the pyrite concentrate only by sphalerite. The presence of pyrite in the source materials, galena and chalcopyrite was established.

Electron microscopic studies were carried out on a JEOL ISM – 25S analyzer at 1500x magnification. Microscopic study of the original ore sample, sized into classes: +0.05 and –0.05 and divided into heavy and light fractions, made it possible to establish the mineralogical composition of the presented sample of zinc-oligonite ore. The mineralogical analysis of pyrite concentrate showed that pyrite is predominantly in the form of free crystalline, cubic grains (74.6%), in the form of fine dissemination in quartz (1.8%), dissemination in calcium hemihydrate and calcium sulfate (21.7%). Sphalerite, galena and chalcopyrite in free grains and inclusions make up 1.4%. Iron carbonates and hydroxides do not exceed 0.5%. The original ore before roasting was crushed, crushed and dispersed to a particle size of 0.1–0.25 mm and combined with pyrite flotation concentrate class 0.074 mm 90%.

Wet magnetic separation was carried out on an electromagnetic separator at a magnetic field strength of 100–120 kA/m.

The magnetic susceptibility of materials was analyzed on a KLY-2 susceptibility instrument (AGICO), Czech Republic: sensitivity is 1×10^{-6} SI units (in scanning mode 1×10^{-5} SI units); operating frequency 10 kHz.

Flotation enrichment of the non-magnetic fraction from the separation of cinders was carried out on a laboratory flotation machine of the FL-237 type with a working chamber volume of 0.5 dm³ and 1.0 dm³, subject to $S:L$ equal to 1:(2.0–2.5).

The high temperature sulfidizing roasting was carried out in a fluidized bed furnace. The scheme of the enlarged laboratory installation for roasting in a fluidized bed furnace is shown in **Fig. 1**. The installation of a fluidized bed furnace includes the following main components and mechanisms: the reactor of the “fluidized bed” furnace with an adjustable continuous system for loading the charge and unloading the cinder; gas duct with a system of coarse and fine dust collection, condensation of sublimates and absorption of sulfur dioxide from exhaust gases, air heating units and furnace reactor, a system for controlled supply and control of air blast flow, a control unit and temperature control in the furnace.

The reactor of a fluidized bed furnace of rectangular cross section with a hearth area of 120 cm² is made of XI8H90T stainless steel, and the hearth is made of stainless heat-resistant mesh with a hole size of up to 5 microns. The charge is loaded into the reactor from above in a non-breakthrough mode using two screw feeders driven by reversible motors of the KD-30-U4 type. The rotation speed of the screws is selected depending on the specified material loading mode and is controlled by changing the voltage supplied to the motors from a laboratory autotransformer.

Table 1
Chemical composition of zinc-oligonite ore and pyrite concentrate

Component	Content, %	
	Ore	Pyrite concentrate
Zinc	1.8–2.5	0.32–0.35
Iron	7.5–11.5	38–40
Sulfur	1.8–3.2	45–47
Lead	0.06–0.1	0.21–0.23
Copper	0.01–0.05	0.35–0.39
Manganese	0.9–0.95	–
Silicon oxide	65–67	4–5.7
Calcium oxide	0.5–0.7	4.2–4.6
Aluminium oxide	9.6–10	1.3–1.7

The unloading of the cinder from the furnace into a sealed hopper is carried out by a horizontal auger located 15 cm from the level of the hearth. The height of the discharge window may vary depending on the material being fired and the specified mode of operation of the furnace.

Exhaust gases from the reaction zone through the furnace charge enter a heated gas duct equipped with three cascaded cyclone chambers for coarse and fine dust collection, a sublime condenser and an absorber of fine dust and sulfur dioxide. In accordance with the program of work, experiments were carried out on an enlarged-laboratory installation of a fluidized-bed furnace to test the operating parameters of the sulfidizing roasting of zinc-oligonite ore at the Zhairam deposit.

The preparation of the mixture of a given composition was carried out by thoroughly mixing the original ore with a particle size of 0.1–0.25 mm with a pyrite concentrate with a particle size of 0.074 mm 90%, taken in the required ratios. The finished charge was loaded into the furnace feed hopper.

