MINISTRY OF EDUCATION AND SCIENCE OF THE REPUBLIC OF KAZAKHSTAN

Satbayev University

Institute of Metallurgy and Industrial Engineering

Department of Metallurgy and Mineral Processing

Galipauly Shyngys

GRADUATE WORK

Extraction of lead from lead slag

5B070900 – Metallurgy

Almaty 2020

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ALLOWED TO PROTECT
Head of the Department of MaMP
candidate of technical sciences
__________M. Barmenshinova
«____» _________2020

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Extraction of lead from lead slag

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Performed Galipauly Shyngys

Scientific adviser
candidate of technical sciences,
associate professor
_________N. Dosmukhamedov
«___»___________2020.

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«AFFIRM»
Head of the Department of MaMP
candidate of technical sciences
__________M. Barmenshinova
«____» _________2020

THE TASK
for diploma work

To the student: *Galipauly Shyngys*
Subject: *«Extraction of lead from lead slag»*
Approved by *order of the Rector of the University* No. 762-b of 01.27.2020
Deadline for completion of work is May 20, 2020.
Initial data for the thesis: *Industrial data of Kazzinc LLP*
Summary of thesis:
a) A literature review of the current state of lead production and methods for processing intermediate products and working materials of lead production;
b) Metallurgical calculations;
List of graphic material: ___ *slides of the presentation* of work are presented
Recommended basic literature: *from 20 titles.*

SCHEDULE

preparation of thesis

Name of sections, list of issues addressed	Dates for the Supervisor	Note
Introduction	11.03.2020	
Literature review	25.03.2020	
Metallurgical calculations	08.04.2020	
Conclusion	22.04.2020	

Signatures

consultants and the normontroller for the finished diploma work indicating the sections of work related to them

Name of sections	**Consultants, F.N. (academic degree, rank)**	**Date of signing**	**Signature**
Norm controller	A. Taimassova		

Scientific adviser __________________ N. Dosmukhamedov

The student accepted the task _____________ Sh. Galipauly

The date «3» February 2020

АҢДАТПА

Дипломдық жұмыста 38 парақ, 3 сурет, 11 кесте, 20 атаудан тұратын библиография бар.

Түйінді сөздер: қорғасын, мырышты шлактар, тотықсыздану, фьюмингование, материалдық баланс, жылу балансы.

Түсті металлургия шлактарын өңдеудің қазіргі жай-күйін әдеби талдау негізінде қорғасын өндірісінің құрамында мырыш бар шлактарды қайта өңдеу бойынша зерттеу бағыты таңдап алынды.

Жұмыста металлургиялық есептер, оның ішінде қалпына келтіру атмосферасы жағдайында қорғасын өндірісінің құрамында мырыш бар қождарының түю процесінің материалдық және жылу теңгерімі жүргізілді.

АННОТАЦИЯ

Дипломная работа содержит 43 листов, 3 рисунков, 11 таблиц, библиографию из 20 наименований.

Ключевые слова: свинец, цинксодержащие шлаки, восстановительное обеднение, фьюмингование, материальный баланс, тепловой баланс.

На основании литературного анализа современного состояния переработки шлаков цветной металлургии выбрано направление исследований по переработке цинксодержащих шлаков свинцового производства.

В работе проведены металлургические расчеты, в том числе материальный и тепловой баланс процесса обеднения цинксодержащих шлаков свинцового производства в условиях восстановительной атмосферы.

ABSTRACT

The thesis contains 43 pages, 3 drawings, 11 tables, and a bibliography of 20 titles.

Keywords: lead, zinc-containing slags, reducing depletion, fusing, material balance, heat balance.

Based on a literary analysis of the current state of non-ferrous metallurgical slag processing, the direction of research on the processing of zinc-containing slags of lead production has been selected.

The work carried out metallurgical calculations, including the material and heat balance of the depletion of zinc-containing slag of lead production in a reducing atmosphere.

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INTRODUCTION

The growth of the world population significantly exacerbates the problem of depletion of natural resources and increasing production waste.

The annual economic damage caused by consumption and environmental pollution from industrial waste is estimated at 10% of GDP (gross domestic product). The solution to the problem of resource conservation is possible with the integrated use of technical, organizational, economic factors and the acceleration of scientific and technological progress.

One of the serious environmental problems is the dumps of the Ust-Kamenogorsk metallurgical complex of «Kazzinc» LLP. Despite the modernization, including the replacement of obsolete lead production processes and equipment with Isasmelt technology, the problem of processing waste, in particular zinc-containing slag, remains relevant. The search for new methods of both current and accumulated slag waste is of paramount importance for the enterprise.

1 Current state of the lead production

Currently, the mining and metallurgical complex is one of the basic industries of the Republic of Kazakhstan, which plays an important role in the formation of macroeconomic indicators of the country.

Today, of the 11 billion tons of minerals mines in the world, our republic accounts for more than 250 million tons. It provides 11th place in the world. And Kazakhstan ranks first to 19th for 37 types of products. Thus, in terms of reserves of tungsten and vanadium ores, the Republic ranks first in the world, chromium – containing ores – second (23 %), and manganese-third. Kazakhstan accounts for 19 % of the world's lead reserves, 13 % – zinc, 10 % - copper and iron.

Kazakhstan has large reserves in expanding the mineral resource base of non-ferrous metallurgy. Large proven reserves of almost all non-ferrous and rare metals are concentrated in the bowels of the Republic.

The main branches of non – ferrous metallurgy in Kazakhstan are lead, copper, aluminum and titanium-magnesium. Each of these industries has significant reserve deposits and is of great importance to the country's economy.

Today, the non-ferrous metallurgy of Kazakhstan consists of 8 sub-sectors, which include: 40 underground and 30 open-pit mines, 21 processing plants, 11 metallurgical plants. Multinational companies created in industries and integrated into industrial associations have a positive reputation on the world market and make a significant contribution to the country's economy.

Kazakhstan is one of the largest producers of zinc and lead. In terms of confirmed zinc reserves approaching 35 million tons, Kazakhstan ranks first in the world. According to the US geological survey, Kazakhstan has the second largest lead reserves in the world.

According to VNIItsvetmet, active reserves of zinc in Kazakhstan, after revaluation, account for 88,7 % of its total reserves, and similar data for lead – 66,8 %.

Such reserves could in principle ensure the sustainable development of the lead-zinc industry in Kazakhstan for several decades to come. The problem is that in addition to the low content of useful components, a negative factor is the lack of reserve deposits with active reserves in the field of old mining enterprises (Karagailinsky GOK). The stress state is typical for the mineral resource base in the sphere of activity of some mining complexes of the Ore Altai.

Lead, zinc and copper concentrates are supplied to «Kazzinc» LLP, where silver, cadmium, selenium, tellurium, indium, and mercury are extracted from them along the way. Sulfide sulfur is captured for the production of sulfuric acid.

Today, «Kazzinc» LLP producers the main of non-ferrous metals based on lead and zinc, which is a large integrated global producer of zinc with a large share of the associated production of copper, precious metals and lead. All enterprises of the company are located in Kazakhstan exactly in five cities. Now the company includes the following units:

a) Zyryanovsky mining and processing complex (Zyryanovsk, East Kazakhstan region), including Maleevsky and Grekhovsky mines, processing plant;

b) Ridder (former Leninogorsk) mining and processing complex (Ridder, East Kazakhstan region), including the Tishinsky and Ridder-Sokolny mines, an enrichment plant;

c) a metallurgical complex, which includes a zinc plant in Ridder, and zinc and lead plants in Ust-Kamenogorsk;

d) refining production (administratively located within the plant).

Technological schemes for the production of lead from sulfide lead concentrates can be represented in the form of three groups of technological processes. The first group unites the technological redistribution of crude lead. The second group consists of refining operations of rough lead. The third group covers technological processes aimed at the processing of intermediate products (dust, sublimates, slag, gases, smelters, floats, etc.) of the first two groups, with the aim of additional extraction of lead and other valuable satellites (zinc, copper, gold, silver, cadmium, bismuth, antimony, arsenic, tellurium, indium, etc.).

Lead has a number of unique properties: high ductility, ductility, density, low melting point, fluidity, lack of solubility of iron, as well as extreme resistance to corrosion and protection against the penetration of various types of radiation. These physicochemical properties determine the wide demand for it in various industries, both in the form of metal of acceptable purity and alloy component.

Hydrometallurgical methods for the extraction of lead, due to technological imperfections, are uncompetitive with respect to pyrometallurgical methods, therefore, they are currently not widely used.

