Processing of the zinc-lead-bearing flotation middlings by sulfidizing roasting with pyrrhotites production by predicted properties

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The accumulated amount of lead-zinc ore flotation tailings in the dumps of concentrating plants today can be considered as independent man-made deposits. In addition to their resource value as sources of lead and zinc, as well as associated gold, silver, cadmium, selenium and other metals, tailings are an environmentally hazardous source of heavy metal pollution of ground and surface waters. The environmental hazard of stale tailings is exacerbated by the fact that they occupy large areas that cannot be used for agricultural or other purposes of the national economy. Wastes of flotation enrichment of lead-zinc ores significantly differ from the source material not only in the content of minerals, but also in the degree of oxidation of their surface, fractional composition, and the presence of a significant amount of mineral intergrowths. In view of this, the use of existing flotation technologies is ineffective for obtaining standard lead and zinc concentrates from enrichment tailings. This paper describes the technology that has been developed for processing of zinc and lead-bearing enrichment wastes by sulfidizing roasting followed by magnetic and flotation concentration of cinders. It was found that, as a result of the sulfidizing- pyrrhotizing roasting process, the flotation ability increases for lead compounds and decreases for iron compounds, while the magnetic susceptibility of lower iron sulfides formed during roasting increases. It has been established that sulfidizing takes place with sufficient completeness, and during subsequent flotation, it is possible to extract up to 95% of zinc and up to 80% of lead into sulfide concentrate. These results have a technological advantage in contrast to the other methods that have been used. It was found that at roasting temperatures of 700–800 °C, pyrrhotites have a maximum magnetic susceptibility of 3.75, 5.43 and 2.18 SI units for $Fe_{0.855}S$, $Fe_{0.888}S$ and $Fe_{0.909}S$, respectively. Technological recommendations are acceptable for similar raw materials.

Key words: zinc, lead-bearing wastes; pyrrhotites, sulfidizing roasting, flotation beneficiation, magnetic susceptibility, sulfidizing.

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1. Introduction

Increasingly poorer and more refractory complex polymetallic ores with a low mineral composition are becoming a secondary source of lead and zinc. A feature of refractory ores is the variability of their composition, the content of dissolved salts and ocher-clay mud, as well as the complexity of the mineral composition [1]. Non-ferrous metals and minerals are represented in these ores by numerous associations: sulfides, carbonates, sulfates, alumino-silicates, oxides, hydroxides and other mineral compounds with different wettability. This does not allow choosing a universal flotation mode that would ensure the extraction of all mineral forms of lead into concentrates. In addition, ores are characterized by small inclusions, the presence of ore minerals in the form of thin smears or peripheral films ranging in size from 1 to 4 μm [2, 3]. Direct use of enrichment processes does not give positive results [4, 5]. Direct pyro- and hydrometallurgical methods for processing refractory polymetallic ores have not been developed to the level of industrially recommended ones.

The best performance in the processing of oxidized and mixed ores is achieved by using preliminary activation of the feedstock by oxidizing or sulphatizing roasting, followed by processing of the activated product [6, 7].

Directions are being formed that are characterized by a selective change in the natural technological properties of minerals before enrichment. This is carried out by controlled physical and physico-chemical influences that change the composition, structure of the crystal lattice and surface properties of minerals. One of these areas is sulfidizing, which can be carried out both by hydrome-

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tallurgical and pyrometallurgical methods. Autoclave sulfidizing is inefficient due to the batch nature of the process and the low productivity of equipment for large-scale production. Sulfidization by sulfate-reducing bacteria makes it possible to restore the flotation activity of oxidized lead minerals due to the formation of sulfide and sulfur films on the surface of minerals [8, 9]. Alternative technologies are biological leaching technologies, but currently they have a number of difficulties with access to large-scale production and climatic conditions at the site of production organizations [10].

Sulfidization of polymetallic raw materials with elemental sulfur can be carried out both in melts and in the solid phase. During sulfidization of oxidized minerals: zincite, smithsonite, cerussite with pyrite and sulfur in the temperature range of 500–700 °C, the degree of sulfidization reaches 90–95%. By flotation of oxidized lead-silver ores sulfidizied with pyrite at 700–800 °C in an inert medium, up to 75% of lead can be extracted into a concentrate [11].

Wastes from the flotation enrichment of lead-zinc ores differ significantly from the source material not only in content and composition, but also in the degree of oxidation of their surface, fractional composition and the presence of a significant amount of mineral aggregates [4, 12–15].

The disadvantages of collective waste flotation is the lack of positive recovery results due to the presence of a high content of metal oxides. During flotation, most of these compounds remain in the chamber product. Even with fine grinding and high consumption of reagents during flotation, no more than 10% of zinc is extracted into the sulfide product [5, 6, 16–20].

Preliminary sulfidization during flotation makes it possible to largely overcome the difficulties associated with the specific features of the material composition of these ores [21–25].

Sulfidization is usually carried out with the help of sodium sulfide, sodium hydrosulfide, or a mixture of them, supplied at many foreign factories in the form of a ready-made reagent [26–30].

