

## TECHNOLOGY OF SULFIDIZING-PYRRHOTIZING ROASTING OF LEAD FLOTATION TAILINGS

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**ABSTRACT.** Processing of refractory, pyrite-containing raw materials is most expediently carried out by a combination of pyrometallurgical and hydrometallurgical processes. During pyrometallurgical processing, pyrite undergoes changes leading to a change in the chemical and physical properties of the processed products. The results of the technology for the integrated processing of oxidized polymetallic ores and intermediate products by sulfidizing roasting with pyrite concentrate, followed by magnetic and flotation dressing, are presented. Based on thermodynamic calculations, it follows that the interaction of sulfate with pyrite proceeds at temperatures of 540 °C and higher with the formation of pyrrhotite (Fe<sub>7</sub>S<sub>8</sub>); Fe<sub>7</sub>S<sub>8</sub> interacts with sulfate at a temperature of 460 °C with the formation of lower iron sulfides; sulfidization of lead and zinc oxides and carbonates with pyrite with the formation of the corresponding sulfides is carried out at temperatures above 300 °C. The research results are aimed at solving the problem of additional extraction of lead and zinc. In this work introduced the conditions for Zn extraction up to 95 % and Pb to 80 % to sulfide concentrate.

**Keywords:** pyrite concentrate, sulfidizing roasting, thermodynamic calculations, sulfidization, lead flotation tailings

## ТЕХНОЛОГИЯ СУЛЬФИДИРУЮЩЕГО-ПИРРОТИНИЗИРУЮЩЕГО ОБЖИГА ХВОСТОВ СВИНЦОВОЙ ФЛОТАЦИИ

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**РЕЗЮМЕ.** Переработку труднообогатимого, пиритсодержащего сырья наиболее целесообразно осуществлять комбинацией пирометаллургических и гидрометаллургических процессов. При пирометаллургической обработке пирит претерпевает изменения, приводящие к изменению химических и физических свойств продуктов обработки. Представлены результаты технологии комплексной переработки окисленных полиметаллических руд и промпродуктов сульфидирующим обжигом с пиритным концентратом, с последующим магнитным и флотационным обогащением огарка. На основании термодинамических расчетов следует, что взаимодействие сульфата с пиритом протекает при температурах 540 °C и выше с образованием пирротина Fe<sub>7</sub>S<sub>8</sub>; Fe<sub>7</sub>S<sub>8</sub> взаимодействует с сульфатом при температуре 460 °C с образованием низших сульфидов железа; сульфидирование оксидов и карбонатов свинца и цинка пиритом с образованием соответствующих сульфидов вероятно при температурах выше 300 °C. Результаты исследований направлены на решение проблемы дополнительного извлечения свинца и цинка. Разработаны условия извлечения в сульфидный концентрат Zn до 95 %, Pb до 80 %.

**Ключевые слова:** пиритные концентраты, сульфидирующий обжиг, термодинамические расчеты, сульфидирование, хвосты свинцовой флотации

## Introduction

Lead and zinc are important materials supporting modern society and nowadays, both of which are mainly extracted from sulfides by pyrometallurgy method, published by Balarini (2008). With the exploitation of resources in the world, the primary resources are soon going to be insufficient to meet the demand, and the Pb–Zn oxide ore usually containing 1 % – 5 % Pb and 1 % – 20 % Zn, may be the second source to offer the above metals. However, it seems to be difficult for valuable metal recovery from the refractory ore characterized by complex composition and high content of slime, published by Peng (2003).

The main use of lead is rechargeable batteries (automobile) of all types and sizes, with the exception of mobile devices. Car production in China over the past 5 years has increased from 18 million to 28 million units per year. Only China created a 13 % increase in world car production with a total increase of 19 %. And it was he who ensured the stability of lead prices (Liu, 2018). Lead is the only stock exchange metals with a share of recycling exceeding 50 % of the market.

The lead deficit in the world market in May 2017 amounted to 37.2 thousand tons and continues to persist.

