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Metallurgy

Mechanism and technological results of sulfidation roasting of oxidized lead compounds

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ABSTRACT

The paper presents the results of a critical analysis of existing technologies for processing lead-zinc ores and industrial products; the relevance of the research lies in the development of methods aimed at additional extraction of zinc and lead in conditions of a rapid decrease in the content of lead and zinc in ores. The paper presents research on the thermodynamic justification of sulfiding roasting, the results of the development of technology for intensifying the process of processing poor, difficult-to-process complex lead-zinc ores and middlings through preliminary thermal activation by sulfiding roasting in a fluidized bed furnace. The mechanism of sulfidation of oxylead compounds has been established according to the scheme: $PbO \rightarrow PbO \cdot PbSO_4 \rightarrow PbSO_4 \rightarrow PbS$. The results of the physicochemical study of roasting products, as well as the results of magnetic enrichment of cinders, are presented. The results of magnetic separation of cinders after heat treatment of industrial products show that it is possible to separate up to 70% of iron in the form of pyrrhotite into a magnetic product, while the pyrrhotite content in the magnetic product is up to 98.2%. The paper presents a new technological scheme for processing lead-zinc industrial products from enrichment to obtain pyrrhotites with predicted properties.

Keywords: lead, lead-containing waste, refractory ores, sulfidizing roasting, fluidized bed furnaces, sulfidation, pyrite

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Introduction

Currently, not only in Kazakhstan but also in the world, zinc and lead are the most important metals that form modern industry, the metallurgical industry and the circular economy (circular economy) of different countries of the world (Circular Economy (CE)) [1]. The main amount of lead (over 65%) is used for the production of batteries, a significant part of which is used for the manufacture of electrical cable sheaths. Zinc is used mainly (up to

50%) as anti-corrosion coatings and for galvanizing surfaces. Also, a significant amount of zinc is consumed in the production of various types of alloys with the addition of aluminum, copper and magnesium, which have good casting properties. Innovative uses of zinc have increased by 30% since 2015 as nanomaterials in the form of zinc ferrites, zinc-ion batteries provide higher power density and longer life. The innovative use of lead is also growing by more than 10% each year through its use as

nanostructured lead electrodes to operate lead-acid batteries.

According to the content of basic metals, lead-zinc ores are classified into: rich with a lead content above 4% or with a total content of lead and zinc above 7%; medium quality (ordinary), containing from 2 to 4% lead or a total of lead and zinc from 4 to 7%; poor with a lead content of 1.2 - 2% or a total lead and zinc content of 2 - 4%. Over the past 10 years, since 2013, ores with a lead and zinc content of less than 2 - 3.5% have been used in the industry.

Zinc and lead are extracted mainly from sulfide raw materials using pyrometallurgical technologies, however, a decrease in the liquid concentration of lead and zinc in sulfide ores has been recorded in many deposits around the world. Due to the increasing consumption of natural resources in the world, primary resources will soon become insufficient to meet the demand for lead, and Pb-Zn oxide ore, typically containing 1%-5% Pb and 1%-20% Zn, may become a valuable source to meet in need of the above metals. Extracting valuable metals from refractory ores, characterized by a complex composition and high content of carbonates and silicon, seems to be the most difficult task. Lead and zinc are mainly found in the form of carbonates in the ore, and in recent years many technologies such as flotation or flotation combined with gravity separation, hydrometallurgy and pyrometallurgy have been tried to treat such refractory ore.

Difficulties in processing such raw materials arise at all stages of processing, at the flotation stage, there is a problem with the use of Na₂S as a sulfidizer, the consumption is too high due to non-selective adsorption on sludge, and desliming is required before flotation, while the loss of metals in the fine fraction remains high [[2], [3]].

To solve these problems, various hydrometallurgical processes, including acid and alkaline leaching, have been introduced. Sulfuric acid leaching seems to be the most promising for zinc recovery from economic and environmental points of view. However, Pb-Zn oxide ore usually contains large amounts of silica, which can also dissolve and then gel, preventing the leach solution from separating from the residue. In addition, a significant amount of carbonate containing gangue will react with acid, resulting in high operating costs.

The mechanochemical process of processing non-ferrous metal oxides by grinding with sulfur and iron powders at room temperature turned out to be unfeasible in practice due to the high energy costs

required to obtain a satisfactory degree of sulfidation [[4], [5], [6]].

Hydrothermal sulfidation has also been proposed for the treatment of zinc-containing compounds [[7], [8], [9]], but it remains a major challenge to achieve satisfactory recovery due to artificial sulfides characterized by fine crystallization.

A feature of difficult-to-process ores is the complex mineralization of valuable components, significant oxidation and mutual germination of minerals. The practice of processing plants has shown that direct processing of such ores using enrichment methods, even when selecting a reagent regime and improving enrichment schemes, does not give satisfactory results. From the analysis of literary sources and the practice of domestic and foreign enterprises, it follows that a solution to this problem must be sought in the development of combined technologies.

Of particular relevance is the use of preliminary preparation of ores for enrichment through thermal activation of non-ferrous metal minerals. Among them, the method of activating and high-temperature roasting of ore minerals has a significant effect.

Thermodynamic justification of sulfiding friction of oxidized lead compounds

The most promising technology for processing oxidized and mixed polymetallic ores is a technology that involves preliminary sulfidation of oxidized compounds of non-ferrous metals with pyrite or elemental sulfur under pyrrhotinizing roasting conditions, followed by the separation of non-ferrous metals into appropriate concentrates.

The use of partial pressure diagrams has been used by many authors, however, to substantiate the sulfidation process, it is necessary to establish data under the conditions being developed [10].

When processing oxidized lead-zinc ores, the composition is mixed, i.e. sulfide-oxide, or predominantly oxide. Middlings are also mixed and oxidized in composition: FeS₂, PbO, PbCO₃, PbS, PbSiO₃.

To study the thermodynamics of physical and chemical transformations, the HSC-5 software package developed by Outocumpu Ou was used.