Three types of smelting lead from sulfide concentrates: reactive, precipitation and reduction. At present, precipitation melting, including the interaction of lead sulfide with iron, has lost its significance. The production of lead by reaction melting is based on the chemical interaction between its sulfide and oxide or sulfate. The course of these reactions should be preceded by a partial oxidative roasting of the initial concentrate, carried out previously or in the same apparatus in which the reaction interaction takes place. Reaction smelting can be carried out by KIVCET, QSL processes. Widely used reducing smelting carries out in shaft furnaces. Before smelting, lead sulfide concentrates calcines with simultaneous sintering. A classic example of lead smelting in shaft furnaces is the Imperial Smelting (ISP) process. The lead bullion contains 2–10% impurities. Copper, antimony, arsenic, bismuth, gold, silver, etc. are present as impurities in lead bullion. Refining of lead bullion can be carried out by pyrometallurgical and electrolytic methods. Electrolysis is economically justified only with a small content of impurities, therefore, its use in practice is limited.

1.1 Characteristic of the products

Lead bullion contains from 93 to 98% of the base metal. Impurities found in lead bullion are contained within, %: copper 1-5; antimony 0,5-2,0; arsenic 0,2-2,0; tin 0,1-0,2; bismuth 0,05-0,4; tellurium 0,005-0,1. In addition, lead bullion contains silver (1-5 kg/t), gold (1-30 g/t), slag-forming components (0,3-0,8 %) and sulfur (from 0,1-0,3% for mine melting to 3-5% for autogenous methods). Lead bullion does not meet the requirements of the standard in its composition, and its physical and chemical characteristics are not suitable for any consuming industry.

Slag is a multi-component non-metallic melt. The composition of the slag factory (little Zinkovich): silicon oxide – 25-35%, iron oxide – 20-50 %, calcium oxide – 5-20%, others – 10-15%.

High-zinc slags have the condition:

$ZnO + SiO_2 = 41\text{-}42$ % and $ZnO + CaO \leq 29\text{-}30$ %.

In total, oxides of calcium, iron, silicon and zinc or calcium, iron and silicon (in low-zinc slags) make up 85-90% of the weight of the slag.

Matte of lead smelting. In lead smelting, the purpose of obtaining matte is to remove copper from the process in the form of its sulfurous compound. At the same time, lead smelting matte contains copper and lead sulfides, as well as zinc, silver, and antimony sulfides. There are also dissolved metals in matte: iron, copper, lead, and gold.

The lead content in matte depends on the amount of copper and iron sulfides. Zinc in matte is mainly contained in the form of its own sulfide, which is limited to dissolving in iron and copper sulfides. When the matte is cooled, zinc sulfide falls out of the solution. The factory matte contains, %: 5-40 copper, 10-35 lead, 2-8 zinc, 15-50 iron and 15-26 sulfur (average 20).

Speyza of lead smelting. The basis of speyza are compounds of arsenic and antimony with iron. Speyza heavier than matte but lighter than lead. Melting speyza lead in the case when the raw materials are Nickel or Cobalt which are readily soluble in spate. In speise there are also arsenides and antimonides of lead and copper, and precious metals. Obtaining speyza during mine melting is undesirable because of the" smearing " of metals on the products of melting, its aggressiveness to the material of the furnace and the difficulty of processing.

Dust and gases. The dust and gas mixture obtained as a result of mine sinter melting is subjected to separation. The purified gas, as having no value, is released into the atmosphere, and the captured dust is divided into coarse and fine.

Coarse dust is captured in cyclones and dust chambers and its composition differs little from that of the initial charge. It contains, %: 55-65 lead, 12-20 zinc, 6-8 sulfur, 0,1-1,5 iron and 0,5 arsenic. Coarse dust is sent into circulation in the agglomeration charge.

Fine dust is captured in bag filters and electrofilters and contains a noticeable amount of rare and scattered element compounds, its composition is as follows, %: 50-60 lead; 2-20 zinc; 0,3-4,5 cadmium; 0.005-0.13 thallium; 0,002-0,01 indium; 0,03-1,3 selenium; 0,015 tellurium; 0,3-7,0 arsenic. This dust serves as the raw material for the extraction of rare and scattered elements, therefore sends for separate processing.

1.2 Methods for impoverishing slags

Lead mine smelting slags contain 10-14 % zinc, 1-2 % lead, 0,5 % copper, as well as cadmium, tin, indium, thallium, germanium and precious metals.

Processes are used to extract zinc and lead:

1) Flotation method of impoverishing slags;
2) Fumigation of slags;
3) Electrothermal method.

1.2.1 Flotation method of impoverishing slags

Due to various types of slags, non-ferrous metallurgy offers various options for flotation enrichment of slag for subsequent recovery of metals. So, depending on the rate of slag cooling, there are slags that have passed the stage of slow cooling and quickly cooled slags. The first is used for crushing, multi-stage grinding in closed circuit with spiral classifiers, basic and control flotation of copper minerals, intermediate and tails, prechistoy flotation concentrate basic flotation of the copper, cosmelenia intermediates and flotation. Slags before enrichment are processed-slowly cooled, which ensures the formation of large crystals of sulfides and facilitates their further extraction. Slag flotation is performed in mechanical and pneumomechanical flotation machines. The technology allowed to obtain rich copper concentrates with high copper extraction. Slags that have been stored for a long time in dumps, so-called man-made deposits, are characterized by a very weak crystallization, thin inclusions of copper minerals in the glassy mass of slag-forming minerals. Therefore, the flotation process had to be upgraded technologically. The process chain exactly repeats the flotation of slags subjected to slow cooling, but the control copper flotation is carried out in a field with low turbulence of pulp flows in conditions of high air saturation of the pulp. Grinding of the initial slag is carried out in three stages, and the first stage of grinding in a ball mill is carried out in an open cycle. This is due to the fact that slags that have not passed the preliminary slow cooling operation are subjected to enrichment. In this regard, slags have a high hardness and after the first stage of grinding, the number of opened grains ready for flotation is less than 15 %. Operation of the mill in a closed cycle with classifiers leads to a large circulation load (up to 500 %) and reduces the processing capacity of the initial slag.

1.2.2 Electrothermal method

In an electric furnace, due to heating by electricity, the consumption of coke required for reduction reactions is reduced to a minimum (4-5 % of the load weight). In this case, the partial pressure of zinc vapors in the gas phase approaches the theoretical one. Further cooling of the gas creates favorable conditions for the condensation of zinc in the form of metal. For the first time this method has been applied in the United States. In the Soviet Union, this method was studied by M. M. Lakernik and others in relation to the slags of the Leninogorsk lead plant, which contain 11 % zinc and 3 % lead. Zinc vapors condense in a liquid condenser, which is irrigated with liquid zinc. The zinc sublimate is 85 %, of which about 83 % condenses into a liquid metal. The power consumption is 1200 kWh per ton of zinc.

1.2.3 Fumigation of slags

Slag fusing is a method for extracting volatile components from molten slags containing zinc, lead or tin. Slag containing lead and zinc is blown at 1200-1250°C with a carbon-air mixture (coal dust can be replaced with natural gas), resulting in the reduction of zinc and lead oxides. Metal vapors are removed with gases and, interacting with carbon dioxide, form oxidized fumes, which are captured by bag filters after cooling in the recovery boiler. The process is carried out in a rectangular shaft furnace with 40-50 lances. To obtain pure zinc oxide and separate lead oxides from it, the distillates are calcined in a tube furnace.

1.3 The selection and justification of the study

In this paper, the choice of a method for impoverishing copper-rich slags is justified, and the possibility of reducing the impoverishment of copper-rich oxidized slags with natural gas is evaluated.

Non-ferrous metallurgy enterprises in Kazakhstan produce 600-800 thousand tons/year of slag. The technology of depletion of lead production slags by fusing, which operates at «Kazzinc» LLP, is aimed exclusively at extracting zinc. This technology is one of the most environmentally harmful and has a number of significant disadvantages: it requires complex preparation of a dust-air coal mixture, accompanied by a high dust yield. At the same time, the waste slags contain high content of non-ferrous metals, %: 0,1 Pb; 0,3 Cu; 2,5 Zn. Thus, the technology does not fully solve the problem of complex extraction of non-ferrous metals and utilization of slag, but only by extracting zinc, it transfers it from one state to another, requiring further processing to the necessary stage of utilization.