The “roasted layer” from the previously roasted material (cinder) 1.0–1.5 kg was laid down on the bakestone before launching of the furnace. The conditions of the roasting for “roasted layer” and charging of the “fresh” ores mass and pyrite concentrate were constant, the addition of pyrite concentrate varied from 50 to 75, the roasting indicators calculated by the ratio $NMeO/NFeS_2$, by the

degree of sulfidizing, %, while the best indicators of the roasting is temperature interval 700–800 °C.

Simultaneously with the heating of the furnace to a given temperature, the air blast flow rate was set, which varied on average from 8.0 to 20 l/min. Upon reaching the specified temperature in the cinder layer, the charge was loaded into the furnace with simultaneous adjustment of the screw rotation speed to provide the specified productivity. After the furnace bath was filled up to the unloading window, the unloading auger was turned on, and after a 2–3-fold exchange of material in the reaction zone, the selection of the calcined cinder into the sealed hopper began.

In the course of the ongoing research, the influence of temperature on the degree of sulfidizing of zinc oxides in the range of 650–800 °C, the influence of the composition of the charge and the sulfur potential in the system were studied. The charge composition varied depending on the percentage of pyrite concentrate addition from 50 to 75%. The ratio of pyrite concentrate to ore is 1:1 and 2:1. The change in sulfur potential, depending on the ratio of pyrite concentrate to ore, was determined by calculation, depending on the amount of oxygen supplied with air blast and the amount of sulfur introduced with the charge per unit time; in this case, the blast flow rate varied from 10 to 20 l/min, and the charge load from 10 to 60 g/min. Sulfur potential means thermodynamic conditions in the S – O system or phase equilibria in the