As a result, it is promising to use combined methods for processing oxidized and mixed polymetallic ores and intermediate products, including sulfidizing roasting followed by enrichment of cinders [7, 8, 31–37].

The innovation of this study is the development of a method for thermal treatment of flotation middlings with subsequent sulfidizing of the cinder due to the pyrite contained in the middlings; no analogues of the technology have been found in the literature.

2. Materials and experimental methods

2.1. Materials

The raw materials used were an intermediate product of flotation concentration of lead-zinc ore from Ridder concentration plant of Kazzinc LLP. Pyrite contained in the wastes was used as a sulfidizer. *X*-ray phase analysis of the middling product showed the following mineral composition: FeS_2 (54%), $ZnCO_3$, ZnO, $ZnO{\cdot}2SiO_2$, $ZnSiO_3$, ZnS, PbO, $PbCO_3$, PbS, $PbSiO_3$. Elemental analysis composition: Zn — 0.38%; Pb — 0.07%; Fe — 13.0%; S — 7.20%. Results of mineralogical analysis of samples introduce at **Fig. 1**.

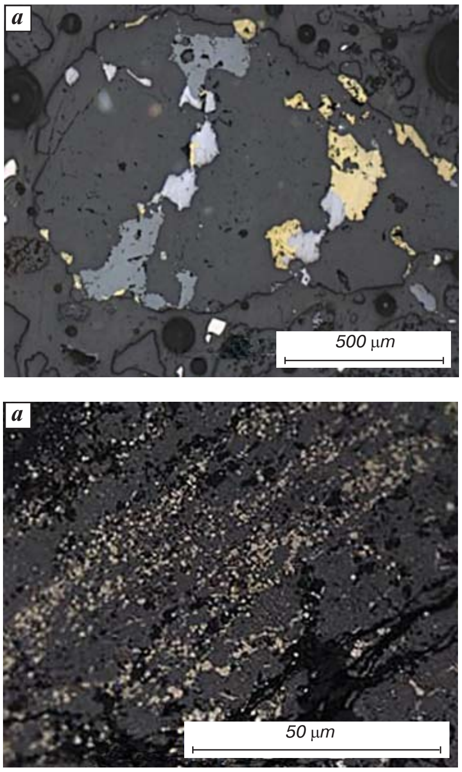

Fig. 1. Results of mineralogical analysis of samples:
a – wastes of lead-zinc ore dressing; *b* – oxidized compounds of lead-zinc ore dressing wastes

The composition of pyrite contained in the wastes is following: monomineral pyrite — 99.05% pyrite, 53.9% iron and 45.15% sulfur. Mineralogical analysis did not reveal the presence of non-ferrous minerals in the mineral, the field of view is 0.3 mm, the quartz content is 0.85%. Grains of monomineral pyrite are represented by elongated, rarely isometric, acute-angled fragments ranging in size from hundredths of a millimeter to 0.1–0.2 mm. The magnetic susceptibility of the initial material was analyzed on a susceptemeter KLY-2 (AGICO) with a sensitivity of $3\text{–}5{\cdot}10^{-8}$ SI, the specific magnetic susceptibility of the initial pyrite = $= 1.8\text{–}2{\cdot}10^{-6}$ units SI/g.

2.2. Experimental methods

The electrokinetic potential of the pyrrhotite suspension was determined by macroelectrophoresis. The electrophoretic mobility of the pyrrhotite suspension was measured using the Rabinovich and Fadiman apparatus using the moving boundary method. The electrokinetic potential was calculated using the Smoluchowski equation [38–41]. Macroelectrophoresis was used to study four samples of pyrrhotite, which differed in structural composition: 1, $Fe_{0.85}S$; 2, $Fe_{0.86}S$; 3, $Fe_{0.87}S$; and 4, $Fe_{0.89}S$. To prepare a suspension, the samples were first crushed and fractions less than 0.044 mm were taken, suspensions were prepared by adding 50 ml of distilled water to a 0.5 g sample and stirred on a magnetic stirrer for 10 minutes. Such a suspension was prepared for each sample of pyrrhotite depending on the pH of the medium at 5, 7, 9, 11, and 13.

X-ray diffraction analysis was carried out on an automated DRON-3 diffractometer with (CuK_α-irradiation, β-filter. Conditions for recording diffraction patterns: $U = 35$ kV; $I = 20$ mA; shooting θ-2θ; detector 2 deg/min. A BRUKER D2 *X*-ray phase analyzer was also used, Cu/Ni radiation, A = 1.54184 A, 30 kV, 10 mA, 2θ-5-70, time 1720 s) and SEM - EDS (JEOL - JSM-6010PLLIS/LA).

Electron microscopic studies were carried out on a JEOL ISM - 25S at 1500x magnification. Wet magnetic separation was carried out on an electromagnetic separator at a field strength of 40–80 kA/m (500–1000 Oersted) and a current strength of 0.25 to 2.0 A.