Despite the extensive and practical material available in the technical literature, the search for effective schemes for processing copper-smelting slags is still of great interest. Moreover, given the prevailing role of dissolved losses of copper in slags in the form of its oxide, it can be argued that of all the known methods of impoverishing slags, the most effective are the reduction methods.

To solve this problem, thermodynamic analysis of the interaction of slag components with natural gas and metallurgical calculations for the depletion of slags were performed.

2 Lead production technology in the conditions of «Kazzinc» LLP and methods for their processing

Ust-Kamenogorsk metallurgical complex consists of a zinc plant with a capacity of 190 thousand tons/year, lead plant with a capacity of 144 kt/y, copper production capacity of 70 kt/y, plant on production of precious metals and sulfuric acid plant.

2.1 General technological scheme of lead production

The General scheme of lead production includes the following closely related technological processes: sintering firing, mine reduction melting for matte and refining of lead bullion. The General technological scheme of mine recovery melting is shown in figure 1.

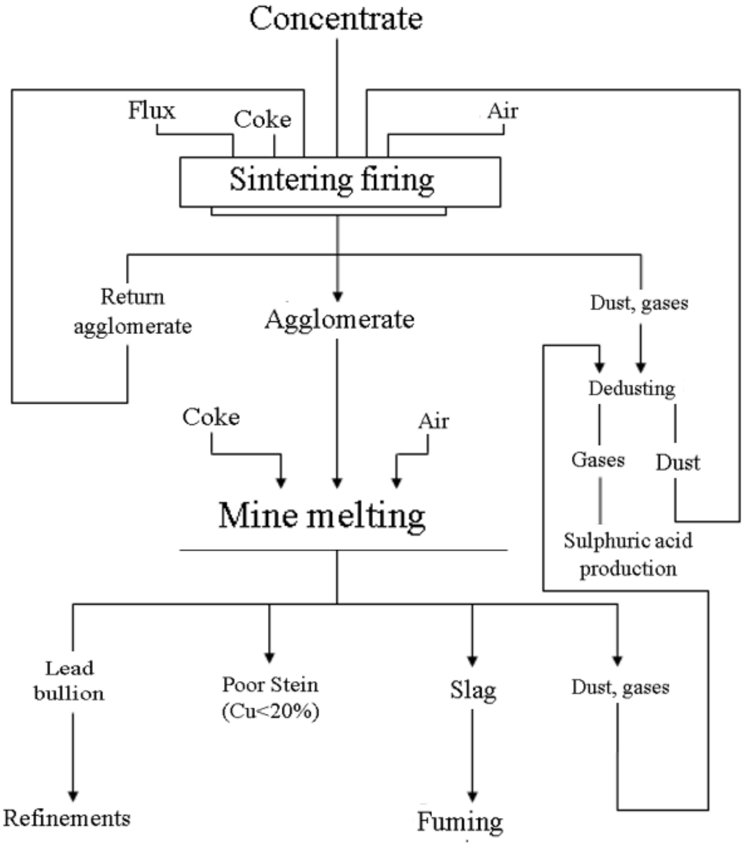


Figure 1 – Technological scheme of mine reduction smelting

The sinter reduction smelting process receives the agglomerate composition, %: Pb 45-50; S 6-8; CaO 10-20; FeO 25-35; SiO_2 20-25.

The process of mine melting is characterized by an insignificant yield of matte. The composition of the resulting slags is as follows, % (wt.): Pb-1,7; ZnO-22; Cu-0,8; FeO-32; SiO_2 -25; CaO-15.

Lead bullion obtained by smelting sinter contains such impurities as copper, antimony, arsenic and other elements. Composition of draft lead, %: 91-96 Pb; 2,5-3,0 Cu; 0,5-2 As; 0,5-2 Sb. Copper present in lead bullion is removed in the form of copper slips during refining, which, according to the technology currently existing at the plant, are sent for separate processing into mine contractile melting.

Slag is a multicomponent melt formed from gangue oxides and specially introduced fluxes. Zinc-containing slag, to extract zinc from them, is supposed to be sent for processing by fuming.

In the process of mine smelting, favorable conditions are not created for the sublimation of arsenic. In dust passes only 35 % of arsenic from its total content. Up to 30 % of arsenic is concentrated in matte, which greatly affects the quality of the latter. During smelting, with a lack of sulfur in the charge, one should expect strong matte metallization, as a result of which the transition of metallic copper to blister lead increases. It was established in that the strongest correlation of arsenic in matte is observed with copper content. In the case of matte metallization, the probability of the formation of intermetallic compounds increases, which leads to an increase in the arsenic concentration in matte.

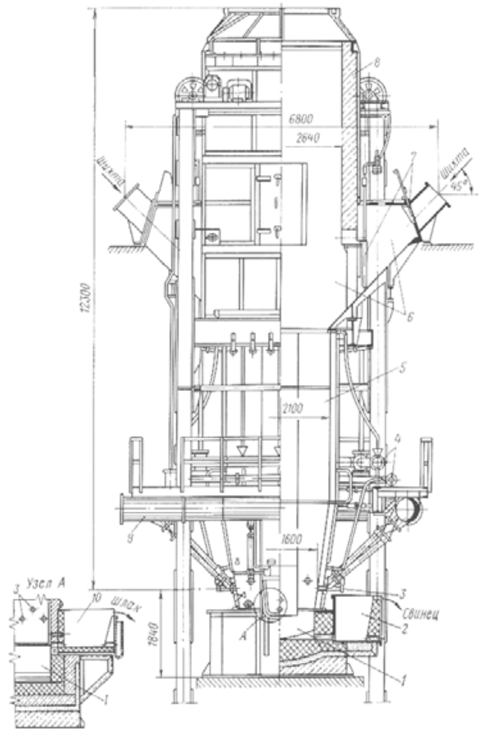
During the smelting process, the matte yield is negligible. The copper content in them is low and varies insignificantly - from 15 to 20 %. The ratio of copper to lead in these mattes is at the level of 1,0. The decrease in the copper content in matte can be explained by a significant redistribution of it in rough lead. The mattes obtained in the process of mine smelting are practically unsuitable for further processing by conversion, due to the low copper content (up to 20 %) and high concentrations of impurities - lead, arsenic and antimony. The sum of antimony and arsenic in mattes is 1,5 %. Together with impurities, a significant amount of lead passes into matte, thereby reducing the quality of the resulting polymetallic mattes. The resulting copper-lead mattes are sent for separate processing in a shaft furnace together with other intermediate products and working materials of lead production.

The obtained data indicate that the decrease in lead recovery in the rough metal is mainly due to its losses with matte and slag.

The presence of lead in the matte reduces the quality of the products obtained, reduces the extraction of lead into the rough metal, and also complicates the further processing of copper-lead matte during the conversion process to obtain rough copper.

2.2 Theory and practice of mine recovery melting

Reducing melting is the most common process for producing lead, which is characterized by versatility and high technical and economic indicators. At present, in most lead plants, recovery melting is carried out in mine furnaces (Fig. 2), since it is easy to create and regulate the recovery atmosphere.



1-hearth; 2-black lead extraction siphon; 3-tuyere; 4-water cooling system collector; 5-furnace shaft; 6-grate; 7-loading gate; 8 - roof of the grate; 9-blowing grate; 10-slag removal siphon

Figure 2 – Cross section of the mine furnace

The starting materials for melting are lead agglomerate, coke, and air. The agglomerate contains lead, related metals (copper, zinc, gold, silver, bismuth, etc.) and all the necessary components for the formation of slag. Sinter and coke are loaded into the furnace in layers. In the lower part of the furnace (furnace) liquid products of melting accumulate: rough lead, matte, slag. Above the slag layer is a charge column, the lower part of which (0.5–1.0 m) consists of red-hot coke (the focus of the furnace). To Gorenje coke through tuyeres in the furnace is supplied with compressed air. As a result of intensive coke Gorenje the temperature in the focus of the furnace reaches 1500°C. Incandescent furnace gases, passing through the charge column, heat it and participate in the reduction reactions of oxidized compounds of lead and other metals. At the exit from the furnace (in the grate), the gases have a temperature of 200-400°C. The charge column (4-6 m) slowly descends (about 1 m/h) as the coke burns out and the melting products are melted, and it is replenished with the next loads of agglomerate and coke. The liquid products of melting flow down and are collected in the inner furnace, where, due to the difference in density, they are stratified and released from the furnace as they accumulate.