Lead prices in 2019 rose to \$ 1.949.5 per tonne (London Metal Exchange, LME). Kazakhstan increased lead exports by 74 %. The main importers of raw materials are Vietnam and Spain. Extraction of lead in lead concentrate for 2 months of the current year amounted to 15 thousand tons - 8.7 % more than a year earlier. The production of lead concentrates increased by 18.7 % - up to 57.1 thousand tons. Lead use for domestic needs of the Republic of Kazakhstan immediately increased by 20 % year-on-year, to 24.2 thousand tons in 2018. Zinc is the fourth most used metal in the world. World zinc consumption amounts to about 13.0 million tons per year. The average annual growth rate of the zinc market is about 3.5 %. Between 2013 and 2018, zinc consumption in China more than doubled to 5.6 million tons, and the average annual growth rate was about 10 %, (Liu, 2018).

About 50% of the world's zinc is used as electroplated coatings to protect steel and other metals from corrosion, 17% is spent on the production of zinc alloys and 17% on the production of brass and bronze.

Currently, world zinc consumption is 11 million tons, and also grows annually regardless of the state of the world economy, and often outstrips the growth of gross national product. Despite the decrease in export volumes of zinc ores and concentrates in physical terms, in monetary terms, supplies to foreign markets brought Kazakhstan immediately \$ 239.5 million, which is 29.9 % more than in 2018. Due to rising zinc prices (\$ 2,351 per tonne), zinc export revenues in Kazakhstan increased 1.5 times. Zinc per capita consumption is growing at 1.8% per year, with zinc consumption growing in developed countries faster (International Zinc Association).

The best indicators for the processing of oxidized and mixed ores are achieved by using the preliminary activation of the feedstock by oxidizing or sulfating roasting followed by processing of the activated product, however, these methods have not been applied in industry (Ejtemaei, 2011).

New processing? Directions are formed, characterized by a selective change in the natural technological properties of minerals before enrichment. This is carried out by dosed physical and physico-chemical effects 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 hydrometallurgical and pyrometallurgical methods. Autoclave sulfidization due to the periodicity of the process and the low productivity of equipment for large-capacity production is ineffective. Sulfidization by sulfate-reducing bacteria allows the flotation activity of oxidized lead minerals to be restored due to the formation of sulfide and sulfur films on the surface of minerals (Hosseini, 2011). However, there are no recommendations on the use of such a method in industry, as a critical analysis of technologies has shown.

Sulfidization of polymetallic raw materials with elemental sulfur can be carried out both in melts and in the solid phase (Keqing, 2005). The Australian Bureau of Mines has developed a sulfidization process with elemental sulfur and sulfur dioxide gas with the addition of pyrite to the batch. The resulting cinder is subjected to flotation (Qiu, 2007).

In the process of beneficiation of mixed polymetallic ores, a significant amount of middlings and tailings are formed, the flotation processing of which is ineffective. At the same time, in the froth flotation products, in addition to oxidized compounds of zinc and lead, a significant amount of pyrite is concentrated, (Chepushtanova, 2012; 2015). We studied the possibility of thermal treatment of flotation middlings with zinc sulfidization due to pyrite contained in the middlings, the composition and magnetic properties of pyrrhotite formed as a result of roasting.

The paper presents the results of technological studies of the process of thermal treatment of flotation middlings with zinc sulfidization due to pyrite contained in the middlings, the composition and magnetic properties of pyrrhotite formed as a result of roasting, with the study of the effect of temperature, duration and composition of the gas phase on the process.

The aim of the research was to determine the possibility and conditions of magnetic enrichment of sulfidized cinders.

## Materials and methods

The following materials were used as starting materials: intermediate product of flotation concentration of lead-zinc ore, consisting of a foam product of lead cleaning (40 %) and

tailings of lead flotation (60 %), containing Pb - 1.86, Zn - 4.33, Fe - 34.88, S - 36.60, CaO - 3.50, SiO<sub>2</sub> - 14.27, Al<sub>2</sub>O<sub>3</sub> - 1.52, MgO - 1.30 %, (the pyrite content in the original samples was 71.48 %); pyrrhotite containing 96,5 % iron sulfide Fe<sub>0,855</sub>S.