The magnetic susceptibility of materials was analyzed on a KLY-2 susceptibility instrument (AGICO), Czech Republic: sensitivity is $1 \cdot 10^{-6}$ SI units (in scanning mode $1 \cdot 10^{-5}$ SI units); operating frequency 10 kHz. The dependences of the magnetic susceptibility of sulfidizied products were measured by the Faraday method (magnetic balance) to determine the force acting on a sample placed in an inhomogeneous magnetic field created by an electromagnet. The magnetic susceptibility of the studied samples was determined by formula [42]:

$$\chi_{sample} = \frac{\Delta F_{sample}}{\Delta F_{standard}} \chi_{standard}. \tag{1}$$

The values ΔF_{sample}, $\Delta F_{standard}$ were determined by weighing the test sample and the standard on an automatic supersensitive balance of the VS 560 brand by Luxx with a current at the poles of an electromagnet of 1 A, which corresponded to the magnetic field strength at the point where the sample was located at 680 kA/m on the basis formulas [42]:

$$\Delta F = \frac{P_1 - P_2 + 0.0013}{P_1 - P_0} \tag{2}$$

P_0 — weight of an empty ampoule, g; P_1 — weight of the ampoule with the sample or standard, g; P_2 — weight of the ampoule with the sample in a magnetic field, and 0.0013 — coefficient that takes into account the diamagnetism of the glass of the ampoule at a current strength of 1 A.

Flotation enrichment was carried out on a laboratory flotation machine FL-237 with a working chamber volume of 50 ml at L:S equal to 9:1, 500 rpm.

Sulfidizing roasting of middlings of lead-zinc flotation was carried out in an electric tube furnace without air access. Experiments were carried out with 10^{-3} kg weights in a fixed bed in an electric furnace Zhengzhou Brother Furnace Co. Ltd (BR-NT) without air access, at a pressure of –0.05 MPa. The exposure time of the samples varied from 15 to 60 minutes; the temperature was controlled from 400 to 900 °C. The results of the experiment are presented in **Table 1**. The mass of the sample was controlled after thermal decomposition by the content of iron and sulfur in the treated product. In the process of decomposition without air access, up to 84–87% of unstable pyrite sulfur was removed within 30 minutes.

Table 1
Temperature dependence of the completeness of pyrite decomposition in vacuum

T, °C	Cinder mass, kg · 10^{-3}	Content in the cinder, wt.%		Fe/S in a cinder	% extraction of labile sulfur into gas
		Fe	S		
650	8.0	34.3	28.7	1.25	60
700	7.0	34.8	29.0	1.30	67
750	7.7	35.3	28.9	1.40	77
800	7.5	36.9	27.4	1.47	83
850	7.8	37.2	27.9	1.46	83
900	7.5	38.1	24.1	1.53	87
950	7.5	37.5	27.1	1.50	84

3. Results and Discussion

In general, the mechanism of sulfidization of oxidized minerals with pyrite is described by equation:

$$2MeO + 3FeS_2 = 2MeS + 3FeS + SO_2 \tag{3}$$

The temperature dependence of the completeness of pyrite decomposition in vacuum is shown in **Table 1.**

The dependence of the completeness of decomposition of pyrite in vacuum on the duration of the experiment is presented in **Table 2.**

Table 2
The results of roasting the middlings of enrichment for 30 minutes

T, °C	m, g	Cinder mass, g / content, %					S extraction into cinder,%
		Fe	S	Zn	Pb	Others*	
600	19.37	2.6/13.4	1.3/6.71	0.074/0.38	0.012/0.06	15.4/79.4	90.3
700	18.24	2.6/14.1	1.01/5.5	0.074/0.40	0.012/0.06	14.53/79.7	72.4
800	18.2	2.6/14.3	0.9/6.5	0.074/0.39	0.012/0.06	14.53/80.2	62.5
900	18.03	2.6/14.4	0.8/4.4	0.074/0.41	0.012/0.06	14.53/80.5	58.5

*Others — waste elements.

The results of electron microscopic analysis **(Fig. 2)** confirm the process of sulfidization of oxidized lead compounds, as a result of the detection of an intermediate product, namely lead sulfate.

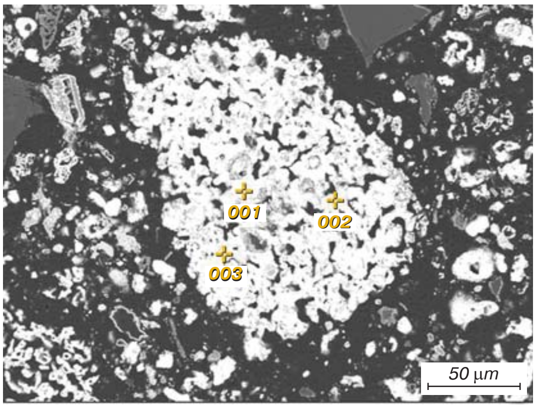

Fig. 2. Micrograph of sulfidizied lead oxide (×450).
Micrograph: 001 – PbS, 002 – $PbSO_4$, 003 – PbO