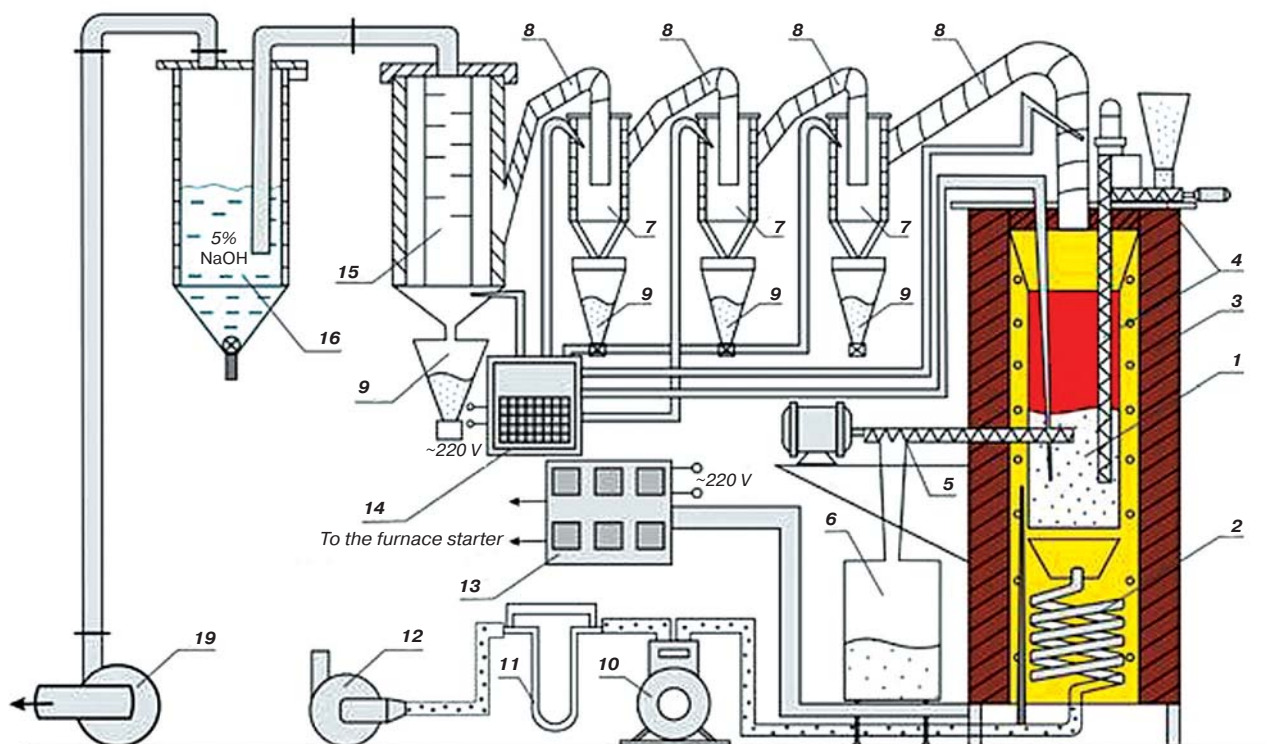


Fig. 1. Large-scale laboratory installation of sulfidizing roasting in a fluidized bed furnace:
 1 – reactor; 2 – air heating unit; 3 – fluidized bed furnace; 4 – loading unit; 5 – unloading unit; 6 – cinder bunker; 7 – cyclone; 8 – heated flue; 9 – dust bunker; 10 – gas meter; 11 – rheometer; 12 – blower; 13 – furnace control unit; 14 – KSP potentiometer; 15 – capacitor; 16 – bubbler; 17 – valve; 18 – adjustable damper; 19 – smoke exhauster

Fe – S – O system in the aggregate, the release and concentration of sulfur (elemental sulfur) directly in the fluidized bed. The source of heat necessary for the dissociation of pyrite is the heat released during the oxidation of the dissociation product, elemental sulfur, directly in the fluidized bed, which makes it possible to minimize its losses. Good conditions for heat and mass transfer, characteristic of a fluidized bed, allow the dissociation of pyrite to be carried out quite intensively. Since the thermal effect of elemental sulfur oxidation significantly exceeds the thermal effect of thermal dissociation, it becomes possible to oxidize in the layer only a part of the sulfur released during dissociation. At the same time, blast oxygen is used by 95% or more to produce gases containing up to 20% sulfur dioxide. In addition, part of sulfur 1–4%, depending on the roasting conditions, is obtained in the form of elemental. It has been established that at 650 °C favorable conditions are created for obtaining the maximum sulfur potential in the system, associated with the kinetic patterns of thermal dissociation of pyrite, oxidation and distillation of dissociated sulfur.

Large-scale laboratory installation of sulfidizing roasting in a fluidized bed furnace, **Fig 1**.

Electron paramagnetic resonance was carried out on a JES-FA 200 setup (Jeol, Japan), recording conditions: frequency 9.445 GHz, in the field $F_c = 340$ mT, sweep 7.50 (mT), modulation frequency and amplitude $F_r = 100$ (kHz). Width = 0.6 (Mt), EPR spectra were recorded at room temperature in the presence of $Mn^{(2+)}$ standard in MgO. Pyrrhotites obtained from 700 to 875 °C during roasting in an air-blast fluidized bed furnace with a composition from $Fe_{0.862}S$ to $Fe_{0.90}S$ were subjected to analysis.

The ξ -potential of lead and zinc sulfides was measured by macroelectrophoresis. Electrophoretic mobility was measured using the apparatus of Rabinovich and Fadiman by the method of moving boundaries. The electrokinetic potential was calculated using the Smoluchowski equation [28–33]. To prepare the suspension, the samples were first crushed and fractions less than 0.044 mm were taken. Suspensions were then prepared for this process by adding 50 ml of distilled water to a 0.5 g sample and stirring on a magnetic stirrer for 10 minutes. Such a suspension was prepared for lead and zinc sulfides depending on the pH of the medium at 5, 7, 9, 11, and 13.

3. Results and discussion

3.1 Results of high temperature sulfidizing roasting in fluidized bed furnace

High-temperature sulfidizing roasting was carried out in an air-blast fluidized bed furnace, which allows creating the best modes of heat and mass transfer, regulation and control of the sulfur potential in the unit, the process took place in an autogenous mode with high productivity.