Mineralogical characteristics of pyrite in the initial samples of the intermediate product:

1) free grains – 90 %; grain size from 5.0·10<sup>-6</sup> to 4.0·10<sup>-5</sup> m, prevailing 2.0·10<sup>-5</sup> m;

2) intergrowths with sphalerite – 6 %; the size of pyrite precipitates is from 5.0·10<sup>-6</sup> to 2.0·10<sup>-5</sup> m, of which the opening is 5%;

3) intergrowths with quartz – 2 %; the size of pyrite precipitates is from 2.0·10<sup>-6</sup> to 4.0·10<sup>-5</sup> m, mostly open;

4) intergrowths with galena - about 1%, the size of precipitates is from 5.0·10<sup>-6</sup> to 2.0·10<sup>-5</sup> m, mostly closed.

## Experiments of heat treatment of middlings in vacuum

The main factors affecting on the rate and completeness of thermal decomposition of pyrite are the conditions of heat transfer, i.e. temperature, and duration of heat treatment.

The grain size from 1.0·10<sup>-5</sup> to 6.0 10<sup>-4</sup> m does not affect the process speed. In studies in a fixed bed, the rate of the process is influenced by the layer thickness, therefore, in the experiments described below, the size of the sample and the method of its placement in the furnace were selected experimentally in order to minimize the effect of this factor (when carrying out decomposition in industrial continuous units, for example, in fluidized bed furnaces, the influence of this factor will not affect), (Sadowski, 2004).

The experiments were carried out with weights of 10·10<sup>-3</sup> kg in a fixed bed, the setup diagram is shown in Fig.1. The residual pressure during the experiments was 1-15 Pa. The time of the experiment was counted after reaching the specified temperature, which was maintained with an accuracy of ± 1 °C.

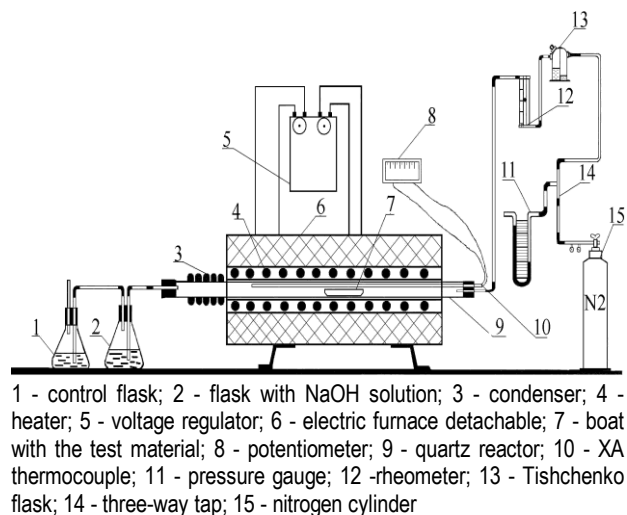


Fig. 1. The scheme of the sulfidizing pyrrhotizing roast setting

## Experiments of heat treatment of middlings in the air

The decomposition was carried out in a fixed bed in quartz test tubes in an atmosphere of gases formed during the decomposition of the middling product, which makes it possible to accurately control the oxygen consumption.

The weight of the sample was taken depending on the volume of the test tube, taking into account the reaction of oxygen from the air in the closed volume of the reaction space.

The amount of labile sulfur in the initial sample exceeded its amount theoretically capable of reacting with oxygen present in the reaction space at the beginning of the experiment.

### Microscopic studies

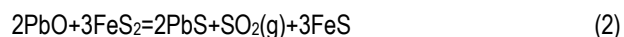
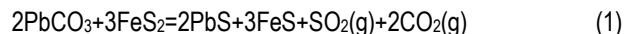
Microscopic studies (fig.3) were performed on a JEOL ISM - 25S 3 scanning electron microscope. Sample size was + 70 - 100 microns, magnification x1500.

### Thermodynamic research

The calculations were performed using by thermodynamic calculation program of the Outokumpu Ou Company; using of phase equilibrium diagrams. On the basis of thermodynamic analysis, it was established that: the homogeneity region of the synthesized pyrrhotite is a continuous series of iron-sulfur compounds; in the Fe-S-O system, the formation of pyrrhotites of composition from FeS to Fe<sub>0,877</sub>S or Fe<sub>7</sub>S<sub>8</sub> is possible.