The formation of sulfides starts from the surface of the initial phase and propagates inside the particle. On **Fig. 2** shows a micrograph of sulfidizied lead oxide (≈630). Based on the results of *X*-ray diffraction studies of lead oxide sulfidization products **(Fig. 3)**, it was found that intermediate lead sulfates are formed during sulfidization. It has been established that *X*-ray phase studies of lead oxide sulfidization products show that intermediate lead sulfates are formed during sulfidization, sulfidation proceeds according to the scheme $PbO \rightarrow PbO\ PbSO_4 \rightarrow PbSO_4 \rightarrow PbS$. The presence of a PbS phase is confirmed by the *X*-ray results, **Fig. 3** clearly shows the PbS phase highlighted in red (COD9008694) showing the most significant 2θ half-angle amplitude (2Theta: 26, 30, 43, 51.53.5). The established decomposition mechanism during sulfidization was not previously presented and confirmed by *X*-ray phase analysis in the literature [43–44].

X-ray phase studies of zinc oxide sulfidization products show that during sulfidization, zinc sulfides are formed according to the scheme $ZnO \rightarrow ZnS$. On the line *X*-ray diffraction patterns of sulfidizied zinc oxides, intermediate sulfates were not observed.

The results of *X*-ray phase studies of sphalerite show 49% free grains – 37% in size ranges from $5.0 \cdot 10^{-6}$ to $2.0 \cdot 10^{-5}$ m and 12% in $2.0 \cdot 10^{-5}$ to $4.0 \cdot 10^{-5}$ m range. It was found that the intergrowths with pyrrhotite are at 19% [size of sphalerite single grains is up to $4.0 \cdot 10^{-5}$ m and the size of the aggregates ranges from $4.0 \cdot 10^{-4}$ to $1.2 \cdot 10^{-4}$ m.], **Fig. 3.** It was found that the zinc sulfide is present as β-modification.

It has been established that when roasting by-products of lead-zinc ore flotation with an increase in temperature from 550 to 900 °C, the degree of zinc and lead sulfidization reaches 85–95% at 700–900 °C. The decomposition of carbonates and the dissociation of pyrite do not have a significant effect on the sulfidation process. Sulfides, which are obtained as a result of sulfidization and as a result of the destruction of intergrowths, have high flotation properties. Pyrite is completely replaced by the pyrrhotite composition $Fe_{0.892}S$ – $Fe_{0.869}S$.

For the first time it was found that the optimal conditions for sulfidization of oxidized lead and zinc compounds in an environment without air access are the duration of 30–60 minutes and the temperature range from 600 to 800 °C. The formation of the most magnetic pyrrhotites of composition $Fe_{0.892}S$ – $Fe_{0.869}S$ occurs in the temperature range of 600–800 °C, with the highest maximum of magnetic susceptibility at a temperature of 750 °C. Studies of magnetic susceptibility have shown that most magnetic pyrrhotites are formed only in this temperature range of 600–800 °C. The properties of the resulting lead and zinc sulfides correspond as closely as possible to analogues of natural sulfides of galena and sphalerite. These results indicate the possibility of applying enrichment methods to the thermally processed product.