Oxidized lead-zinc ore was used as a feedstock, with a zinc content of up to 2.5%, lead up to 0.1%, the degree of zinc oxidation reached up to 60%.

Roasting was carried out in an air-blast fluidized bed furnace at a flow rate of 10 to 20 l/min, at a temperature of 750–800 °C, with a roasting duration of 30–45 minutes. The air blast was supplied from the compressor, regulated by the rotameter valve and controlled according to the readings of the gas meter. To create and maintain fluidization in the reaction space of the furnace, the blast flow rate was regulated from 1.0 to 45 l/min, the optimal blast flow rate for obtaining magnetic pyrrhotites was the blast flow rate from 10 to 20 l/min. The influence of temperature on the degree of sulfidizing of oxides of zinc and lead in the temperature range from 650 to 850 °C, the influence of the composition of the charge and the sulfur potential in the system were determined. The composition of the charge varied according to the pyrite concentrate from 50 to 75%. The ratio of pyrite to ore was 1:1 and 2:1, the molar ratios of $NZnO/NFeS_2$ and $NPbO/NFeS_2$ ranged from 0.08 to 0.2. The change in the sulfur potential was determined by calculation, depending on the amount of oxygen supplied with air blast and the amount of sulfur introduced with the charge per unit time. In this case, the blast flow rate varied from 10 to 20 l/min, and the charge load from 10 to 60 g/min.

The resulting roasting products were subjected to enrichment: magnetic enrichment of cinders and flotation enrichment of the non-magnetic fraction were carried out.

The pyrrhotite obtained in cinders was analyzed for magnetic susceptibility, the degree of lead and zinc sulfidization was determined, the hydrophobicity of the obtained sulfides was determined by the value of the ξ -potential. The results of high-temperature sulfidizing of lead-zinc ore are presented in **Tables 2, 3**.

The experiments on lead and zinc oxide sulfidizing at 600–800 °C and a molar ratio of 0.1 (**Table 3**) show that at temperatures below 700 °C the degree of lead and zinc sulfidizing is low, and the resulting sulfides are characterized by low hydrophobic properties. The extraction of lead and zinc into the flotation concentrate is 30 and 45%, respectively, with their content in the tailings being 35% Pb and 30% Zn.

The best indicators are roasting conditions in the temperature range of 700–800 °C, while zinc and lead sulfides have high hydrophobic properties ($\xi = -350$ mV Zn; $\xi = -340$ mV –Pb), and the resulting pyrrhotites $Fe_{0.75}S$ to $Fe_{0.9}S$ are the most magnetic ($1250-1330 \cdot 10^{-6}$ SI/g). The best indicator of the magnetic susceptibility of pyrrhotites is achieved at 800 °C. In this case, a high yield of the magnetic fraction (95%) and a high extraction of lead (90%) and zinc (95%) are achieved, their losses to tailings are 3% for lead and 2% for zinc. As the temperature rises above 800 °C, the degree of sulfidization is also low. The output of the magnetic fraction in percent was determined relative to the mixture — the ratio of pyrite to ore.

The roasting products were lead and zinc sulfides with low values of ξ -potential (ξ (Pb) = –64 mV; ξ (Zn) = –108 mV). This reduces the extraction of lead and zinc into the flotation concentrate and the quality of the

resulting concentrates (the loss of Pb to tailings is 18%, and that of zinc is 12%).

Thus, the formation of pyrrhotites $\text{Fe}_{0.75}\text{S}$ to $\text{Fe}_{0.9}\text{S}$ with a maximum magnetic susceptibility of $1330 \cdot 10^{-6} \text{ Ci/g}$ is fixed at a temperature of 800°C and $\text{NMeO}/\text{NFeS}_2$ a ratio of 0.14 with a sulfidization duration of 45 minutes, **Table 2**.