Thermodynamic analysis of the behavior of complex oxygen-containing compounds of zinc and lead was performed based on calculations of ΔG^0 and $\log K_p$ of possible reactions. Previous studies have established that the thermal decomposition of

pyrite begins at temperatures of about 600 °C, so we chose a temperature range of 600 - 900 °C for thermodynamic analysis.

Thermodynamic characteristics (Table 1) show that at temperatures of 600 - 900 °C, decomposition of lead zinc carbonates will occur with the formation of zinc and lead oxides, respectively. Aluminates and silicates of zinc and lead are stable at temperatures of 600 - 900 °C.

Thus, oxides, aluminates and silicates of zinc and lead will participate in high-temperature sulfidation processes.

Table 1 - Values of thermodynamic characteristics of the decomposition reactions of oxidized lead and zinc compounds

| Reaction | lgKp/ΔG ⁰ , kJ at T, °C | |
|--|------------------------------------|-------------|
| | 700 | 900 |
| PbCO ₃ = PbO+CO ₂ | 2.80/-52.3 | 3.396/-76.2 |
| PbSiO ₃ = PbO+SiO ₂ | -0.87/16.2 | -0.85/20.4 |
| Pb ₂ O ₃ = 2PbO+1/2O ₂ | 1.19/-22.2 | 1.551/-34.8 |
| PbO ₂ = PbO+1/2O ₂ | 2.056/-9.1 | 2.320/-3.7 |
| Pb ₂ SiO ₄ = 2PbO+SiO ₂ | -2.12/39.6 | -1.979/40.9 |

Phase transformations in the Pb-S-O system

The results of thermodynamic analysis of the Pb-S-O system are presented in Table 2 and Fig. 1. When firing pyrite, elemental sulfur is present in the gas phase and its pressure can reach 10 Pa or more. Therefore, during the thermodynamic analysis of the Pb-S-O system, calculations of logKp and ΔG⁰ of the reactions of the interaction of lead oxides with elemental sulfur and pyrite were performed.

In the Pb-S-O system, the stable condensed phases are PbS, PbO, Pb, PbSO₄, PbO·PbSO₄. Thermodynamic calculations of the potentials of the reactions of sulfidation of lead oxide with elemental sulfur, carried out using the method of reduced potentials, showed that sulfidation in the temperature range of 600-900 °C is thermodynamically possible and can proceed both with the direct production of lead sulfide and with the initial production of a number of intermediate compounds with the subsequent formation of lead sulfide. At low temperatures, the formation of intermediate oxysulfates and lead sulfate is thermodynamically more likely. When the temperature rises to 900 °C, the possibility of direct production of sulfide and the formation of

intermediate metallic lead with its subsequent sulfidation increases significantly.

Table 2 - Values of thermodynamic characteristics of reactions in the Pb-S-O system

| Reaction | lgKp/ΔG ⁰ , kJ/mol at T, °C | |
|--|--|----------|
| | 700 | 900 |
| 4/3PbO+S ₂ =4/3PbS+2/3SO ₂ | 6.9/129 | 5.8/124 |
| PbSO ₄ +S ₂ =PbS+2SO ₂ | 5.3/100 | 6.1/132 |
| 2PbO+PbS=3Pb+SO ₂ | 0.0/0,0 | 1.7/38 |
| 4PbO+S ₂ =4Pb+2SO ₂ | 6.9/129 | 8.0/172 |
| 2Pb+ S ₂ =2PbS | 6.9/129 | 4.6/100 |
| 2PbO+SO ₂ =PbSO ₄ +Pb | 1.6/30 | 0.23/4,9 |
| 12/7PbO+S ₂ =2/7PbSO ₄ +10/7PbS+2/7SO ₂ | 7.3/138 | 5.6/122 |
| 24/9PbO+S ₂ =12/9PbS+2/9SO ₂ +4/9(2PbO*PbSO ₄) | 20.7/385 | 9.1/411 |
| 2PbO+S ₂ +5/2O ₂ =(PbSO ₄ *Pb)+SO ₂ | 30.6/571 | 22.5/485 |
| 4/7(PbO*PbSO ₄)+S ₂ =8/7PbS+10/7SO ₂ | 10.7/198 | 10.6/229 |
| 3PbS+2(PbSO ₄ *PbO)=7Pb+5SO ₂ | 13.3/248 | 21.0/452 |

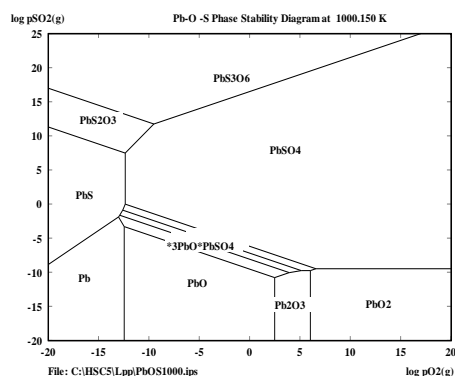


Figure 1 - Diagram of phase equilibria of the Pb-S-O system depending on temperature

Thus, sulfidation of lead oxide in a wide range of sulfur pressures in the gas phase, depending on temperature, can proceed according to the following mechanisms: PbO → PbO PbSO₄ → PbSO₄ → PbS. As the temperature increases, it is preferable to carry out direct sulfidation: PbO → PbS.

Lead-zinc tailings from the Ridder enrichment plant of Kazzinc LLP were used as feedstock. Pyrite contained in the tailings was used as a sulfidizer.

The chemical compositions of lead-zinc flotation tailings and pyrite concentrate are given in Table 3.

Table 3 - Chemical composition of lead-zinc tailings and pyrite concentrate

| Name of elements | Lead-zinc tailings, % | Pyrite concentrate, % |
|------------------|-----------------------|-----------------------|
| Pb | 0.169 | 0.719 |
| Al | 7.548 | 5.049 |
| Cu | 0.9 | 0.548 |
| Fe | 12.947 | 32.946 |
| Si | 49.789 | 22.29 |
| Mn | 0.289 | 1.89 |
| P | 0.69 | 0.39 |
| Cu | 0.09 | 0.48 |
| Zn | 0.52 | 6.49 |
| Mg | 3.3 | 1.702 |
| Fe | 12.88 | 32.89 |

Method of high-temperature sulfidation firing in a fluidized bed furnace

High-temperature sulfidation roasting was carried out in a fluidized bed furnace. A diagram of an enlarged laboratory installation for firing in a fluidized bed furnace is shown in Figure 2.