### Sulfidization of lead oxides and carbonates

The reactions of sulfidization of PbCO<sub>3</sub> with pyrite (FeS<sub>2</sub>) were studied:



Standard changes in free energy ( $\Delta G$ ) for the above reactions in the range from 100 to 1000 ° C were calculated per 2 mol of PbCO<sub>3</sub> and PbO using HSC Chemistry 5. The results show that sulfidization of PbCO<sub>3</sub> and PbO with FeS<sub>2</sub> is thermodynamically possible in the studied temperature range, Fig.2. Regarding the transformation of the iron phases, equations 1 and 2 show relatively large negative values of  $\Delta G$ , with the values becoming more negative with increasing temperature, and therefore the conversion of FeS<sub>2</sub> to FeSO<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> / Fe<sub>3</sub>O<sub>4</sub> is predominant.

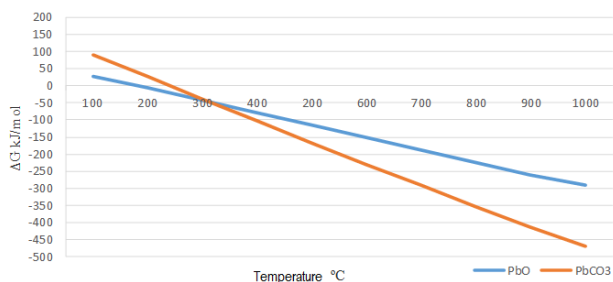


Fig. 2. Standard changes in free energy of possible reactions depending on temperature in the range of 100-1000°C

### Sulfidization of zinc oxides and carbonates

The probability of the formation of various compounds of zinc and iron as a result of interaction and the influence of the process conditions on the composition of the products was studied. The analysis was carried out for oxidizing, reducing and neutral environments of zinc oxide sulfidization with pyrite.

The paper presents calculations of the thermodynamic characteristics of the process of sulfidization of ZnCO<sub>3</sub> to obtain zinc in the form of Zn, ZnO, ZnSO<sub>4</sub>, ZnS; iron - in the form of troilite FeS (the formation of pyrrhotites was not taken into account), FeO, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> FeSO<sub>4</sub>.

During heat treatment, ZnCO<sub>3</sub> dissociates with the formation of ZnO and CO<sub>2</sub> at temperatures of 573 K and higher (ZnCO<sub>3</sub> = ZnO + CO<sub>2</sub>  $\Delta G^0$ , kJ / mol S<sub>2</sub> at a temperature, K 973: -93.4), therefore, in the calculations, oxide ZnO was used as the initial compound.

Since, at high temperatures, thermal decomposition of pyrite occurs with the formation of pyrrhotite and elemental sulfur, we calculated the thermodynamic characteristics of sulfidization of zinc oxides with elemental sulfur.

### Sulfidization in an inert atmosphere

In an inert atmosphere, sulfidizing of zinc oxide in the temperature range 573-973 K is thermodynamically possible in the entire temperature range under study.

Depending on the ZnO / FeS<sub>2</sub> ratio under the initial conditions, the reaction can form various iron compounds - with a decrease in the ZnO / FeS<sub>2</sub> ratio, the reaction products can be not only FeS, but also oxides (from FeO to Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>, and sulfate. At temperatures above 793 K ferrous sulfate is sulfided by pyrite to form FeS.

### Sulfidization in an oxidizing environment

The participation of oxygen in the sulfiding process increases the thermodynamic probability of zinc oxide sulfiding with the formation of iron oxides and sulfates. However, an increase in the amount of oxygen in the reaction shifts the equilibrium of the reaction towards the formation of zinc sulfate (Table 1).

At the same time, it is practically impossible to obtain zinc sulfide as a result of the interaction.