The coke loaded into the furnace is used as fuel and reducing agent. Coke combustion is the main process that occurs during mine smelting, affecting the composition of the gas phase and the specific performance of the furnace. In the region of the tuyeres, the coke is burned by reaction:

$$C + O_2 = CO_2 + 391{,}86\ kJ \qquad (1)$$

$$C + 0{,}5O_2 = CO + 110{,}08\ kJ \qquad (2)$$

Hot gases, rising up, heat the charge, CO_2 interacts with red-hot coke according to the Boudoir reaction:

$$CO_2 + C = 2CO – Q \qquad (3)$$

Carbon monoxide (CO) formed by the reaction (3) is the main reducing agent in the mine furnace. Reduction of metal oxides by carbon oxide occurs as a result of the reaction:

$$MeO + CO \rightleftarrows Me + CO_2 \qquad (4)$$

The reaction (4) is reversible. Depending on the conditions under which the reaction takes place, either reduction of the metal oxide by carbon monoxide or oxidation of the metal by carbon dioxide CO_2 can occur. The direction of the reaction under melting conditions depends on the composition of the gas phase in the furnace. Different concentrations of carbon monoxide and temperatures are required for the reduction of various metal oxides. When reducing melting, it is desirable to restore lead as much as possible, but not to restore zinc to metal. In the case of zinc sublimation, due to its oxidation in the upper part of the furnace, the formation of a refractory paste occurs. In mine smelting, it is also undesirable to reduce iron to metal, since iron, interacting with the carbon of coke, can form a refractory cast iron. As a result, the bottom part of the oven will be formed by the formation of a crust. For selective reduction of lead, without reducing zinc and iron, a certain reducing atmosphere is created in the furnace (no more than 60 % CO). In these circumstances, there is a restoration of the oxide of lead compounds by the reactions:

$$PbO + CO = Pb + CO_2 \qquad (5)$$

$$PbO{\cdot}Fe_2\,O_3 + 2CO = Pb + 2FeO + CO_2 \qquad (6)$$

$$PbO{\cdot}SiO_2 + CO = Pb + SiO_2 + 2CO_2 \qquad (7)$$

Lead sulfate is intensively reduced by carbon oxide to sulfide at 550°C by reaction:

$$PbSO_4 + 4CO = PbS + 4CO_2 \qquad (8)$$

Lead sulfide in the conditions of reducing mine melting is practically not restored and passes into matte. Direct extraction of lead into the rough metal during mine reduction smelting is 90-93%.

During the smelting of lead agglomerate together with lead, oxidized compounds of copper, arsenic, antimony, bismuth and other non-ferrous metals are reduced. These elements dissolve in molten lead, forming a crude metal:

$$Cu_2O + CO = 2Cu + CO_2 \quad (9)$$

$$Cu_2O{\cdot}Fe_2O_3 + 2CO = 2Cu + 2FeO + 2CO_2 \quad (10)$$

$$Cu_2O{\cdot}SiO_2 + CO = 2Cu + SiO_2 + 2CO_2 \quad (11)$$

$$As_2O_5 + 5CO = 2As + 5CO_2 \quad (12)$$

$$Sb_2O_5 + 5CO = 2Sb + 5CO_2 \quad (13)$$

$$Bi_2O_3 + 3CO = 2Bi + 3CO_2 \quad (14)$$

If a lot of sulfur is left in the sinter, then copper oxide reacts with sulfides of other metals by the reactions:

$$Cu_2O + FeS = Cu_2S + FeO \quad (15)$$

$$Cu_2O + PbS = Cu_2S + PbO \quad (16)$$

Copper metal formed by reactions (9) - (10) can interact with sulfides of other metals, for example, with iron sulfide by the reaction:

$$2Cu + FeS = Cu_2S + Fe \quad (17)$$

Which during melting will lead to the formation of an alloy of sulfides of copper, iron, lead – matte.

At a temperature of 1100°C, the process of formation of liquid slag begins, ending with the complete melting of the charge. Oxides of calcium, silicon, aluminum, and magnesium pass into slag.

In lead reduction smelting, higher iron oxides are reduced to FeO. Iron oxide, interacting with quartz, forms silicates ($2FeO \cdot SiO_2$):

$$2Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \quad (18)$$

$$Fe_3O_4 + CO = 3FeO + CO_2 \quad (19)$$

$$2FeO + SiO_2 = 2FeO{\cdot}SiO_2 \quad (20)$$

Iron silicates are the basis of the slag melt from lead mine smelting. Oxidized zinc compounds under melting conditions practically do not recover. Their recovery requires a strong reducing atmosphere and high temperature. Therefore, most of the zinc in the form of oxide and silicate passes into the slag, dissolving in it. Zinc is concentrated in slag with a degree of recovery of up to 90%. Noble metals are 98-99% recovered in crude lead.

2.3 Characterization of high-copper lead production slags and methods for their depletion

One of the promising areas of slag waste processing is the use of modern bubbling processes using multi-chamber melting units, where the corresponding depletion of slags is consistently carried out in order to minimize the loss of non-ferrous metals with slags. Despite the uniqueness and originality of the proposed solutions, each method is characterized by a complex hardware design and is accompanied by large material and energy costs.

When reducing the depletion of slag in one stage, you can get an iron-copper alloy (copper cast iron), which is later used as a wear-resistant material for the production of crushing bodies: balls, rods, armor plates of ball mills, impellers and stators of flotation machines. Despite the positive results obtained, the disadvantages of the method include insufficient study of the behavior of impurities (lead, zinc, arsenic).

Of interest is the method developed in Canada for processing copper-smelting slags with sequential recovery of all metals Strategic Udi process. The complex technology consists of several electric furnaces. The first furnace is used for reducing slag melting with the addition of coke, lime and pyrite in order to deeply impoverish the slag by copper and drive zinc into dust. As a result of impoverishment, poor matte with a content of up to 5 % copper and 11-15% iron is obtained, as well as ferrous slag, which is sent to the second electric furnace and processed into pig iron (1-1.25% C, 0.12% P, 0.3% S) to produce silicate-calcium slag. The process is carried out with the addition of lime and coke. Cast iron from the second furnace in liquid form is sent to the third electric furnace, where it is further processed into steel. Silicate-calcium slag is used for the production of building materials. In the process of such processing, 5.5 tons of slag (0.5% Cu, 2% Zn, 33% Fe) at a consumption of 4.7 tons of limestone, 0.44 tons of pyrite and 0.6 tons of coal were obtained from 2 tons of steel, 0.15 tons of zinc oxide, 0.15 tons of sulfur, 0.025 tons of copper and 5 tons of silicate-calcium slag.

The advantage of this method of impoverishing slags is the low volume of waste gases and the possibility of flexible regulation of recovery conditions, but it is economically justified in places with a low cost of electricity. The disadvantages of the method of impoverishing slags in an electric furnace include the lack of intensive mixing of the melt and the bottom phase, in which valuable components are extracted, which reduces the rate of separation of valuable components into the target product and slows down the processes of formation and separation of phases. These disadvantages can be attributed, perhaps, to all known works devoted to the deep depletion of copper slags with solid reducing agents. However, such complex schemes combine high economic efficiency and minimal environmental harm, due to a sharp reduction in the number of waste products.

The most suitable method for impoverishing non-ferrous metal-rich slags is reducing impoverishment.

In practice, there are already various designs of devices for bubbling impoverishment of slags, which differ in the way of feeding the blast (upper, side) and hardware design. In particular, technologies have been developed for impoverishing copper slag in Ausmelt furnaces, fuel oil furnaces at the Houma plant in China, as well as in furnaces with a design similar to the horizontal Converter – Horno de Limpieza de Escoria (HLE) at the El Teniente plant of Codelko.

A common advantage of bubbling depletion technologies is their high productivity, achieved by accelerating the flow of all physical and chemical processes using intensive mixing of the melt, as well as relatively low energy costs.

The disadvantages of these methods include the short-lived linings of aggregates in conditions of intensive mixing of the slag melt. In addition, the frequency of processes currently used (Ausmelt, HLE) creates certain inconveniences, especially in large-scale production with a large number of rich slags formed.

Thus, from the analysis we can conclude that the reduction of copper-rich slag depletion can be carried out in one stage with the production of copper cast iron and demetallized silicate part, which can be used for the production of building materials. From these positions, the most successful are continuous-action capped devices, among which the most optimal, for the organization of the process, is the Vanyukov furnace (VF).