The installation of a fluidized bed furnace includes the following main components and mechanisms: a fluidized bed furnace reactor with an adjustable continuous system for loading the charge and unloading the cinder; a gas duct with a system for coarse and fine dust collection, condensation of sublimates and absorption of sulfur dioxide from exhaust gases, air heating units and the furnace reactor, a system for adjustable supply and control of air blast flow, a control unit and control of the temperature regime in the furnace.

The reactor of the fluidized bed furnace of rectangular cross-section with a hearth area of 120 cm² is made of XI8N90T 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 engines of the KD-30-U4 type. The rotation speed of the screws is selected depending on the specified loading mode of the material and is regulated by changing the voltage supplied to the motors from a laboratory autotransformer.

The cinder is unloaded from the furnace into a sealed bunker by a horizontal auger located 15 cm from the hearth level. The height of the discharge

window can vary depending on the material being fired and the specified operating mode of the furnace.

The exhaust gases from the reaction zone through the furnace charge enter a heated flue, equipped with three cascaded cyclone chambers for coarse and fine dust collection, a sublimation condenser and an absorber for fine dust and sulfur dioxide. Through the work program, experiments were carried out at the enlarged laboratory installation of a fluidized bed furnace to test the operating parameters of sulfiding roasting of zinc-oligonite ore from the Zhairam deposit.

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

Before starting the furnace, a "bed" of previously burned material (cinder) weighing up to 1.0-1.5 kg was laid on the hearth. The firing conditions for the "bed" and the supply of "fresh" mass of ore and pyrite concentrate remained unchanged, the addition of pyrite concentrate varied from 50 to 75%, the firing parameters were calculated based on the NMeO/NFeS₂ ratio, the degree of sulfidation, %, with the best indicators being the firing conditions in the temperature range 700 – 800 °C.

Simultaneously with heating the furnace to a given temperature, the air blast flow rate was set, which on average varied from 8.0 to 20 l/min. Upon reaching the specified temperature in the cinder layer, loading of the charge into the furnace began with simultaneous adjustment of the screw rotation speed, ensuring the specified productivity. After the furnace bath had reached the unloading window, the unloading screw was turned on and after 2-3 times the exchange of material in the reaction zone, the selection of burnt cinder into a sealed bunker began.

During the preparation of the furnace for operation, a vacuum was established in the flue duct and under the roof of the furnace and an alkaline solution was poured into the bubbler to neutralize the gases. Unloading of collected dust from cyclones and sublimations from the condenser was carried out after each experiment before switching to another firing mode.

The unloaded firing products (cinder, dust, sublimates) were weighed, averaged and selected

for chemical analysis for zinc, sulfur and iron. Individual samples were subjected to mineralogical and X-ray phase analyses.

The progress of the technological process was monitored according to the following parameters: blast flow rate, charge loading rate, temperature in the fluidized bed and the gas duct, and composition of roasting gases and roasting products.

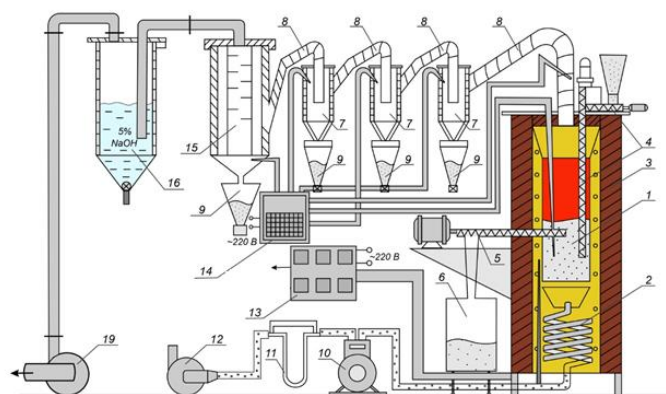
During the ongoing research, the influence of temperature on the degree of sulfidation of zinc oxides in the range of 650-800°C, the influence of the composition of the charge and the sulfur potential in the system were studied. The ratio of pyrite concentrate to ore is 1:1 and 2:1.

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 loading varied from 10 to 60 g/min. By sulfur potential we mean thermodynamic conditions in the S-O system or phase equilibria in the Fe-S-O system in an aggregate, the release and concentration of sulfur (elemental sulfur) directly in the fluidized bed. The source of heat required for the dissociation of pyrite is the heat released during the oxidation of the dissociation product - elemental sulfur directly in the fluidized bed, which allows its losses to be reduced to a minimum.

Good conditions of heat and mass transfer, characteristic of a fluidized bed, allow for quite intensive dissociation of pyrite. Since the thermal effect of the oxidation of elemental sulfur significantly exceeds the thermal effect of thermal dissociation, it becomes possible to oxidize only part of the sulfur released during dissociation in the layer. In this case, 95% or more per cent of the blast oxygen is used to produce gases containing up to 20% sulfur dioxide. In addition, part of the sulfur 1-4%, depending on the firing conditions, is obtained in the form of elemental sulfur.

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 laws of thermal dissociation of pyrite, oxidation and distillation of dissociated sulfur.

Enlarged laboratory installation for sulfidation firing in a fluidized bed furnace, Figure 2.