Table 1. Thermodynamics of the interaction of ZnO and FeS<sub>2</sub> at the O<sub>2</sub> presence

N	Reaction	$\Delta G^0$ , kJ/моль S <sub>2</sub> , 973, K
1	ZnO+FeS <sub>2</sub> +O <sub>2</sub> =ZnS+FeO+SO <sub>2</sub>	-245.5
2	ZnO+FeS <sub>2</sub> +3O <sub>2</sub> =ZnSO <sub>4</sub> +FeO+SO <sub>2</sub>	-760.3
3	ZnO+2FeS <sub>2</sub> +6O <sub>2</sub> =ZnSO <sub>4</sub> +Fe <sub>2</sub> O <sub>3</sub> +3SO <sub>2</sub>	-801.1
4	ZnS+3Fe <sub>2</sub> O <sub>3</sub> +1.5O <sub>2</sub> =ZnSO <sub>4</sub> +2Fe <sub>3</sub> O <sub>4</sub>	-332.9
5	ZnS+2O <sub>2</sub> =ZnSO <sub>4</sub>	-904.0
6	ZnO+2FeS <sub>2</sub> +6O <sub>2</sub> =ZnSO <sub>4</sub> +Fe <sub>2</sub> O <sub>3</sub> +3SO <sub>2</sub>	-1602.2
7	ZnO+3FeS <sub>2</sub> +8.5O <sub>2</sub> =ZnSO <sub>4</sub> +Fe <sub>3</sub> O <sub>4</sub> +5SO <sub>2</sub>	-2313.6
8	2ZnO+4S+O <sub>2</sub> =2ZnS+2SO <sub>2</sub>	-111.6

Thus, sulfidization of lead and zinc oxides and carbonates by pyrite with the formation of the corresponding sulfides is thermodynamically probable at temperatures above 300 °C. In this case, pyrite decomposes to FeS, Fe<sub>7</sub>S<sub>8</sub> or Fe<sub>0,877</sub>S.. Those, during sulfidization of oxidized compounds of lead and zinc, pyrrhotite may form within its homogeneity region.

On the basis of thermodynamic analysis, the technological parameters of sulfidizing-pyrrhotizing roasting with the production of non-stoichiometric pyrrhotites were selected and they are???

## Results and discussion

### Heat treatment of middlings in vacuum

The experimental results are presented in table 2.

Table 2. Dependence of the decomposition completeness of pyrite in vacuum on the temperature, at time?

Temperature, °C	Weight of the cinder, kg · 10 <sup>-3</sup>	Content in the cinder, weight, %		Fe/S in the cinder	% extraction of labile sulfur to 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

After the end of the experiment, the sample was cooled under vacuum. The weight of the sample after decomposition and the content of iron and sulfur in the processed product were monitored.

In a vacuum with the duration of the decomposition process of 30 minutes, it is possible to drive away up to 84-87 % of the labile sulfur of pyrite. An increase in the decomposition temperature above 800 °C does not increase the extraction of sulfur into the gas, in addition, at temperatures above 850 °C, the initial product is enlarged. This means that increasing the process temperature above 900 °C is impractical, since it does not lead to an increase in sulfur recovery.

The increasing of duration more than 15 minutes, as can be seen from the data (table 3), does not significantly affect the degree of sulfur recovery in the gas. This suggests that at constant temperature and gas phase composition are obtained pyrrhotite approximately the same composition, and hence properties of pyrrhotite should be close.

Mineralogical studies of samples of industrial products obtained by decomposition in vacuum gave the following results: during the decomposition process at a temperature of 750 °C, pyrite is 75-80 % replaced by pyrrhotite, which forms semi-oval sinuous-oblong and worm-like secretions??? ranging from 5.0·10<sup>-6</sup> to 1.0·10<sup>-5</sup> m, grouped into aggregative clusters (several dozen pieces) ranging from 4.0·10<sup>-5</sup> to 8.0·10<sup>-5</sup> – 1.0·10<sup>-4</sup> m across. The resulting pyrrhotites have a composition of Fe<sub>0.892</sub>S - Fe<sub>0.869</sub>S.

Table 3. Dependence of the completeness of pyrite decomposition in a vacuum on the duration of the experiment, at temperature?

Duration, min	Weight of the cinder, kg · 10 <sup>-3</sup>	Content in the cinder, weight, %		Fe/S in cinder	% extraction of labile sulfur to gas
		Fe	S		
15	7.9	35.1	28.1	1.36	72.0
30	7.9	34.8	29.0	1.30	67.0
60	7.9	35.6	28.4	1.40	76.0
90	8.0	35.6	28.2	1.37	73.0
120	7.9	35.4	28.0	1.37	74.5

Sphalerite undergoes minor changes: the same sharp-angled fragments of its grains as in the original (not subjected to heat treatment) product; their size and distribution pattern does not change in the cinder – in aggregate and other

complex aggregates, sphalerite occupies the same position. The contours of the boundaries between sphalerite grains and semi-oval pyrrhotite secretions that replaced pyrite are still complex, sinuous and have the character of close contact.