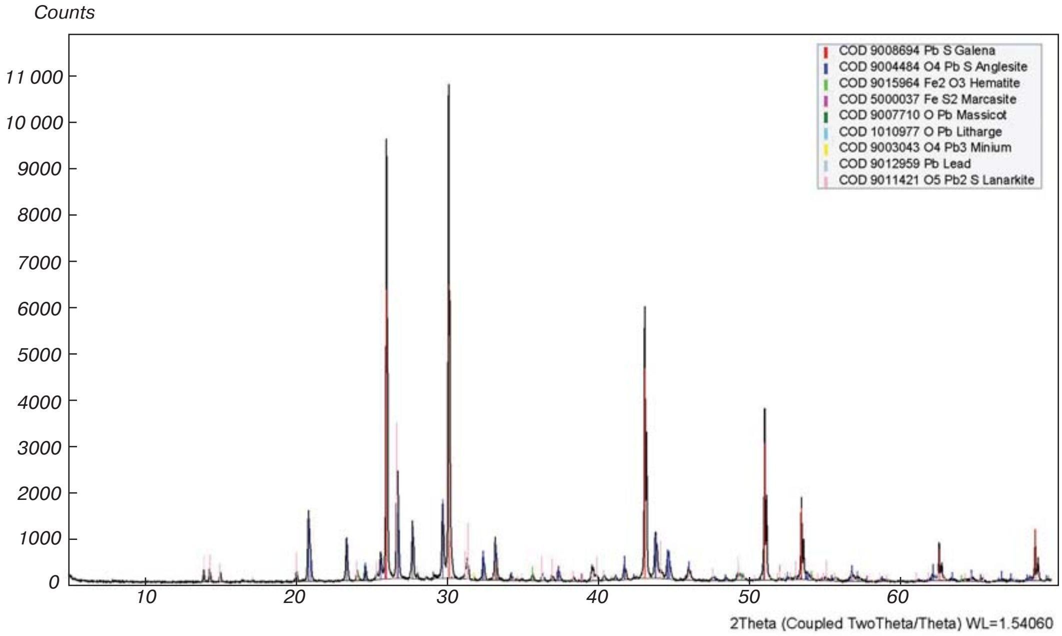

Fig. 3. XRD results of sulfidizied lead oxide cinders

3.1. Electro-kinetic characteristics of sulfidization products of oxidized compounds of lead and zinc.

The electro-kinetic characteristics of sulfidization products were studied by macro-electrophoresis. The ζ-potential of zinc oxide sulfidization products has a greater negative value than for lead oxide sulfidization products, which indicates its higher level of hydrophobicity. The ξ-potential values for the products of zinc carbonate sulfidization (from –1 mV until –0.3 mV at the temperatures from 550 to 750 °C) are close to the values of the ζ-potentials of zinc oxide sulfidization (from –0.5 mV to –0.3 mV at the temperatures from 550 to 750 °C). **Fig. 4** shows the nature of the change in the ζ-potential that has a parabolic appearance for all temperatures in the range 550–750 °C over time. Sulfidization of zinc carbonate begins after its decomposition. The resulting zinc sulfide corresponds to the β-modification sphalerite.

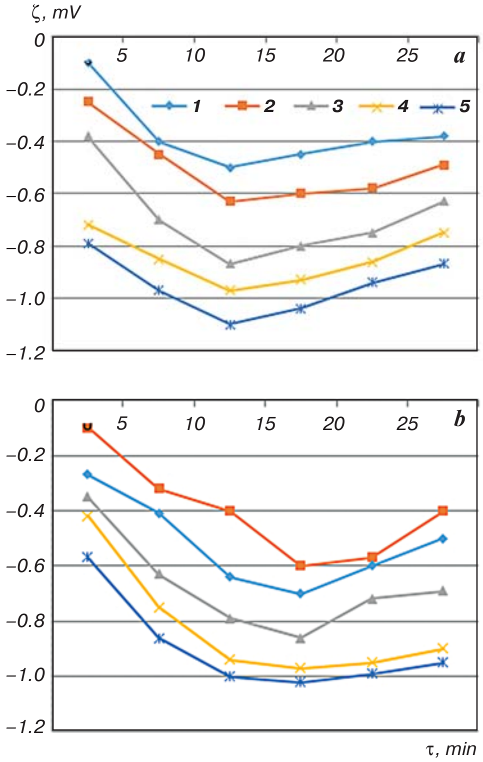

Fig. 4. Dependence of the ζ -potential of the sulfidization products of zinc oxide (*a*) and carbonate (*b*) on the duration, °C: *1* — 550; *2* — 600; *3* — 650; *4* — 700; *5* — 750

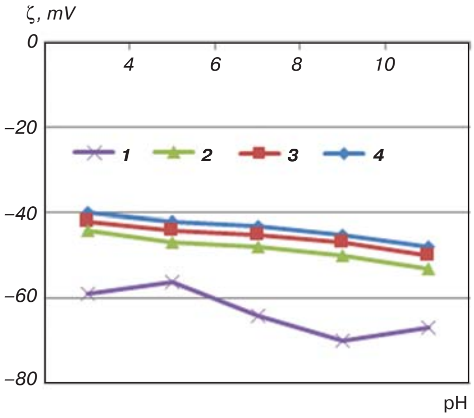

Fig. 5. Change in the electro-kinetic potential of a suspension of pyrrhotites of various compositions, depending on the pH of the medium:
1 – $Fe_{0.85}S$; *2* – $Fe_{0.86}S$; *3* – $Fe_{0.87}S$; *4* – $Fe_{0.89}S$

When lead carbonate is sulfidizied with elemental sulfur at a temperature of 650–700 °C, sulfides are formed that have a high degree of hydrophobicity. With an increase in the duration, a certain amount of the sulfate is first formed; the amount of this sulfate then decreases to almost traces, and the amount of the formed sulfide increases.

3.2. Measurement of electro-kinetic potentials by the method of macro-electrophoresis of pyrrhotites of various compositions.

To determine the possibility of flotation separation of the products of roasting pyrite-containing materials (middlings of flotation concentration), we studied the electro-kinetic characteristics of pyrrhotites of various compositions.

From the results of measuring the electro-kinetic potential of the pyrrhotite suspension, follows that: ζ-potential in all pyrrhotites increases with an increase in pH from 5 to 13, the electrophoretic rate also increases with an increase in pH from 5 to 13. With a decrease in the sulfur content in pyrrhotite, ζ-potential decreases from 52.1 mV for pyrrhotite $Fe_{0.85}S$ to –40.8 mV for pyrrhotite $Fe_{0.89}S$, as shown in **Fig. 5**.

As a result, the floatability of pyrrhotite decreases with decreasing sulfur content in its composition. This means that the ζ-potential of lead and zinc sulfides is equal to –15.6 and –13.8, flotation separation of low-sulfur pyrrhotite and non-ferrous metal sulfides is possible.

To determine the technological characteristics of the products of sulfidization of lead-zinc flotation wastes with pyrite concentrate, studies on the processing of cinders, followed by magnetic and flotation concentration of cinders, were presented.