- 1 – reactor; 2 – air heating unit; 3 – fluidized bed furnace; 4 – loading unit; 5 – unloading unit; 6 – cinder hopper; 7 – cyclone; 8 – heated flue; 9 – dust bin; 10 – gas meter; 11 – rheometer; 12 – blower; 13 – furnace control unit; 14 – potentiometer KSP; 15 – capacitor; 16 – bubbler; 17 – valve; 18 – adjustable damper; 19 – smoke exhauster

Figure 2 - Enlarged laboratory installation for sulfidation roasting in a fluidized bed furnace

Component distribution and firing material balance

According to the balance, the cinder yield is 56-65% of the original charge, 20-21% dust yield and 15-23% loss with gases in the form of fine dust up to 3-4% and sulfur dioxide. An increase in temperature from 650 to 750°C leads to a decrease in the yield of cinder and an increase in gas formation, which is easily explained by the kinetic laws of the processes of dissociation and oxidation of pyrite, as well as a more complete decomposition of carbonate compounds. When the pyrite ore ratio is increased to 2:1, the distribution of products is similar to the 1:1 ratio.

The distribution of sulfur in the roasting products, depending on the temperature, changes in the direction of increasing sulfur oxidation with increasing temperature and its removal with gases in the form of sulfur dioxide up to 50%. In this case, the sulfur content in the cinder varies from 16.6 to 15.8% (1:1) and from 19.8 to 18.6% (2:1), and the iron content from 26 to 27% and from 31 to 33 % respectively. The inversely proportional change in the contents of sulfur and iron in the cinder is associated with the kinetic laws of thermal dissociation of pyrite, when the removal of sulfur from pyrite occurs at a very high speed and the oxidation of pyrrhotite begins.

Table 4 - Results of spectral analysis

| Elements | Contents of elements, %, 10 ³ | | |
|------------|--|--------|--------|
| | Ore | Pyrite | Cinder |
| Zinc | 2000 | 100 | 1000 |
| Lead | 120 | 60 | 100 |
| Copper | 6 | 150 | 150 |
| Manganese | 1000 | 80 | 200 |
| Arsenic | 10 | 80 | 30 |
| Nickel | 4 | 8 | 10 |
| Strontium | 20 | - | 10 |
| Barium | 100 | 100 | 400 |
| Titanium | 100 | 60 | 100 |
| Vanadium | 4 | - | 2 |
| Chromium | 2 | - | - |
| Zirconium | 10 | - | 6 |
| Antimony | 2 | 10 | 4 |
| Tin | 0.2 | - | - |
| Cobalt | 3.0 | 5.0 | 8.0 |
| Molybdenum | 0.4 | 2.0 | 3.0 |
| Cadmium | 3.0 | - | 3.0 |
| Beryllium | 0.2 | - | - |
| Bismuth | - | - | 0.6 |
| Germanium | 0.15 | 15.0 | - |
| Gallium | 0.8 | 0.4 | 1.0 |
| Thallium | 0.6 | 0.4 | 0.5 |
| Gold | - | 0.8 | 0.8 |
| Silver | 1.0 | 8.0 | 6.0 |

The distribution of zinc among the roasting products, depending on the temperature and the pyrite-ore ratio, varies slightly and lies in the range of 83-86% in cinder and 14-17% in dust. Losses of zinc in the form of sublimates and fine dust do not exceed 2-3%. The dust removed from the reactor is mainly dust from pyrite concentrate, which is finer ground than ore, as confirmed by the results of mineralogical analysis. As a result, an increase in the content of pyrite concentrate in the charge leads to an increase in the extraction of zinc and iron in the dust, which is due to the close intergrowth of zinc with pyrite in the initial concentrate.

Measurements of the composition of the gas phase showed that the oxygen content (arrived with air blast) in the exhaust gases does not exceed 0.2-0.4%, while the sulfur dioxide content varied from 8 to 18% depending on the amount of air blast supplied.

The distribution of rare and trace elements among the firing products was assessed based on the results of a full spectral analysis presented in Table. 4.

From the data obtained, we believe that part of the rare and trace elements, under certain process conditions, is concentrated in dust and roasting sublimes, which determines the practical value of separate processing of dust. This work does not involve the task of processing the resulting dust; these studies are planned to be carried out in future projects.

Characteristics of firing products and evaluation of the results obtained

Based on the results of the phase analysis of zinc compounds, the degree of sulfidation during the firing process was determined. At the same time, the extreme nature of zinc sulfidation was established at all pyrite concentrate: ore ratios depending on temperature. The maximum degree of sulfidation is 88% at a temperature of 650°C and a ratio of 2:1 - concentrate: ore. This is because at 650°C favourable conditions are created for obtaining the maximum sulfur potential in the system, associated with the kinetic laws of thermal dissociation of pyrite, oxidation and distillation of dissociated sulfur. With increasing temperature, the established proportions shift towards increasing the rate of pyrite dissociation and removal of unreacted sulfur, which leads to the interaction of blast oxygen with pyrrhotite and the resulting zinc sulfide.

Mineralogical analysis, carried out by dividing samples into light and heavy fractions, showed that in cinders of sulfiding roasting zinc is represented by sphalerite, which is present 60-70% in the form of independent grains and 30-35% in the form of small anhedral dissemination in carbonate waste rock fragments. Sphalerite inclusions in pyrrhotite are observed. An increase in the pyrite content in the charge leads to an increase in both free grains of zinc sulfide and those bound in pyrrhotite. Carbonate zinc in the fired products did not come into view, and X-ray phase analysis did not show peaks characteristic of it. Formations of zinc-containing aluminosilicates, which were probably previously present in the ore, are found in single grains. Individual grains of galena (traces) are observed in a free state and in intergrowths with pyrrhotite, but cerussite is not found.

The cinder under study under the binocular is a black sooty material, in which porosity and a cellular structure are observed and consists mainly of pyrrhotite and a fine black mass. In polished sections, pyrrhotite is presented in a wide variety of forms with intricately sinuous outlines. Myrmikitic and eutectoid types of intergrowth with sooty

material are noted. There are grains of three component compositions. When observed in immersion oil, pyrrhotite, a finely dispersed, matte gray and intermediate product with finely aggregated secondary pyrite, is identified in them. The intermediate product has less reflectivity and better seed ability from the action of concentrated nitric acid. Pyrrhotite in these grains forms peripheral rims and branching veins in the grain, the gaps which are made of fine aggregate mass.

Copper is present in the form of chalcopyrite with a film of black-blue chalcocite, which was found in the original ore. However, after heat treatment of chalcopyrite, chalcocite formations began to stand out brighter than in the original ore. Formations of the second phase, represented by cubanite, appeared and an increase in the chalcocite structure was observed.