The behavior of sphalerite is characterized as follows:

- 1) free grains - 49 %; of them the size from 5.0·10<sup>-6</sup> to 2.0·10<sup>-5</sup> m - 37 %, from 2.0·10<sup>-5</sup> to 4.0·10<sup>-5</sup> m -12 %;
- 2) accretions with pyrrhotite – 19 %; the size of sphalerite secretions from 5.0·10<sup>-6</sup> to 2.0·10<sup>-5</sup> m. single grains up to 4.0·10<sup>-5</sup> m of them open - 12 %. closed - 7 %;
- 3) splices with pyrrhotite and galenite – 13 %; the size of the splices from 4.0·10<sup>-5</sup> 8.0·10<sup>-5</sup> before 8.0·10<sup>-5</sup> · 1.2·10<sup>-4</sup> m. sphalerite size up to 3.0·10<sup>-5</sup> m mostly closed;
- 4) accretions with quartz-12 %; size of sphalerite discharge from 7.0·10<sup>-6</sup> to 3.0·10<sup>-5</sup> m. open - 8 %. closed - 4 %;
- 5) accretions with pyrrhotite and quartz – 7 %. the size of sphalerite discharge from 5.0·10<sup>-5</sup> to 2.0·10<sup>-5</sup> m. mostly closed.

The color of sphalerite grains becomes slightly lighter than in the original industrial product, they appear thin, but quite bright reflexes, and at large magnifications (x 950 and x 1425) in the immersion oil, even without structural etching, the internal structure of individual large grains of sphalerite secretions is clearly visible: it is visible that they are composed of the thinnest (2.0·10<sup>-6</sup> – 5.0·10<sup>-6</sup> m) xenomorphic grains with prizing boundaries between them, which create internal reflexes. Obviously, part of the iron entering the sphalerite lattice leaves the crystal lattice during firing???. Zinc sulfide has a β-modification.

Thus, it is established that the sulfidizing roasting of oxidized ore allows to obtain zinc sulfides similar in their properties to those obtained from pure compounds, while pyrrhotites of the composition Fe<sub>0.892</sub>S - Fe<sub>0.869</sub>S with pronounced magnetic properties are formed. Sulfidizing roasting is advisable to be carried out at a temperature of 650-700 °C, for a duration of 30 minutes.

When the temperature of heat treatment of industrial products increases to 950 °C, the nature of changes in the mineralogical composition is similar. Pyrite is completely replaced by pyrrhotite, which is present almost exclusively in the form of separated semi-oval and dump secretions and inclusions sized from 5.0·10<sup>-6</sup> – 8.0·10<sup>-6</sup> up to 4.0·10<sup>-5</sup> m. Hematite was not detected.

As can be seen from the mineralogical analysis, pyrite is almost completely replaced by pyrrhotite, such results indicate the possibility of applying enrichment methods to the heat-treated product. An increase in the temperature of heat treatment above 900 °C leads to some enlargement of the material, to its partial agglomeration, which indicates that it is not advisable to increase the temperature of the process to this level.

#### Heat treatment of industrial middlings in the air

The results of the experiments showed that during of the 30 minutes at a temperature of 700-750 °C, the decomposition of pyrite, which is part of industrial products, occurs by 89-98 % (table 4). There is no sintering of the products. Pyrrhotites of the composition Fe<sub>0.892</sub>S - Fe<sub>0.869</sub>S are formed, the magnetic susceptibility of which is equal to 1330 - 1020 ·10<sup>-6</sup> SI / g.

Table 4. The dependence of the completeness of the decomposition of pyrite from the temperature

Temperature, °C	The content in the cinder, %		Fe/S in the cinder	% extraction of labile sulfur to gas
	Fe	S		
700	41.67	24.40	1.70	89.0
750	42.50	22.75	1.8	98.0
800	41.57	24.43	1.70	88.0
900	41.52	24.52	1.69	87.0

Mineralogical analysis shows that the replacement of pyrite with pyrrhotite occurred by 95-98 %, and all free grains were completely replaced. The presence of a small amount of hematite, which replaces pyrrhotite, was detected.