3.3. Magnetic enrichment of cinders

Literature data and our research indicate that pyrrhotites obtained in the process of thermal dissociation have magnetic properties and therefore can be isolated into a separate product by magnetic separation, as shown in **Table 3**. As the research results indicate, during the thermal treatment of flotation middlings, 95–98% of pyrite goes into pyrrhotite was established by *X*-ray analysis of cinders.

With increasing temperature, the yield of the magnetic fraction increases, as shown in Table. 3. If at 600 °C the yield of the magnetic fraction is 14.2-13.7%, then at 900 °C, the yield is 37.6-33.0%. At high temperatures of 800–900 °C with an increase in the process duration of more than 30 minutes, the yield of the magnetic fraction decreases from 36.5-37.6 with a roasting duration of 15 minutes to 30.4-32.5. It was established that with an increasing of the duration of roasting, the degree of sulfur gasification increases. The extraction of iron into magnetic products increases with an increasing of the duration of roasting at 800 °C from 80.7% to 96.2%, while the extraction of sulfur remains at the level of 48.6%. The extraction of zinc in a non-magnetic product is 86.5% and that of Pb is 100%, as shown in **Table 4**.

Table 5 presents the results of enlarge research on the magnetic separation of sulfidizing roasting products. Pyrrhotites obtained by thermal dissociation of pyrite under various conditions in terms of their magnetic susceptibility, according to the technological classification of minerals [9], can be attributed to highly magnetic materials mined in separators with a relatively low magnetic field strength of 40–120 kA/m (1200–1500 E). From the results of wet magnetic separation of the cinder (the content of pyrrhotite in the cinder is 42.0%), it can be seen that with an increase in the magnetic field strength from 40–80 kA/m (from 500 to 1000 Oe), the extraction of pyrrhotite into the magnetic fraction increases with 62.4 to 69.20%, **Table 5.** Thus, it has been established that the proposed combined technology of thermal treatment of flotation middlings with subsequent sulfidizing of the cinder due to the pyrite contained in the middlings makes it possible to obtain pyrrhotites with a predictable composition and properties.

3.4. Flotation beneficiation of non-magnetic fraction

The sulfides obtained as a result of sulfidizing and as a result of the destruction of intergrowths have high flotation properties. At the same time, pyrrhotite is hydrophilic and exhibits low flotation properties. By accounting for this difference in the properties of the obtained roasting products, we studied the process of flotation separation of compounds that make up the non-magnetic fraction of magnetic enrichment. The resulting non-magnetic product was subjected to flotation.

The results of the flotation separation of non-magnetic products showed that with an increase in the temperature and duration of roasting, the yield of the froth increases. At a roasting temperature of 600 °C, the yield of the froth is 36.82% (15 min), and at 800 °C, the yield is 53.89% (60 min), as shown in **Table 6**.

It was found that the content of non-ferrous metals in the froth increases with increasing temperature and duration of the wastes roasting. So, at 600 °C and 15 minutes of roasting, the zinc content in the froth is 0.7%, was defined by chemical analysis; with a roasting duration of up to 60 minutes, it reaches 1.41%, was defined by chemical analysis. At a roasting temperature of 800 °C and a roasting duration of 60 minutes, the zinc content is 6.7% and the lead content is 1.4%.

It was found that the extraction of lead and zinc into the froth increases with an increase in temperature and duration of roasting. At 600 °C, the extraction of zinc is up to 60%, and that of lead is 75%. High extraction rates are observed at high temperatures; for example, at a roasting temperature of 800 °C, the extraction of zinc into the froth reaches up to 90% and that of lead reaches 78%. It was found that the through-extraction of zinc is 84.77% and that of lead is 80%.

Table 3

Magnetic and non-magnetic product yields depending on temperature and duration of roasting (%)

T, °C	Roasting duration, min							
	15		30		40		60	
	*MF**	*NMF*	*MF*	*NMF*	*MF*	*NMF*	*MF*	*NMF*
600	14.2	85.61	11.7	87.92	13.1	86.65	13.7	85.68
700	15.01	84.99	15.94	84.06	14.98	85.02	16.89	83.11
800	36.5	63.5	32.6	67.4	30.4	69.6	32.5	67.5
900	37.6	62.4	34.6	65.4	32.5	67.5	33.0	67.0

**MF* — magnetic fraction; *NMF* —non-magnetic fraction.

Table 4

Extraction of iron, sulfur, zinc, and lead into the products of magnetic enrichment of cinders obtained by roasting wastes at 800 °C, shown in percentages

Element	*T*, °C / roasting duration, min.							
	800/15		800/30		800/40		800/60	
	*MF**	*NMF*	*MF*	*NMF*	*MF*	*NMF*	*MF*	*NMF*
Fe	80.7	20.8	88.4	11.6	92.3	7.69	96.2	3.84
S	47.2	55.5	48.6	48.6	48.6	34.7	48.6	20.8
Zn	13.5	86.5	13.5	86.5	13.5	86.5	13.5	86.5
Pb	–	~100	–	~100	–	~100	–	~100