The volume of carbonate rocks with sulfide dissemination decreases from 80% to 25% in the heavy fraction and from 95% to 25% in the light fraction for materials larger than 0.05 mm. In the heavy fraction of materials less than 0.03 mm, only sooty material with pyrrhotite (100%) was found, and in the light fraction, carbonates are represented by 50%, while in the original ore, carbonates are present in the heavy fraction by 73%, and in the light fraction by 73%. 80%.

It should be noted that after firing, sphalerite is present only in material larger than 0.05 mm. It follows from this that the newly formed zinc sulfides and the original sphalerite are enlarged to 50-60 microns.

The X-ray fluorescence analysis of sulfidation cinders confirmed the presence of the identified phases of mineralogical analysis, Figure 3.

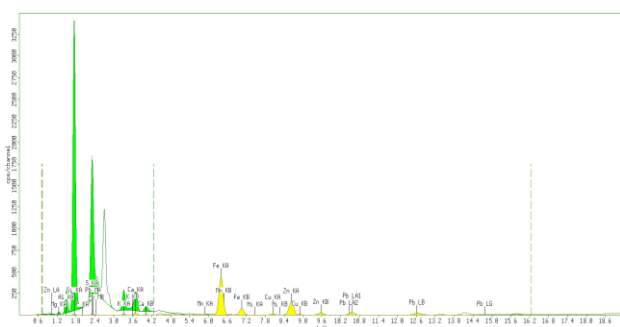


Figure 3 - Results of X-ray fluorescence analysis of sulfidation cinders

From the results of X-ray fluorescence analysis, it is clear that with increasing temperature the amount of sulfide decreases (the intensity of zinc

peaks decreases), which is due to the excess of the rate of pyrite dissociation over the rate of sulfidation. The product of pyrite dissociation are pyrrhotites of composition $Fe_{0.62}S$ to $Fe_{0.9}S$, which have high magnetic properties. There are no zinc carbonate compounds, which indicates the complete decomposition of these compounds.

Mineralogical analysis of cyclone dust showed that they are 50-70% represented by pyrrhotite with sooty material, 3-4% undecomposed pyrite with limonite films, 15-37% carbonates and about 10% quartz. Sphalerite and other sulfides in the dust of the first two cyclones are present in the signs, and only in the third cyclone, their amount reaches 1-3%.

Pyrrhotite with sooty material is most concentrated in the second cyclone (67-68%). The carbonate content increases as the cyclones pass and in the third reaches 35-37%. On the contrary, the amount of quartz decreases and only traces are found in the third cyclone. In the first cyclone, hematite was found in the heavy fraction with a particle size of more than 0.05 mm, the origin of which can be attributed to both direct dust entrainment and oxidation of pyrrhotite.

The results of X-ray diffraction analysis of roasting dust showed the presence of pyrrhotite, hematite, magnetite, quartz and sphalerite in the dust, which confirms the data of mineralogical analysis.

The qualitative and quantitative characteristics of the roasting products presented according to mineralogical, X-ray diffraction and chemical phase analyzes allow us to conclude that sulfiding roasting of acidified lead-zinc ore together with pyrite concentrate proceeds most fully and efficiently at a temperature of 650 °C and a pyrite:ore ratio of 1:1 and 2:1. As a result of heat treatment of ore under these conditions, almost complete destruction of non-ferrous metal carbonates is achieved, the opening of zinc intergrowths with pyrite and waste rock, an increase in grain size both in size and in connection with the components of the charge, deep sulfidization of oxide particles of non-ferrous metals and the conversion of iron into form magnetic pyrrhotite, which makes it possible to separate it from cinders using magnetic enrichment methods.

Thus, the large-scale laboratory studies carried out on the sulfidation roasting of lead-zinc ore in a fluidized bed furnace made it possible, based on the results of the balance of metals, their distribution

and the qualitative characteristics of the roasting products, to establish optimal conditions for conducting the sulfidation process.

Enrichment of roasting products

The results of previous studies [[11], [12], [13], [14], [15], [16], [17], [18]] and the study of the characteristics of roasting products showed that sulfides of non-ferrous metals obtained by sulfidation of oxides and carbonates have high hydrophobic properties, and pyrrhotite, a product of pyrite decomposition, has a significant magnetic susceptibility. All this predetermines further methods for processing sulfidation products. The preliminary removal of magnetic pyrrhotite into a separate product during magnetic enrichment will make it possible to obtain a commercial iron-containing product and zinc-enriched material for flotation processing.

Results of magnetic enrichment of cinders

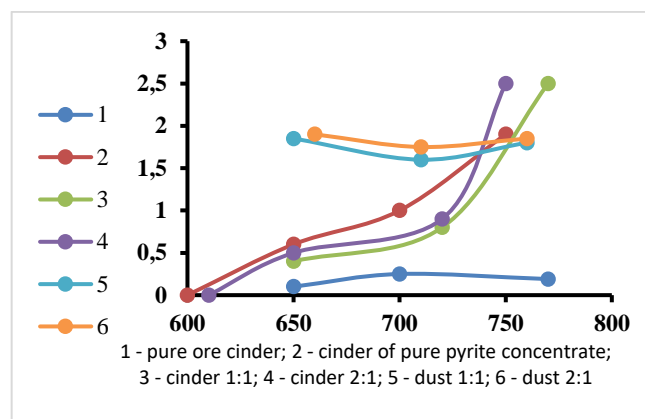
The magnetic properties of the resulting firing products (cinder, dust) were studied on a KLY-2 cappameter (Czech Republic) with a sensitivity of $3 \cdot 5 \cdot 10^{-8}$ SI, which makes it possible to obtain magnetic susceptibility values characterizing the magnetic properties of the substance. The results of magnetic susceptibility measurements are graphically presented in Fig. 4.