2.4 Fumigation of zinc-containing slag

2.4.1 Theory and practice of the process

The essence of the fuming process is as follows. Air mixed with a reducing agent (coal dust or natural gas) is blown into a bath of molten slag containing metal oxides. The amount of air insufficient for complete combustion of the reducing agent, so the carbon dust is burnt to carbon monoxide, and natural gas to carbon monoxide and hydrogen, which restores present in the slag metal oxides. The main reactions are as follows:

$$C + O_2 = CO_2 \tag{21}$$

$$CO_2 + C = 2CO \tag{22}$$

$$CH_4 + 0{,}5\ O_2 = CO + 2H_2 \tag{23}$$

$$ZnO + CO = Zn_{vapor} + CO_2 \tag{24}$$

$$ZnO + H_2 = Zn_{vapor} + H_2O \tag{25}$$

Similarly, lead compounds are restored. Iron is partially reduced to metal, which reacts with oxides and sulfides of lead and zinc by reactions:

$$PbO + Fe = Pb + FeO \tag{26}$$

$$PbS + Fe = Pb + FeS \tag{27}$$

$$ZnS + Fe = Zn + FeS \tag{28}$$

Of the components of liquid slag heated to a temperature of 1250-1300°C, cadmium, zinc, lead sulfide, lead oxide and lead (by decreasing vapor elasticity) have a noticeable volatility. The elasticity of zinc oxide vapors at these temperatures is very small and therefore it is not possible to disperse it. In this regard, it is advisable to restore the zinc oxide and drive it away in the form of steam (the boiling point of zinc is 906°C), for which it is necessary to create an appropriate reducing atmosphere in a liquid bath.

The blowing of the slag carries out for 1.5-3.0 hours. The sublimation of lead and cadmium during fusing does not determine by the duration of the process. The main amount of lead is distilled from the slag in 30-40 minutes of purging, which is due to the high volatility of lead oxide and sulfide vapors. The distillation of cadmium completes within the first minutes.

When fuming, copper and precious metals remain in the slag, which is one of the disadvantages of the process. To extract them, it is recommended to process liquid slags after purging with sulfides in the presence of a reducing agent in order to separate copper, silver and gold into matte or alloy.

Oxides in the slag, such as CaO and FeO, contribute to the distillation of zinc, and the presence of Fe_2O_3 and SiO_2 in the slag reduces the rate and degree of its distillation. Slags containing more than 30-35% SiO_2 are so viscous that they cannot be processed into a fuming furnace.

After fuming, the slag from the furnace sends to the dump. Gases after burning volatiles from slag and carbon monoxide have a temperature of more than 1200°C, so they diverters to waste heat boilers. Under the boiler, they cools to 320°C and then additionally give off heat in the economizer (up to 120°C) to heat the boiler feed water, from where they come to the dust filters in bag filters.

The practice of the process. In a preheated furnace, 35-90 tons of liquid slag are poured and compressed air through a specially designed tuyeres with a diameter of 55-100 mm (11-36 pieces are installed on the longitudinal walls of the furnace) is blown into coal, crushed to 200 mesh (0.07 mm, 85%) . The process is periodic. The cycle includes four stages: slag pouring, heating it, recovery and distillation, and slag discharge. Slag directly from the settling tank of melting furnaces or from the mixer is poured into the slag sublimation kiln via a water-cooled loading chute. The pouring window is located at an altitude of 1.5-2.0 m from the hearth of the furnace. The furnace is filled with slag to the level of 0.9-1.6 m.

When recovering with natural gas, tuyeres are installed for the furnace (one for each box) through which converted gas supplies. Zinc and lead are distilled off in a liquid bath. At the stage of heating the slag, 80-100% of the air necessary for combustion is fed into the furnace (excess coefficient 0.8-1.0). In this case, all solid particles of slag are melted. The temperature of the bath rises to 1250°C. At the recovery stage, air supplies to the bath with a coefficient of excess of 0.6-0.75.

The use of coal dust requires the construction and operation of expensive and explosive installations for grinding and drying coal, transporting and dosing it when fed into the furnace. Coal dust in the slag bath does not burn out completely, its mechanical removal reaches 25% of the total consumption. This complicates the utilization of heat of the exhaust gases, the capture and subsequent processing of sublimates. Replacing coal dust with natural gas reduces investment by eliminating the preparation and supply of coal dust, can increase productivity, reduce fuel costs, simplify the automatic control system, improve sanitary conditions and increase the culture of production.

To intensify the fuming process, the blast is heated, enriched with oxygen, water vapor is used in the blast to increase the reducing ability of the gas by decomposing it ($H_2O + C = H_2 + CO$), metal reducing agents are used (for example, the magnetic fraction of clinker is the residue from slag Waelz) etc.

2.4.2 Main technological indicators of the process

The advantages of the fuming process are that:

1) no preparation of raw materials for processing, because liquid slag uses;
2) the heat of the liquid slag uses to conduct the process;
3) most of the heat from fuel combustion and metal vapor oxidation uses under boilers, which increases the efficiency of the plant;
4) high recovery of metals from slag.

Main characteristics of the process:

The productivity of the device - 25-45 tons of slag per day;
Fuel consumption - 20-25 % of the slag weight;
The blast flow rate – 450 m^3/min;
The temperature – 1300^0C.
Metal extraction:
  lead to dust – 90-98%,
  zinc to dust – 88-94%,
  germanium - 60%.

3 Reducing depletion of high-copper Isasmelt slags

3.1 Thermodynamic calculations of recovery of high-copper slags with natural gas

The most rational and effective way is the reductive depletion of slag using natural gas, which involves the selective separation of metals into target products.

To identify the mechanism of reduction of non-ferrous metal oxides, iron and arsenic by natural gas, a thermodynamic analysis of the reactions of the interaction of components of slag with natural gas was carried out, which is given in table 1.

Table 1 - Calculated values of Gibbs energy (ΔG^0T) for high-temperature processing of high-copper slag with natural gas

Reaction	Gibbs energy, ΔG^0T, kJ / mol			
	Temperature, K			
	1273	1473	1573	1273…1573
$3Cu_2O$(liquid) + CH_4 = 6Cu (liquid) + CO g + $2H_2O$ g	- 395,8	–456,5	–481,2	ΔG^0T=- 33,2 - 0,286 • T
3ZnO (liquid) + CH_4 = 3Zn g + CO g + 2 H_2O g	3,5	–133,6	–201,5	ΔG^0T= – 881,06 –0,689 • T
3PbO (liquid) + CH_4 = 3Pb g + CO g + 2 H_2O g	–141,2	–253,2	–308,1	ΔG^0T = 585,6 – 0,572 • T
$2As_2O_5$ (liquid) + CH_4 = $2As_2O_3$ g + CO_2 g + 2 H_2O g	–943,2	-1064,0	-1122,7	ΔG^0T= –171,76 – 0,605 • T
3FeO (liquid) + CH_4 = 3Fe (liquid) + CO g + 2 H_2O g	–105	–167,0	–197,6	ΔG^0T = 291,3 – 0,311 • T

The calculated values of the Gibbs energy change for the reduction of non-ferrous metals and arsenic oxides by natural gas (Table 1) show the possibility of deep reduction of non-volatile arsenic (V) oxide by natural gas to its volatile oxide (III). The ΔG^0T values of reaction (4) at given temperatures are no less than two times (in absolute value) higher than $\Delta G^0 T$ values of reduction reactions of non-ferrous metal and iron oxides (Table 1), which indicates a high probability of reduction of As_2O_5 to volatile arsenic oxide (As_2O_3) and its removal with exhaust gases.

The thermodynamic probability of copper recovery from its oxide during the processing of slag by natural gas is very high. The decrease in Gibbs energy by reaction (1) ΔG^0 1573K = –481.2 kJ/mol is more than twice the change in Gibbs energy obtained by the reduction of copper oxide with coal (ΔG^0 1573K = –192.3 kJ /mol). In the absence of coal and a collecting metal phase, one should not expect the release of copper into an independent bottom phase due to the relatively low copper content in the initial slag. In this case, metallic copper, which is formed in a small amount by reaction (1), is present in the slag in the form of finely dispersed metal inclusions.

The intensive bubbling of slag melt by natural gas creates favorable conditions for the coalescence of a fine suspension of metallic copper. As a result, an independent bottom phase (alloy) is formed. In this case, the residual copper content in the slag is determined only by its insignificant solubility.

Providing deep reducing conditions (coal addition, natural gas purging) significantly increases the thermodynamic probability of zinc oxide and lead reduction. The calculated values of the Gibbs energy loss of reactions (2) and (3) at a temperature of the slag depletion process (1300°C) exceed $\Delta G^0 1573$ of reaction (5) - reduction of iron oxide by natural gas. The probability of reduction of iron from its oxide will be subordinate due to insufficient excess of coal and low temperature. In addition, the formation of metallic iron will be difficult as long as copper, lead and zinc oxides are present in the slag. The minimum amount of metallic iron passing from slag to alloy by reaction (5) will not have a significant effect on the quality and properties of the resulting alloy.