The results of electron microscopic analysis confirm the results of the mineralogical analysis of the roasted middling, Fig.3.

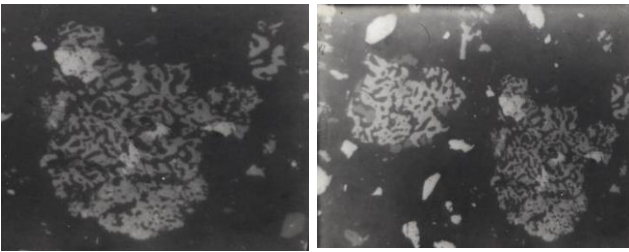


Fig. 3. Large skeletal-frame allocation of pyrrhotite

As a result of thermal decomposition, there is no noticeable decryption of pyrite particles, but it transforms into pyrrhotite of the skeletal-frame form, which can be seen from Figure 3.

#### Enlarged tests on magnetic separation of sulfidizing roasting products of lead flotation middlings

Literature data and our research indicate that pyrrhotites obtained during thermal dissociation have magnetic properties and can therefore be separated into a separate product by magnetic separation. According to research results, 95-98 % of pyrite is converted to pyrrhotite during heat treatment of industrial flotation products.

For the parameters determination of dry and wet magnetic enrichment were performed the research with a mechanical mixture of pyrrhotite (30 %) and lead flotation tailings (70 %) and products of sulfidizing roasting of industrial products of enrichment.

The researches were carried out for separating of the mechanical mixture of pyrrhotite and lead flotation tailings for the establishing of the operating parameters of the magnetic separator.

Pyrrhotite contained 96,5 % iron sulfide  $Fe_{0,855}S$  and had a magnetic susceptibility of  $1000 \cdot 10^{-6}$  SI/g. Particle size in pyrrhotite was 15 % - 44 microns, and in tailings 30 % - 44 microns. The initial pyrrhotite product contained 56 % iron, and the lead flotation tailings contained 20,75 %, in the form of non-magnetic pyrite and 2,93% zinc. The content of the mixture: zinc-2,15 %, iron-30,34 %.

The field strength at the electromagnetic separator varied from 40-80 kA/m (500-1000 Oersted), and the current strength – from 0.25 to 2.0 A (table 5).

Table 5. Results of experiments on magnetic separation of an artificial mixture of pyrrhotite and lead flotation tailings

Name of produce	Current, A	Exit, %	$Fe_{1-x}S$ , %	Extraction $Fe_{1-x}S$ , %
Magnetic fraction	0,25	35.15	77.7	91.15
Non-magnetic fraction		64.85	4.10	8.85
<b>TOTAL</b>		100.0	-	100.0
Magnetic fraction	1,0	32.15	81.20	87.29
Non-magnetic fraction		67.85	5.60	12.71
<b>TOTAL</b>		100.0	-	100.0
Magnetic fraction	2	33.40	81.70	91.11
Non-magnetic fraction		66.60	4.0	8.89
<b>TOTAL</b>		100.0	-	100.0

From the data shown in table 5, it can be seen that the separation of pyrrhotite and tailings practically does not depend on the current strength and magnetic field strength on the separator and is carried out with a high degree. Extraction of pyrrhotite in the magnetic product is 91.15 %.

Further, enlarged tests were carried out for wet magnetic separation of the stub obtained from the sample product. The initial sample contained, %: lead cleaning (40 %) and tails of lead flotation (60 %), Pb – 1.86, Zn – 4.33, Fe – 34.88, S – 36.60, CaO – 3.50,  $SiO_2$  – 14.27,  $Al_2O_3$  – 1.52, MgO – 1.30 %. The pyrite content in the initial samples is 71-72 %.

The original sample was subjected to heat treatment at a temperature of 700 °C for 30 minutes without air access to the reaction zone. The sample was cooled together with the furnace, the resulting cinder was sent to magnetic separation. The content of pyrrhotite in the cinder is 42,0 %. Magnetic field strength 40-80 kA/m (500 -1000 Oe) (table 6).