Shown in Fig. 4. The dependences show that with increasing temperature, the magnetic susceptibility of the dissociation products of pyrite concentrate increases from 0.5 SI units at 650 °C to 1.78 SI units at 750 °C, and for cinders with an initial pyrite: ore ratio of 1:1 from 0, 3 SI units at 650 °C to 0.98 SI units at 750 °C.

The original pyrite concentrate and zinc-oligonite ore have a zero magnetic susceptibility value, and the roasting product of the original ore has a low magnetic susceptibility value, which ranges from 0.01-0.2 SI units when the temperature changes from 650 to 750 °C [[18], [19], [20], [21], [22], [23], [24]].

The results obtained indicate that the magnetic susceptibility of roasting products depends on the completeness of pyrite dissociation. An increase in the value of magnetic susceptibility with increasing temperature can be associated both with a change in the composition of pyrrhotite and with an increase in the amount of pyrrhotite in the materials (curves 2,3,4) during the sulfidation of iron oxides. The magnetic susceptibility of roasting dusts for

charges with pyrite:ore ratios of 1:1 and 2:1 is characterized by parabolic dependences with temperature changes.



Thus, it has been established that sulfides of non-ferrous metals and waste rock have low magnetic susceptibility values compared to pyrrhotite. These properties of the components in the roasting products make it possible to separate them using magnetic separation and extract magnetic pyrrhotite into the magnetic fraction, and leave non-ferrous metal sulfides in the magnetic separation tailings.

Based on the above, sulfiding roasted cinders were subjected to wet magnetic separation at a magnetic field strength of 100-120 kA/m. Table 5 shows the results of magnetic separation for the extraction of iron into a magnetic product.

Table 5 - Results of magnetic separation of cinders

| Product name | Experimental conditions | | Magnetic fraction, iron extraction, % | Non-magnetic fraction, iron extraction, % |
|--------------|-------------------------|-------------------|---------------------------------------|---|
| | °C | Pyrite: ore ratio | | |
| Cinder 1 | 650 | 1:1 | 88.4 | 11.6 |
| | | 2:1 | 90.4 | 9.6 |
| Cinder 2 | 700 | 1:1 | 91.4 | 8.6 |
| | | 2:1 | 96.4 | 3.6 |
| Cinder 3 | 750 | 1:1 | 96.6 | 3.4 |
| | | 2:1 | 97.2 | 2.8 |
| Cinder 4 | 650 | 1:1 | 91.7 | 8.3 |
| | | 2:1 | 91.48 | 8.52 |
| Cinder 5 | 650 | 1:1 | 90 | 10 |
| | | 2:1 | 96 | 4 |

The presented results of magnetic separation show that in the selected range of magnetic field strength, more than 90 - 92% of the iron from roasting cinders is extracted into the magnetic product. It is noted that part of the iron present in the ore is also released into the magnetic product, because a small percentage of iron remains in the non-magnetic fraction compared to the original ore.

The results of spectral analysis of the magnetic and non-magnetic fractions (Table 6) showed that non-ferrous and rare metals are mainly concentrated in non-magnetic fractions.

Table 6 - Results of spectral analysis

| Firing products | Contents of elements, %, 10 ³ | | | | | | | | | |
|--|--|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| | Zn | Pb | Cu | Mn | As | Ni | Sr | Ba | Ti | V |
| Cinder | 1000 | 100 | 150 | 200 | 30 | 10 | 10 | 400 | 100 | 0 |
| Magnetic fraction | 300 | 60 | 100 | 200 | 20 | 10 | 10 | 150 | 100 | 2 |
| Non-magnetic fraction | 1000 | 200 | 300 | 400 | 100 | 5 | 30 | 500 | 200 | 4 |
| Contents of elements, %, 10 ³ | | | | | | | | | | |
| Elements | Zr | Sb | Co | Mo | Cd | Bi | Ga | Tl | Au | Ag |
| Cinder | 5 | 4 | 8.0 | 3.0 | 3.0 | 0.6 | 1.0 | 0.5 | 0.8 | 6.0 |
| Magnetic fraction | 5 | 4 | 10 | 2.0 | 2.5 | 0.3 | 1.0 | 0.3 | 0.8 | 5.0 |
| Non-magnetic fraction | 15 | 20 | 3.0 | 5.0 | 4.0 | 1.6 | 0.8 | 1.5 | 0.6 | 4.0 |

The results of spectral and chemical analyzes show that some of the zinc with a content of 0.2-0.3% is extracted into the magnetic fraction. Mineralogical analysis shows that zinc in the magnetic fraction is present in close contact with pyrrhotite. Apparently, this zinc was present in the original pyrite and remained in close association with it after firing.

The magnetic fraction by size is divided into a class of more than 0.05 -27% and a class of less than 0.05 mm - 33%. In the heavy fraction of the class greater than 0.65 mm, up to 5% of undecomposed pyrite and up to 3% of sphalerite were found. The main mass consists of sooty material with pyrrhotite composition $Fe_{0.855}S$, $Fe_{0.862}S$, $Fe_{0.877}S$, $Fe_{0.901}S$, $Fe_{0.911}S$, and in the class less than 0.05 mm, all material is represented by pyrrhotite, the composition of which is pyrrhotite $Fe_{0.855}S$, $Fe_{0.862}S$, $Fe_{0.877}S$, $Fe_{0.901}S$, $Fe_{0.911}S$. A fine-grained aggregate of quartz-mica composition is also extracted into the magnetic fraction.

The non-magnetic fraction is represented by rock fragments with fine dissemination of sulfides in the heavy fraction of 0.05 mm class, as well as free

grains of sphalerite, chalcopyrite and minor galena, sooty material with pyrrhotite and pyrite in the form of cubic crystals are present. The gangue consists of fine-aggregate quartz-mica materials and carbonates, and grains of feldspars and quartz are observed. The extraction of zinc into the non-magnetic fraction was over 88 - 90%, and the extraction of lead was 100%.

Thus, magnetic separation makes it possible to sufficiently isolate magnetic pyrrhotite from roasting cinders and concentrate non-ferrous metals in a non-magnetic fraction for their extraction by flotation methods.