3.2 The selection of optimal parameters for depletion of high-copper slags with natural gas

Based on the results of thermodynamic analysis *technological modes* and *optimal parameters* for impoverishing slags with natural gas in the presence of coal were selected.

Process mode:

Use natural gas to regulate the heat balance of the process. The melting process is carried out to obtain a copper-ferrous alloy with a low iron content of ~ 2%. The copper-ferrous alloy obtained after melting can be used as intended for producing copper or for making various materials (balls for mills, etc.).

Slag after melting is used to obtain building materials (cement, etc.).

The resulting stream are used to produce lead and zinc.

Optimal parameters of the enterprises:

– Natural gas consumption – 30% more than the stoichiometrically necessary amount for reducing arsenic, lead and zinc;

- Coal consumption – 20% more than the stoichiometrically necessary amount for the recovery of copper and magnetite;

- Melting temperature – 1300°C.

3.3 Metallurgical calculations of the depletion process of high-copper slag

3.3.1 Calculating the material balance of the process

We calculate for 100 kg. of slag. Calculations for zinc-containing lead smelting slag of the following composition, %: 0.7 Cu_2O; 0.4 PbO; 5.56 ZnO; 33.7 SiO_2; 50.3 FeO; 3.1 CaO; 2.5 Al_2O_3; 0.6 MgO; 3.08 the rest-other (table 2).

Table 2 – Chemical composition of slag

Elements	Content, % (mass.)
Cu_2O	0,7
PbO	0,4
ZnO	5,56
As_2O_5	0,06
FeO	50,3
SiO_2	33,7
CaO	3,1
Al_2O_3	2,5
MgO	0,6
Other	3,08
Total	100

From practice data, the mineralogical composition of lead production slags is shown in table 3.

Table 3 – Mineralogical composition of slags

Name	Cu	Pb	Zn	As	Fe	Si	Ca
Slags	Cu_2S Cu_2O	PbO	ZnO	As_2O_5	FeS FeO Fe_3O_4	SiO_2	CaO

The rational composition of the slag is shown in table 4.

A detailed calculation of the rational composition of the slag is shown in Appendix A.

Table 4 - Rational composition of slag

Minerals	Components												
	Cu	Pb	Zn	As	S	Fe	O_2	SiO_2	CaO	Al_2O_3	MgO	Other	All
Cu_2O	0,54						0,07						0,61
Cu_2S	0,08				0,02								0,10
PbO		0,37					0,03						0,40
ZnO			4,47				1,06						5,56
As_2O_5				0,05			0,02						0,07
FeS					00,6	1,05							1,65
FeO						34,47	9,85						44,32
Fe_3O_4						3,60	1,37						4,97
SiO_2								33,7					33,70
CaO									3,10				3,10
Al_2O_3										2,50			2,50
MgO											0,6		0,60
Other												2,42	2,42
Total	0,62	0,37	4,47	0,10	0,62	39,12	12,44	33,7	3,10	2,50	0,60	2,42	100,0

Calculation of natural gas requires for the recovery of $As_2 O_5$
$2As_2 O_5$ (liquid) + CH_4 = $2As_2O_3$ g + CO_2 g + $2H_2O$ g:

$$M_{As} = (0{,}10 \cdot 16)/459{,}68 = 0{,}002$$

In the beginning we find the total amount of O_2 coming from the initial slag:

$$G_{O2}^{inital\ s.} = G_{O2}^{fin.} \quad (29)$$

Others:

$$G_{others}^{inital\ s.} = 100 - G_{Cu}^{inital\ s.} - G_{Pb}^{inital\ s.} - G_{Fe}^{inital\ s.} - G_{Zn}^{inital\ s.} - G_{S}^{inital\ s.} - G_{As}^{inital\ s.} - G_{O2}^{inital\ s.} - G_{SiO2}^{inital\ s.} - G_{CaO}^{inital\ s.} \quad (30)$$

where: 100 - this is the amount of initial slag, 100 kg.
$G_{Me}^{inital\ s.}$- is the amount of metals in the initial slag, kg.

After that, set the initial values for calculating the material balance. Based on these practices, we set the distribution of components by melting products.

Copper:
Extraction to alloy – 96,40%;
Extraction to slag – 3,60%.

Lead:
Extraction to slag – 7%;
Extraction to dust – 93%.

Zinc:
Extraction to slag – 4,80 %;
Extraction to dust – 95,20%.

Ferrum:
Extraction to alloy – 0,02%;
Extraction to slag – 99,48%;
Extraction to dust – 0,50%.

Arsenic:
Extraction to slag – 4,71%;
Extraction to dust – 95,29%.

Amount and composition of the dust

The amount and composition of dust obtained after melting calculates by the formula:

$$G_{Me}^{dust} = \frac{G_{Me}^{ave.slag} * U_{Me}^{dust}}{100} \quad (31)$$

where G_{Me}^{dust} – amount of metal in the dust (Me – Cu, Zn, Pb etc.);
$G_{Me}^{ave.slag}$ – amount of the metal in the averaged slag;
U_{Me}^{dust} – extraction metals to the dust.

Calculation for lead:

$$G_{Pb}^{dust} = \frac{G_{Pb}^{ave.slag} * U_{Pb}^{dust}}{100} \quad (32)$$

And so for each metal, for O_2 its 1 % of initial amount in the ave. slag.
Then sum up the obtained results and get the total amount of dust without oxidation.

$$G_{dust}^{w.o.O2} = G_{Pb}^{dust} + G_{Pb}^{dust} + G_{Pb}^{dust} + G_{Pb}^{dust} + G_{Pb}^{dust} \quad (33)$$

where G_{Me}^{dust} – amount of metal in the dust.

The results are summarized in table 5.

Table 5 – Amount and composition of the dust

Components	Amount, kg.	Content, %
Pb	0,35	4,34
Fe	0,20	2,46
Zn	4,25	53,50
As	0,04	0,54
SiO_2	0,24	2,97
CaO	0,02	0,20
Al_2O_3	0,01	0,16
MgO	0,003	0,04
S	0,62	7,80
CH_4	0,39	4,89
C	0,37	4,66
O_2	1,31	16,51
Other	0,15	1,93
Total:	7,95	100

The content is calculated using the formula:

$$\% \text{ Me} = \frac{G_{Me}^{dust}}{G_{dust}} \cdot 100 \quad (34)$$

where % Me – content metal the in dust

Amount and composition of the alloy

The composition and amount of the alloy is shown in table 6. Detailed calculation of the composition the alloy is shown in Appendix B.

Table 6 – Amount and composition of the alloy

Components	Amount, kg.	Content, %
Cu	0,60	98,30
Fe	0,007	1,28
Other	0,003	0,42
Total	0,61	100

Amount and composition of the slag

The composition and amount of slag is shown in table 7. Detailed calculation of the composition of slag is shown in Appendix C.

Table 7 – Amount and composition of the slag

Components	Amount, kg.	Content, %
Pb	0,03	0,03
Fe	38,92	42,24
Cu	0,02	0,02
Zn	0,21	0,23
As	0,002	0,002
SiO_2	33,46	36,32
CaO	3,08	3,35
Al_2O_3	2,49	2,70
MgO	0,60	0,65
O_2	10,92	11,85
Other	2,40	2,60
Total	92,3	100

The calculation of the require coal for the reduction of Cu_2O, ZnO, and Fe_3O_4 in the initial slag calculates using the formula:

$$G_C^{coke} = \frac{G_{PbO} * Mc}{M_{Pb} + M_O} = 0,05 \qquad (35)$$

where G_C^{coke} – the amount of C in the coal to recovery;

G_{PbO} – the amount of metals in the slag;

M_C – molar mass of carbon;

M_{PbO} – molar mass of lead.