**MF* – magnetic fraction; *NMF* – non-magnetic fraction

Table 5

Results of experiments on wet magnetic separation of cinder

Product name	Current strength, A	Output, %	Contention $Fe_{1-x}S$, %	Extaction $Fe_{1-x}S$, %
Magnetic fraction	0.25	30.50	85.50	62.40
	0.5	27.50	98.10	64.20
	1.0	35.30	79.60	66.90
	2.0	30.0	97.0	69.20

Table 6

Froth and chamber product yield depending on temperature and duration of wastes roasting, shown in percentages

τ, min	15		30		40		60	
T, °C	*Froth**	*CP*	*Froth*	*CP*	*Froth*	*CP*	*Froth*	*CP*
600	36.82	63.18	29.83	70.17	20.0	80.0	15.20	84.80
700	33.49	66.51	35.79	64.21	39.46	60.54	40.85	59.15
800	38.87	61.13	38.79	61.21	46.88	53.12	47.0	53.0
900	43.0	57.0	48.13	51.87	50.56	49.44	53.89	46.11

**Froth* – foam product; *CP* – chamber product

Removal of metals from waste by flotation in a direct one-stage cycle results in the removal of more than 84% of zinc and about 80% of lead in the foam. The content of Zn and Pb in the foam reaches 6.7% and 1.4%, respectively, while the initial content in the waste is 0.38% Zn and 0.08% Pb.

3.5. Study of the magnetic susceptibility of sulfidizied products and pyrite decomposition products

Due to the fact that the magnetic fraction can be used for various technological needs, including the production of magnetic carriers, we studied the properties and compositions of the obtained pyrrhotites. The relevance of studying the properties of pyrrhotites is indicated by the following scientific works [45, 46]. The resulting pyrrhotites in the separation of the magnetic separation point to the difference in composition and high magnetic susceptibility.

The study of the magnetic susceptibility of sulfidizied products and pyrite decomposition products was carried out on the separated pyrrhotite of the magnetic product. It was found that the composition of the gas phase does not have a decisive effect on the composition and magnetic susceptibility of the cinder. When the temperature changes from 600 to 850 °C and the duration changes from 10 to 60 minutes, the iron content in the resulting pyrrhotite changes from 54.30% to 60.91%, as shown in **Table 7**.

Table 7
Composition of pyrrhotites in the cinder

Pyrrhotites composition in cinder	Fe atomic fraction in pyrrhotite, percentage	Atomic relation S : Fe
$Fe_{0.833}S$	45.44	1.20
$Fe_{0.835}S$	45.50	1.197
$Fe_{0.837}S$	45.56	1.194
$Fe_{0.855}S$	46.09	1.169
$Fe_{0.857}S$	46.14	1.169
$Fe_{0.860}S$	46.23	1.163
$Fe_{0.875}S$	46.66	1.142
$Fe_{0.888}S$	47.03	1.126
$Fe_{0.889}S$	47.06	1.124
$Fe_{0.90}S$	47.36	1.111
$Fe_{0.909}S$	47.61	1.100
$Fe_{0.954}S$	48.82	1.048

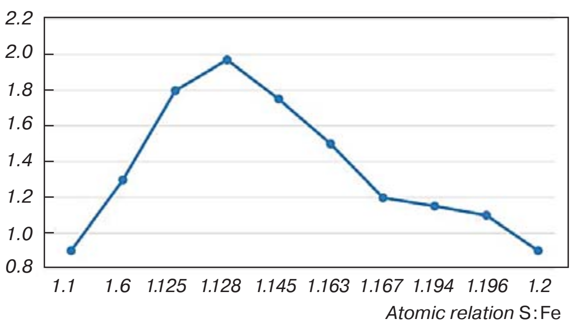

Fig. 6. Dependence of the magnetic susceptibility of pyrrhotite in the cinder on the atomic ratio of S : Fe

The relevance of studying the properties of pyrrhotites is indicated by the following scientific works [48–51]. The study of the magnetic susceptibility of pyrrhotites, especially those obtained during the technological process, during sulfidizing roasting is relevant, because pyrrhotite should be considered as a complete product for subsequent use in various industries. The obtained magnetic pyrrhotite concentrate can be used for the production of abrasives, high-quality ferrous sulfate, for land reclamation, for the production of magnetic media and other purposes. Hydrometallurgical processing of the pyrrhotinized product ensures the production of sulfur from pyrite concentrates in elemental form.

The dependence of the magnetic susceptibility of pyrrhotite in the cinder on the S : Fe atomic ratio is shown in **Fig. 6**.