3.2 Results of electron paramagnetic resonance (EPR)

The results of EPR showed that in the spectrum of pyrrhotite $\text{Fe}_{0.862}\text{S}$, obtained at 800°C during roasting in a fluidized bed furnace, two signals are observed in a field of 338–340 mT, the value of the g factor is about 2.00. In pyrrhotite of the composition $\text{Fe}_{0.90}\text{S}$, a total increase in both signals in a field of 338–341 mT is observed; due to superposition, they appear as one broad signal. Thus, the presence of magnetic properties characteristic of ferro and paramagnets is subjected to EPR spectra, it has been established that in the high-temperature region, iron sulfides can exhibit changes in properties from paramagnetism to ferromagnetism with the maximum spectrum of ferromagnetic properties being achieved in the production

temperature range from $800\text{--}875^\circ\text{C}$, it was also established that the amplitude of the magnetism spectra depends on the composition of pyrrhotites and the amount of sulfur in pyrrhotite.

3.3 Results of wet magnetic separation of cinders

Cinders of sulfidizing roasting were subjected to wet magnetic separation at a magnetic field strength of 100–120 kA/m. **Table 4** shows the results of magnetic separation for the extraction of iron into a magnetic product.

The presented results of magnetic separation show that in the selected range of magnetic field intensity, more than 95% of iron from roasting cinders is extracted into the magnetic product. The results of the spectral analysis of the magnetic and non-magnetic fractions showed that non-ferrous and rare metals are mainly concentrated in the non-magnetic fractions. Magnetic separation makes it possible to isolate magnetic pyrrhotite from roasting cinders with sufficient completeness and to concentrate non-ferrous metals in a non-magnetic fraction for their extraction by flotation methods.

Table 2

Indicators of high-temperature sulfidizing of lead-zinc ore with pyrite at 800°C

Ratio $\text{NMeO}/\text{NFeS}_2$		Degree of sulfidizing, %		ζ – potential, mB		Magnetic susceptibility, 10^{-6} Si/g	Pyrrhotite Fe_{1-x}S	Exit of magnetic fraction, %	Extraction, %		Content in wastes, %	
Pb	Zn	Pb	Zn	Pb	Zn				Pb	Zn	Pb	Zn
0.08	0.08	80	85	–338	–348	820	$\text{Fe}_{0.901}\text{S}$	50	70	80	3	8
0.1	0.1	80	84	–340	–350	890	$\text{Fe}_{0.885}\text{S}$	95	90	95	5	2
0.12	0.12	78	74	–340	–120	920	$\text{Fe}_{0.877}\text{S}$	90	85	91	4	3
0.14	0.14	65	65	–130	–100	1330	$\text{Fe}_{0.862}\text{S}$	85	80	90	4	3
0.2	0.2	35	40	–33	–13	900	$\text{Fe}_{0.855}\text{S}$	80	70	70	15	10

Table 3

Indicators of high-temperature sulfidizing of lead-zinc ore with pyrite at a molar ratio of 0.1 $\text{NMeO}/\text{NFeS}_2$ and a duration of 45 minutes

$T, ^\circ\text{C}$	Degree of sulfidizing, %		ζ – potential, mB		Magnetic susceptibility, 10^{-6} Si/g	Pyrrhotite Fe_{1-x}S	Exit of magnetic fraction, %	Extraction, %		Content in wastes, %	
	Pb	Zn	Pb	Zn				Pb	Zn	Pb	Zn
600	26	30	–50	–57	800	$\text{Fe}_{0.911}\text{S}$	10	30	45	35	30
650	51	54	–75	–240	820	$\text{Fe}_{0.901}\text{S}$	80	70	80	20	15
700	80	84	–340	–350	890	$\text{Fe}_{0.855}\text{S}$	95	90	95	3	2
750	48	69	–170	–280	920	$\text{Fe}_{0.877}\text{S}$	97	85	90	10	6
800	38	44	–64	–108	1330	$\text{Fe}_{0.862}\text{S}$	97	80	90	18	12

Table 4

Results of magnetic separation of cinders

Product name	Experiment conditions		Magnetic fraction		Non-magnetic fraction	
	$T, ^\circ\text{C}$	Pyrite : ore ratio	Quantity, kg	Extraction Fe, %	Quantity, kg	Extraction Fe, %
Cinder 1	650	1:1	0,584	65,4	0,0907	13,6
		2:1	0,027	90,4	0,077	9,6
Cinder 2	700	1:1	0,086	91,4	0,086	8,6
		2:1	1,035	96,4	0,038	3,6
Cinder 3	800	1:1	0,043	96,6	0,029	4,4
		2:1	1,046	97,2	0,03	2,8