Then Cu_2O:

$$G_C^{coke} = \frac{G_{Cu_2O} * Mc}{M_{Cu} * 2 + M_O} = 0,05 \qquad (36)$$

Also ZnO:

$$G_C^{coke} = \frac{G_{ZnO} * Mc}{M_{Zn} + M_O} = 0,62 \qquad (37)$$

Similarly, Fe_3O_4 :

$$G_C^{coke} = \frac{G_{Fe_3O_4}^{\text{общ,рац,сос}} * M_C}{(M_{Fe} * 3 + M_{O_2 * 4})} = 0,25 \qquad (38)$$

Then summarize the amount of C:

$$G_C^{coal} = G_c^{(160)} + G_c^{(161)} + G_c^{(161)} + G_c^{(161)} = 0,97 \qquad (39)$$

According to practice results, C is taken 1.5 more of the required amount.

$$G_C^{coal} = G_C^{coal} \cdot 1,5 = 1,46 \qquad (40)$$

where G_C^{coal} – from formula (3.11)

Composition of coal: C- 75 %; others- 25 %:

$$G_{\cdot}^{coal} = \frac{G_C^{coal}}{\%G_{coal}^{\cdot}} \cdot 100 = 1,9 \qquad (41)$$

where $G_{\cdot}^{coal}$ – total amount of coal;
G_C^{coal} – amount of C from formula (12);
$\%G_{coal}^{\cdot}$ – content of C in coal.

Other 25 % goes to the slag.

$$G_{other}^{coal} = G_{coal}^{\cdot} \cdot 0,12 = 0,23 \qquad (42)$$

Calculation of the amount of blast and the resulting exhaust gases.

The composition and amount of exhaust gases are shown in the table 8. A detailed calculation of the exhaust gases is shown in Appendix D.

Table 8 – Amount and composition of the exhaust gases

Components	Amount, kg.	Composition, %	Volume, м^3	Content, %
SO_2	1,12	7,74	0,43	3,78
N_2	9,28	64,18	8	70,42
CO_2	1,79	12,37	0,94	8,27
CO	2,27	16,69	1,99	17,51
Total:	14,46	100,00	11,36	100,00

The obtained results are summarized in the total material balance of melting, which is shown in table 9.

Table 9 – Material balance of the depletion process

Products	All		Cu		Pb		Zn		As		Fe		S	
	%	G	%	G	%	G	%	G	%	G	%	G	%	G
Loaded:														
Slag	99,12	99,80	0,62	0,62	0,37	0,37	4,48	4,47	0,046	0,045	39,20	39,12	0,62	0,62
Natural gas	0,39	0,40												
Coal	0,49	0,49												
Total:	100	100,69		0,62		0,37		4,47		0,045		39,12		0,62
Received:														
Allay	0,61	0,61	98,3	0,60							1,282	0,0078		
Slag	92,31	92,13	0,02	0,02	0,03	0,03	0,23	0,21	0,00232	0,00214	42,24	38,92		
Dust, gas	7,96	7,95			4,34	0,35	53,50	4,25	0,54	0,0433	2,46	0,20	7,80	0,62
Total:	100	100,69		0,62		0,37		4,47		0,045		39,12		0,62

Products	SiO_2		CaO		Al_2O_3		MgO		CH_4		C		O_2		Other	
	%	G	%	G	%	G	%	G	%	G	%	G	%	G	%	G
Loaded:																
Slag	33,77	33,70	3,11	3,10	2,51	2,50	0,60	0,60					12,25	12,23	2,42	2,42
Natural gas									98	0,39					2	0,008
Coal											75	0,37			25	0,12
Total:		33,70		3,10		2,50		0,60		0,39		0,37		12,23		2,55
Received:																
Allay															0,42	0,003
Slag	36,32	33,46	3,35	3,08	2,70	2,49	0,65	0,60					11,85	10,92	2,60	2,40
Dust, gas	2,97	0,24	0,20	0,02	0,16	0,01	0,04	0,003	4,89	0,39	4,66	0,37	16,51	1,31	1,93	0,15
Total:		33,70		3,10		2,50		0,60		0,39		0,37		12,23		2,55

3.3.2 Calculating the heat balance of the process

According to practice, to calculating the heat balance was selected the following table values.

Table 10 – Standard data from practice

Temperature of slag	25	t_{charge}	ºC
Temperature of coal	25	t_{coal}	ºC
Heat capacity of coal	0,24	C_{coke}	kcal/(kg.·ºC)
Temperature of atmosphere	25	T_a	ºC
Heat capacity of atmosphere	0,24	C_a	kcal/(kg.·ºC)
Temperature of liquid slag	1200	T_{ls}	ºC
Heat capacity of slag	0,3	C_{ls}	kcal/(kg.·ºC)
Temperature of slag	1250	T_{sl}	ºC
Temperature of slag	0,3	C_{sl}	kcal/(kg.·ºC)
Temperature of exhaust gas	850	t_{gas}	ºC
Heat capacity of SO_2	0,57	$C(SO_2)$	kcal/(m^3 ·ºC)
Heat capacity of N_2	0,244	$C(N_2)$	kcal/(m^3 ·ºC)
Heat capacity of CO_2	0,245	$C(CO_2)$	kcal/(m^3 ·ºC)
Heat capacity of CO	0,245	C(CO)	kcal/(m^3 ·ºC)
Heat capacity of water (steam)	0,428	$C(H_2O)$	kcal/(m^3 ·ºC)
Heat capacity of liquid water	1	$C(H_2O)$	kcal/(m^3 ·ºC)
Heat of evaporation of water at 100 ºC	539	$\lambda(H_2O)$	kcal/kg.

The mass of slag:
All data from the material balance table 9.
Calculation of incoming heat.
Physical heat of slag:

$$Q_s = G_{total} \cdot c_s \cdot (T_s - 20) = 100 \cdot 0{,}3 \cdot (25-20) = 150 \text{ kcal} \quad (43)$$

General formula for calculating incoming heat:

$$Q_{incom} = G_m \cdot c_m \cdot (T_m - 20) \quad (44)$$

where G_m - amount of material;
c_m - heat capacity of the material;
T_m- material temperature.

Q_{incom} - heat introduced by liquid slag at 1200 ºC (amount of liquid slag 1/3) m_{sl} = 33.

$$Q_{l.s} = c_s \cdot m_s \cdot t_s = 0,3 \cdot 33,3 \cdot 1200 = 11988 \text{ kcal} \qquad (45)$$

The heat found in formula (3.17) is in kcal, so all value is translated into kJ. To do this, we multiply the obtained data by 4,134:

$$Q_{kJ} = Q_{kcal} \cdot 4,134 = 11988 \cdot 4,134 = 51\,358,392 \text{ kJ} \qquad (46)$$

Heat from combustion C:

$$C + O_2 = CO_2 + 94,052 \text{ kcal/mol} \qquad (47)$$

$$CO_2 + C = CO + 26,416 \text{ kcal/mol} \qquad (48)$$

$$Q_{CO2} = \frac{94052 * G_C^{CO2}}{M_C + M_{O2} * 2} = 1047 \text{ kcal} \qquad (49)$$

$$Q_{CO} = \frac{26416 * G_C^{CO}}{M_C + M_{O2}} = 682 \text{ kcal} \qquad (50)$$

$$Q_{fuel} = (Q_{CO2} + Q_{CO}) \cdot 4,134 = (1047 + 682) \cdot 4,134 = 9\,934,3 \text{ kJ} \qquad (51)$$

Incoming heat:

$$Q_{incom.} = Q_{fuel} + Q_{l.s} + Q_s = 61\,912,4 \text{ kJ} \qquad (52)$$

Calculation of heat expenditure.
General formula:

$$Q_{expen.} = G_{pr.} \cdot c_{pr.} \cdot (T_{pr.} - 20) \qquad (53)$$

$$Q_{expen.}^{sl.} = G_{sl.} \cdot c_{sl.} \cdot (T_{sl.} - 20) = 92,3 \cdot 0,3 \cdot 1230 = 34\,058,7 \text{ kcal} \qquad (54)$$

$$Q_{expen.}^{al.} = G_{al.} \cdot c_{al.} \cdot (T_{al.} - 20) = 0,61 \cdot 0,44 \cdot 1230 = 330,13 \text{ kcal} \qquad (55)$$

where $G_{pr.}$ −amount of products;
$T_{pr.}$ −temteráture of products;
$c_{pr.}$ – heat capacity of products.