Table 6. Results of experiments on wet magnetic separation of cinder

Name of produce	Current, A	Exit %	Content $Fe_{1-x}S$ , %	Extraction, $Fe_{1-x}S$ %
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

The results show that when the magnetic field strength increases from 40-80 kA/m (500 to 1000 e), the extraction of pyrrhotite in the magnetic fraction increases from 62.4 to 69.20 %.

Thus, magnetic separation of a mixture of ferromagnetic pyrrhotite and intermediate products of flotation enrichment, polymetallic ores allows 91 % of the compacted pyrrhotite to be separated into the magnetic product.

As a result of roasting industrial products in a non-oxidizing atmosphere and subsequent magnetic separation of the cinder, more than 69.20 % of iron in the form of pyrrhotite can

be extracted into the magnetic fraction, the content of pyrrhotite in the magnetic fraction is at the level of 85-97 %. At a magnetic field strength of 40-80 kA/m (500-1000 Oe), it is possible to extract up to 69.20 % of pyrrhotite into the magnetic fraction.

## Conclusion

Enlarged tests of the magnetic separation of sulfidizing roasting products in an environment with a limited amount of oxygen in lead flotation middlings confirm the possibility of separating up to 69 % of iron in the form of pyrrhotite into the magnetic product, with a pyrrhotite content in the magnetic product of up to 97-98 %. The technical and economic efficiency from the introduction of the technology of processing roasting-magnetic beneficiation with sulfidizing roasting on the example of processing tailings with subsequent magnetic separation is achieved through additional extraction of zinc from the lead flotation by-product.

## References

- Balarini J. C., Polli L., Miranda T., Castro R., Salum A. Importance of roasted sulphide concentrates characterization in the hydrometallurgical extraction of zinc [J]. *Minerals Engineering*, 2008, 21(1): 100-110.
- Liu, Wei, Zhu, Lin, Han, Junwei, Jiao, Fen, Qin, Wenqing. Sulfidation mechanism of ZnO roasted with pyrite. *SCIENTIFIC REPORTS*. Web of science. Vol. 8. Article number: 9516 (2018).
- Peng Rong-qiu, Ren Hong-jiu, Zhang Xun-peng. *Metallurgy of lead and zinc* [M]. Beijing: Science Press, 2003. (in Chinese).
- Ejtemaei M., Irannajad M., Gharabaghi M. Influence of important factors on flotation of zinc oxide mineral using cationic, anionic and mixed (cationic/anionic) collectors [J]. *Minerals Engineering*, 2011, 24(13): 1402-1408.
- Hosseini S., Forsberg E. Studies on selective flotation of smithsonite from silicate minerals using mercaptans and one stage desliming [J]. *Mineral Processing and Extractive Metallurgy*, 2011, 120(2): 79-84.
- Keqing F.A., Miller J. D., Jiang Tao, Li Guang-hui. Sulphidization flotation for recovery of lead and zinc from oxide-sulfide ores [J]. *Transactions of Nonferrous Metal Society of China*, 2005, 15(5): 56-79.
- Qiu X., Li S., Deng H., He X. Study of heating surface surface sulfurized flotation dynamics of smithsonite [J]. *Nonferrous Metals Mineral Processing*, 2007, 1: 6-10.
- Sadowski Z., Polowczyk I. Agglomerate flotation of fine oxide particles [J]. *International Journal of Mineral Processing*, 2004, 74(1): 85-90.
- Chepushtanova T.A., Luganov V.A., Mamyrbayeva K., Mishra B. Mechanism of Nonoxidizing and Oxidative Pyrrhotites Leaching. *Minerals & Metallurgical Processing Journal*. August 2012, Thomson Reuter, ISI Web of Knowledge. Vol. 29 № 3. – P. 159-164.
- Chepushtanova T.A., Luganov V.A., Ermolayev V.N., Mishra B., Gyseinova G.D. Investigation of the magnetic and flotation properties of synthesized hexagonal pyrrhotites. *Mineral processing and extractive metallurgy review: an international journal*. 2015, Thomson Reuter. Vol. 36 № 4. – P. 237-241. ИФ – 0,690.