Table 5
Results of flotation enrichment of non-magnetic fraction

Product name	Exit, g	Zinc contention		Iron contention		Extraction	
		%	g	%	g	Zinc	Iron
$T = 80\text{ }^{\circ}\text{C}$, ratio 2:1							
Zinc concentrate	100	23.4	37.44	12.7	20.3	90	21
Control concentrate	150	2.3	1.10	5.4	4.7	2.7	4.6
Wastes	830	0.35	2.9	5.7	72.7	7.3	74.4
Flotation charge*	1040	3.08	41.4	9.3	97.7	100	100

*Flotation charge — cinder sent for flotation after roasting and magnetic separation

3.4 Flotation enrichment of the non-magnetic fraction

Enrichment of the non-magnetic fraction was carried out with the following consumption of reagents: lime — up to 2000 g/t; butyl xanthate — 180 g/t; copper sulphate — 600–800 g/t; blowing agent T-80 — 50 g/t. About 20 kg of non-magnetic fraction was subjected to flotation enrichment, **Table 5**.

As it was established earlier, the extraction of zinc into a foam product from raw zinc-oligonite ore does not exceed 32% with a content of up to 3% zinc. After roasting the ore with pyrite concentrate at a ratio of 2:1 and a temperature of 800 °C during flotation, up to 90% of zinc is extracted into the foam product at its content of 23.4%. These results show the high efficiency of ore activation by sulfidizing roasting. The conducted studies showed high flotation properties of sulfides obtained as a result of sulfidizing roasting of zinc-oligonite ore. The average zinc content in flotation tailings is 0.4–0.5%.

Conclusion

It has been established that the optimal conditions for high-temperature sulfidizing of lead-zinc ore are the molar ratio from 0.1 to 0.14 NZnO/NFeS_2 and NPbO/NFeS_2 ; at the same time, the degree of sulfidizing for zinc reaches from 44–65%, for lead from 38–65%, during sulfidizing, lead and zinc sulfides with high hydrophobic properties are obtained, i. e. $\xi = -340\text{ mV} + (-180\text{ mV})$ and pyrrhotite with a maximum magnetic susceptibility of $1250\text{--}1330 \cdot 10^{-6}\text{ CI/g}$, with a roasting time of 45 minutes, which ensures the yield of the magnetic fraction during magnetic separation of 95%, an increase in the extraction of lead and zinc in flotation concentrate up to 90–95% and improving their quality.

It has been established that the cinders of sulfidizing roasting contain pyrrhotite, which has high magnetic properties, which, during magnetic separation, is extracted into the magnetic fraction by more than 90%.

Flotation enrichment of the non-magnetic roasting fraction carried out in an open cycle made it possible to extract zinc by 80–90% into a foam product containing from 12 to 24% zinc. The maximum extraction of zinc in the foam product corresponds to the cinder obtained by roasting at 800 °C and a ratio of 2:1.

Thus, the studies on the activation of ore by sulfidizing roasting showed the effectiveness of high-temperature

sulfidization technology and the possibility of using it on an industrial scale. On the basis of the balance experiments carried out on sulfidizing roasting at the enlarged laboratory installation of the “fluidized bed” furnace, the material balance of the process was compiled and the distribution of metals was established. The technology is recommended for the design of a pilot plant for the preparation of oxidized ores by high-temperature sulfidization under the conditions of Kazzinc LLP. The technology is patented [32].

Economic calculations show that the unit costs per 1 US dollar of marketable products using the proposed technology of high-temperature roasting in a fluidized bed furnace are lower than the specific costs for existing technologies, which is associated with an increase in the extraction of lead and zinc into a marketable product, the use of a cheap sulfidizer, high productivity fluidized bed furnaces and with an increase in the output of marketable products in the form of magnetic pyrrhotites.

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