Development of a technological scheme for high-temperature sulfiding roasting of oxidized lead-zinc ore in a fluidized bed furnace

Based on the obtained results of processing lead-zinc ore of the Zhairam deposit with a zinc content of 2.5%, lead - 0.1% and the degree of zinc oxidation of more than 60%, a technology has been developed for activating, high-temperature, sulfiding roasting of this ore in a fluidized bed furnace using pyrite concentrate (with sulfur content - 45.15%) as a sulfidizer, Figure 5.

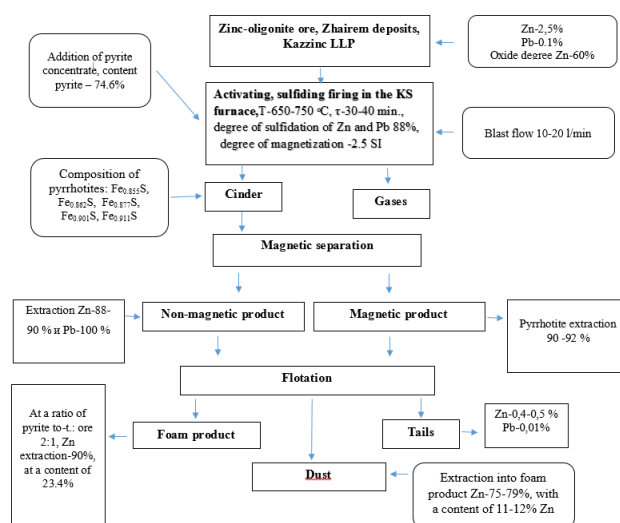
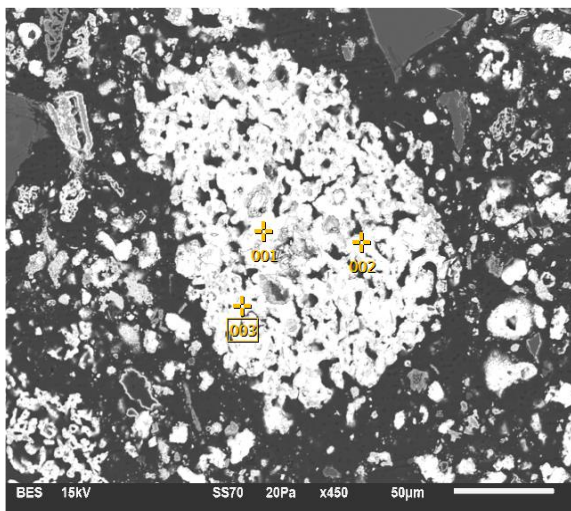


Figure 5 - Flow diagram of the technology for high-temperature sulfiding roasting of oxidized lead-zinc ore in a fluidized bed furnace

The results of electron microscopic analysis (Fig. 6) confirm the formation of lead sulfides; intermediate sulfidation products in the form of lead sulfate were also detected. The formation of sulfides begins from the surface of the initial phase and spreads into the particle. In Fig. Figure 6 shows

a micrograph of the formed sulfides and lead sulfate (≈ 630).

X-ray diffraction studies of sulfidization products show that intermediate lead sulfates are formed during the sulfidization process. It has been established that sulfidation proceeds according to the scheme $PbO \rightarrow PbO \cdot PbSO_4 \rightarrow PbSO_4 \rightarrow PbS$ (activation scheme). The presence of the PbS phase is confirmed by the X-ray diffraction results, Figure 6 clearly shows the PbS phase highlighted in red (COD9008694) showing the most significant amplitude of the 2θ half-angle (2θ : 26, 30, 43, 51.53.5). The established mechanism of decomposition during sulfidation has not been previously presented and confirmed by X-ray phase analysis in the literature.



microphotograph:001 - PbS, 002 - PbSO₄, 003 - PbO

Figure 6 - Micrograph of lead sulfidization products (≈ 450)

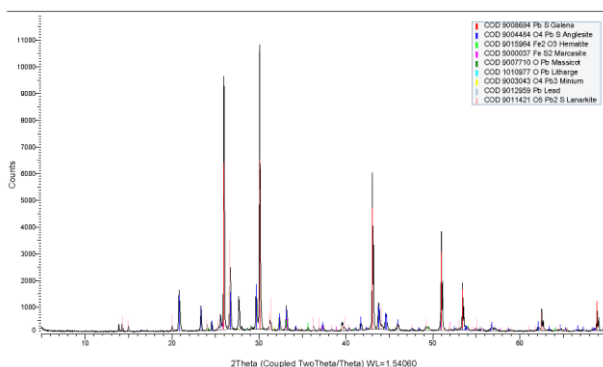


Figure 7 - X-ray results of lead sulfidization products

Thus, sulfidation roasting of lead-zinc flotation tailings with pyrite found in the tailings makes it

possible to obtain lead and zinc sulfides similar in properties to natural sulfides, while pyrrhotites with pronounced magnetic properties of the composition are formed $Fe_{0.892}S-Fe_{0.869}S$ in the temperature range 600-800 °C, which is confirmed by the results of X-ray phase analysis.

Development of a technological scheme for processing lead-zinc enrichment tailings

Figure 8 shows the developed technological scheme for processing lead-zinc tailings and middling products through sulfiding roasting in an environment with a limited amount of oxygen to obtain pyrrhotites with predicted properties. The results of enlarged tests are shown in the technological diagram, Fig. 8. Sulfidation firing was carried out in a fixed bed, in a tube furnace.