Pyrrhotites composition in cinder measure up to atomic relation S : Fe, the results of dependence of the magnetic susceptibility of pyrrhotite in the cinder on the atomic ratio S : Fe we can see on Figure 6. It also shows that the magnetic susceptibility, depending on the composition of pyrrhotite, has an extreme character. From the pyrrhotite composition $Fe_{0.833}S$ to $Fe_{0.888}S$, the magnetic susceptibility increases from 0.90 to 1.89 units CI. With further desulfurization of pyrrhotites from $Fe_{0.888}S$ to $Fe_{0.909}S$, the magnetic susceptibility decreases from 1.89 to 0.97 units. CI. Pyrrhotites of the composition $Fe_{0.941}S$ – $Fe_{0.954}S$, formed during the thermal decomposition of pyrite in the temperature range 900–1000 °C have a magnetic susceptibility of 0.29–0.28 units CI. In composition and magnetic properties, they are close to troilite. It was found that at roasting temperatures of 700–800 °C pyrrhotites have the maximum magnetic susceptibility: $Fe_{0.855}S = 3.75$; $Fe_{0.888}S = 5.43$; $Fe_{0.909}S = 2.18$ units SI, table 6 and figure 6. The resulting pyrrhotites can be extracted on separators with a relatively low magnetic field strength of 96–120 kA/m (1200–1500 Oe).

4. Development of a technological scheme

The **Fig. 7** shows the developed technological scheme for the processing of lead-zinc intermediate products of enrichment by sulfidizing roasting in an environment with a limited amount of oxygen to obtain pyrrhotites of predictable properties. The results of the enlarged tests are shown in the technological scheme, **Fig. 7.** Sulfidizing roasting was carried out in a fixed bed, in a tube furnace.

5. Conclusion

The results of integrated tests showed that the proposed technological scheme for the processing of lead-zinc

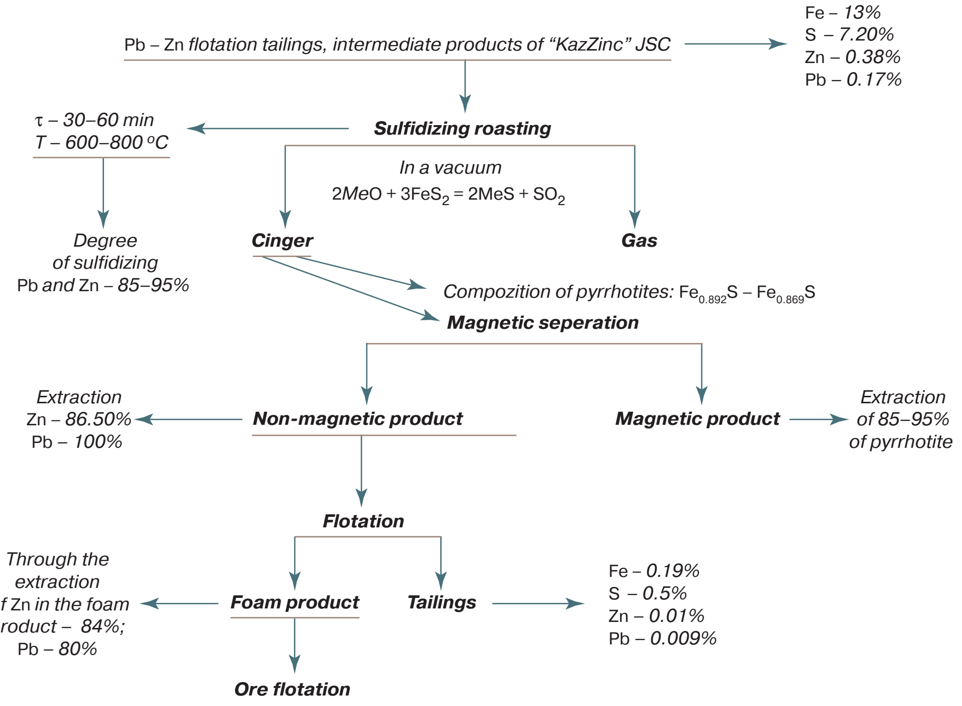

Fig. 7. Technological scheme for the processing of lead-zinc middling products of enrichment with the production of pyrrhotites of predictable properties

middlings of enrichment with the production of pyrrhotites of predictable properties makes it possible to obtain the following results: the degree of sulfidizing of oxidized compounds of lead and zinc reaches from 85 to 95%; the composition of pyrrhotites varies from $Fe_{0.855}S$ to $Fe_{0.96}S$, while it is possible to obtain pyrrhotites with maximum magnetic susceptibility: $Fe_{0.855}S = 3.75$; $Fe_{0.888}S = 5.43$; $Fe_{0.909}S = 2.18$ SI units; extraction of zinc is 86.5% and lead up to 100% in a non-magnetic product; the extraction of pyrrhotite into a magnetic product is up to 90%; optimal temperatures and conditions were developed for obtaining pyrrhotite with a predictable composition.

In contrast to existing technologies, it is proposed to carry out activating sulfidizing roasting of oxidized zinc-lead-containing intermediate products that contain pyrite in their composition. This technology is patented [31]. In this case, hundreds of millions of industrial products obtained from the flotation enrichment of polymetallic ores, which are stored in tailing dumps that violate the ecological balance, can be involved. The proposed technology makes it possible to additionally extract zinc and lead from middlings, significantly increasing the economic effect of production. The unit costs per 1 US dollar of marketable products using the proposed technology are lower than the specific costs for the existing technology, which is associated with an increase in the extraction of lead and zinc into a marketable product and the production of pyrrhotites as an additional marketable product.

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