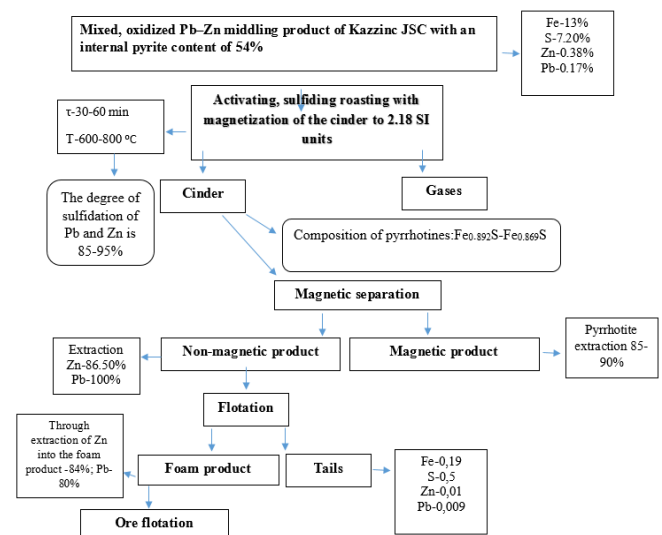


Figure 8 - Technological scheme for processing lead-zinc intermediate products of enrichment to obtain pyrrhotites with predicted properties

The economic effect of the processing technology for the complex processing of oxidized and mixed middling products enriched by sulfiding roasting with subsequent enrichment of the cinder is achieved through additional extraction of zinc from the middling product of lead flotation. A technical and economic calculation showed that with an annual production of 5,000 tons of concentrate, the payback period for the project will be 1.5 years.

Thus, the studies carried out on the activation of middlings by sulfidation roasting showed the effectiveness of the technology and the possibility of using it on an industrial scale; the results can be used in the design of a pilot plant.

Conclusion

It has been established that the sulfidation of lead oxides proceeds from the surface deep into the particle with the formation of a dense microporous sulfide layer, increasing the diffusion resistance, with the simultaneous enlargement of particles, according to the following mechanism: $PbO \rightarrow PbO \cdot PbSO_4 \rightarrow PbSO_4 \rightarrow PbS$. At temperatures above 850 °C, the process progresses according to the scheme: $PbO \rightarrow PbS$.

Thus, a hybrid technology has been developed for activating sulfiding roasting of zinc-containing and lead-containing industrial enrichment products in a fixed layer containing pyrite in its composition of at least 50-54%, used as a sulfidizer; Magnetic separation of cinders after heat treatment of middling products makes it possible to separate up to 70% of the iron in the form of pyrrhotite into the magnetic product, with the pyrrhotite content in the magnetic product being up to 98.2%. This

technology for processing oxidized waste containing zinc and lead can be recommended for processing Kazakh and foreign technogenic deposits.

The proposed technology makes it possible to additionally extract zinc and lead from industrial products, significantly increasing the economic effect of production. The unit costs per 1 US dollar of commercial products using the proposed technology are lower than the unit costs of the existing technology, which is associated with the use of cheaper raw materials in the form of enrichment tailings and the production of pyrrhotites as additional commercial products.

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Тотыққан қорғасын қосылыстарын сульфидтеу арқылы күйдірудің механизмі және технологиялық нәтижелері

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ТҮЙІНДЕМЕ

Жұмыста қорғасын-мырыш кендерін және өнеркәсіптік өнімдерді өңдеудің қолданыстағы технологияларына сыни талдау нәтижелері келтірілген. Зерттеудің өзектілігі – кендегі қорғасын мен мырыш мөлшерлерінің тез азаю жағдайында мырыш пен қорғасынды қосымша өндіруге бағытталған әдістерді әзірлеуде. Жұмыста сульфидтік күйдірудің термодинамикалық негіздемесі бойынша зерттеулер, кедей, қиын байытылатын қорғасын-мырыш кендері мен өнеркәсіптік өнімдерді қайнайтын қабаттағы пеште сульфидті күйдіріп алдын ала термиялық белсендіру арқылы өңдеу процесін интенсификациялау технологиясын әзірлеу нәтижелері берілген. $PbO \rightarrow PbO \cdot PbSO_4 \rightarrow PbSO_4 \rightarrow PbS$ схема бойынша тотыққан қорғасын қосылыстарының сульфидтену механизмі анықталған. Күйдіру өнімдерін физика-химиялық зерттеу нәтижелері, сонымен қатар өртенділерді магниттік байыту нәтижелері келтірілген. Өнеркәсіптік өнімдерді термиялық өңдеуден кейін өртенділерді магниттік бөлу нәтижелері пирротит түріндегі темірді 70% дейін магнитті өнімге бөлуге болатынын көрсетеді, ал магниттік өнімдегі пирротит мөлшері 98,2% дейін болады. Жұмыста қорғасын-мырышты өнеркәсіптік өнімдерді байыту кезінде болжамды қасиеттері бар пирротиттер алу үшін өңдеудің жаңа технологиялық схемасы ұсынылған.

Түйін сөздер: қорғасын, құрамында қорғасын бар қалдықтар, отқа төзімді кендер, сульфидтендіріп күйдіру, сұйық қабат пештері, сульфидтеу, пирит

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Механизм и технологические результаты сульфидирующего обжига окисленных соединений свинца

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АННОТАЦИЯ

В работе представлены результаты критического анализа существующих технологий переработки свинцово-цинковых руд и промпродуктов, актуальность исследований заключается в разработке методов, направленных на дополнительное извлечение цинка и свинца в условиях стремительного снижения содержания свинца и цинка в рудах. В работе представлены исследования по термодинамическому обоснованию сульфидирующего обжига, результаты разработки технологии интенсификации процесса переработки бедных труднообогатимых комплексных свинцово-цинковых руд и промпродуктов за счет предварительной термической активации сульфидирующем обжигом в печи кипящего слоя. Установлен механизм сульфидирования окисленных соединений свинца по схеме: $PbO \rightarrow PbO \cdot PbSO_4 \rightarrow PbSO_4 \rightarrow PbS$. Представлены результаты по физико-химическому исследованию продуктов обжига, а также результаты магнитного обогащения огарков. Результаты магнитной сепарации огарков после термической обработки промпродуктов показывают, что возможно выделить в магнитный продукт до 70 % железа в виде пирротина, при этом содержание пирротина в магнитном продукте составляет до 98,2 %. В работе представлена новая технологическая схема переработки свинцово-цинковых промпродуктов обогащения с получением пирротинных прогнозируемых свойств.

Ключевые слова: свинец, свинецсодержащие отходы, труднообогатимые руды, сульфидирующий обжиг, печи кипящего слоя, сульфидирование, пирит

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