Using the formula (3.25), we calculate the heat for lead bullion, matte, and slag:

$$Q_{en.reac.} = Q_{PbO} + Q_{Fe_3O_4} \qquad (56)$$

$$PbO = Pb + 0.5\ O_2 - 98,942 \qquad (57)$$

$$Q_{PbO} = \frac{98942 * G_{PbO}^{tot.ra.com.}}{M_{Pb} + M_{O_2}} = 177{,}47\ \text{kcal} \tag{58}$$

$$Fe_3O_4 = 3FeO + 0.5\ O_2 - 76{,}908 \tag{59}$$

$$Q_{Fe_3O_4} = \frac{76908 * G_{Fe_3O_4}^{tot.ra.com.}}{M_{Fe} * 3 + M_{O_2} * 4} = 1647{,}6\ \text{kcal} \tag{60}$$

$$Q_{en.reac.} = Q_{PbO} + Q_{Fe_3O_4} = 1825{,}07\ \text{kcal} \tag{61}$$

Formula for gases (SO_2, CO_2, CO, N_2):

$$Q_{(MeO)} = G_{MeO} * c_{MeO}(T_{MeO} - 20) \tag{62}$$

$$Q_{(SO2)} = G_{SO2} * c_{SO2}(T_{SO2} - 20) = 1{,}12 \cdot 0{,}57 \cdot 830 = 529{,}9\ \text{kcal} \tag{63}$$

$$Q_{(CO)} = G_{CO} * c_{CO}(T_{CO} - 20) = 2{,}27 \cdot 0{,}245 \cdot 830 = 461{,}6\ \text{kcal} \tag{64}$$

$$Q_{(CO2)} = G_{CO2} * c_{CO2}(T_{CO2} - 20) = 1{,}79 \cdot 0{,}245 \cdot 830 = 363{,}9\ \text{kcal} \tag{65}$$

$$Q_{(N2)} = G_{N2} * c_{N2}(T_{N2} - 20) = 9{,}28 \cdot 0{,}244 \cdot 830 = 1879{,}3\ \text{kcal} \tag{66}$$

$$Q_{ex.gas} = Q_{SO_2} + Q_{CO_2} + Q_{CO} + Q_{N_2} = 3\ 234{,}7\ \text{kcal} \tag{67}$$

Total heat expenditure:

$$Q_{expen.} = (Q_{sl.} + Q_{al.} + Q_{ex.gas} + Q_{en.reac.}) * 4{,}134 = 61\ 735.9\ kJ \tag{68}$$

Find the final result:

$$Q_{expen.} = Q_{expen.} - Q_{expen.} = 61\ 912{,}4 - 61\ 735{,}9 = 176{,}5\ \text{kJ} \tag{69}$$

If the obtained value is with a minus sing, then add fuel to equalize the values. If we get a number with a plus sign, then we consider the cooling of the furnace with caissons. In our case, the value is with a plus sign, therefore, it is necessary to consider the cooling of the furnace with caissons.

4 Technological scheme of slag processing and the main technological indicators of the process

From the obtained results, the technological scheme (Fig. 3) was constructed which shows the entire processing non-ferrous metallurgy slags with the extraction of valuable metals into target products.

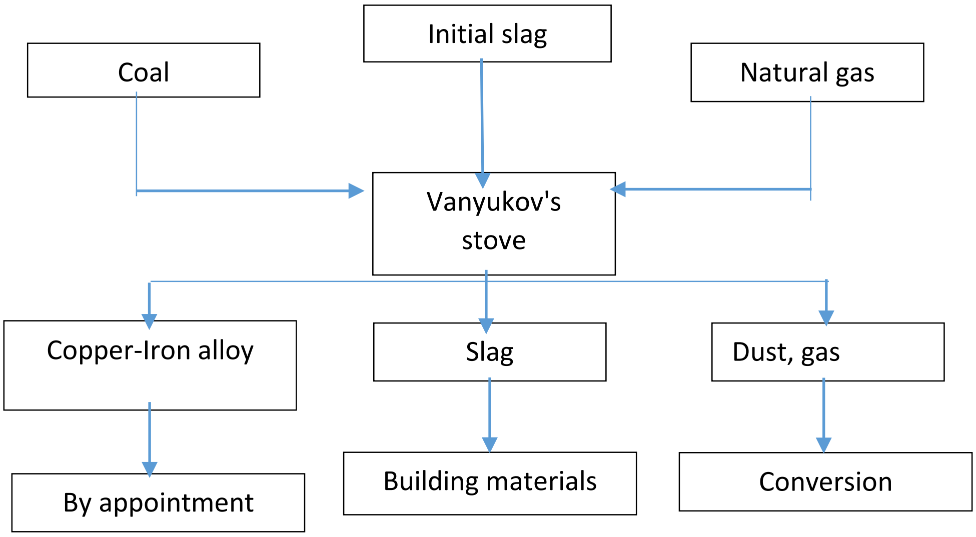


Figure 3 – General technological scheme of slag processing

The main technological values of the depletion process of slags with natural gas are shown in table 11.

Table 11 - Technological values of the depletion process

Name	Values
The extraction of copper in the alloy, %	98,3
Extraction of lead in dust, gases, %	95
The extraction of zinc in the dust, gases, %	92
Extraction of arsenic into dust, %	99
Iron content in the alloy, %	1,28
Natural gas expenditure, kg.	0,4
Temperature,°C	1300

CONCLUSION

Large amounts of accumulated and growing volumes of current slag waste require finding new approaches and solutions for their use as an additional source of raw materials for the extraction of valuable metals. Of particular interest are autogenous smelting slags and continuous conversion, characterized by a complex chemical composition and high copper content.

A thermodynamic analysis of the interaction of slag components with natural gas was carried out in the work. A mechanism has been established for the distribution of non-ferrous metals and arsenic under conditions of depletion of slag by natural gas in the presence of coal. The results obtained are of fundamental importance from the point of view of choosing the optimal technological parameters and modes that ensure the equilibrium distribution of metals between the smelting products during the organization of recovery methods of depletion of high-copper slags.

Based on metallurgical calculations, technological conditions and optimal parameters of the depletion process of high-copper slag are determined. The obtained results of thermodynamic and metallurgical calculations of the method of depletion of high-copper slag allows us to offer a technological scheme of slag processing with selective extraction of copper, lead and zinc into commercial products.

The optimal parameters were selected for the process of reducing depletion of slag by natural gas in the presence of coal and the expected extraction of non-ferrous metals and arsenic in the target products.

The extraction of copper into the alloy was 9 %, lead and zinc to dust – 95 % and 92 %, respectively, of arsenic to dust - 99 %.

The residual metal content in the slag, %: Cu – 0,02; Pb – 0,03; Zn – 0,23.

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Appendix A

From table 2, we know the mineralogical composition of the slag, after calculate the rational composition of the slag.

First of all calculate the mineralogical composition for copper.

$$G_S^{Cu_2S} = \frac{G_{Cu} * M_S}{M_{Cu} * 2} \quad (1)$$

where $G_S^{Cu_2S}$ - the amount of sulfur associated with copper

G_{Cu} - amount of copper in the original slip

M_S - molar mass of sulfur

M_{Cu} - molar mass of copper

In the chemical composition O_2 we find in the end which is associated with all components. Other 100 - ∑ components:

$$G_{O_2}^{Cu_2O.} = G_{Cu}^{int.sl} \quad (2)$$

$$G_{O_2}^{Cu_2\,O.} = \frac{G_{Cu}^{Cu2O.} * M_{O2}}{M_{Cu} * 2} \quad (3)$$

$$G_{Cu_2O} = G_{Cu}^{Cu_2O.} + G_{O_2}^{Cu_2O.} \quad (4)$$

Then PbO:

$$G_{O_2}^{PbO.} = \frac{G_{Pb}^{PbO.} * M_{O_2}}{M_{Pb}} \quad (5)$$

Then find ZnO exactly the same way:

$$G_{Zn}^{ZnO} = G_{Zn}^{int.sl.} \quad (6)$$

$$G_{O_2}^{ZnO} = \frac{G_{Zn}^{ZnO} * M_{O_2}}{M_{Zn}} \quad (7)$$

$$G_{ZnO} = \left(G_{Zn}^{ZnO} + G_{O_2}^{ZnO}\right) \quad (8)$$

Also As_2O_5:

$$G_{As}^{As_2O_5} = G_{As}^{int.sl.} \quad (9)$$

$$G_{O_2}^{As_2O_5} = \frac{G_{As}^{As_2O_5} * M_{O_2} * 5}{M_{As} * 2} \quad (10)$$

$$G_{As_2O_5}=G_{As}^{As_2O_5}+G_{O_2}^{As_2O_5} \quad (11)$$

According to practice, the Fe content in Fe_3O_4 is 20 %.

$$G_{Fe}^{Fe_3O_4}=G_{Fe}^{int.sl.}\cdot 20\ \% \quad (12)$$

$$G_{O_2}^{Fe_3O_4}=\frac{G_{Fe}^{Fe_3O_4}*M_{O2}*4}{M_{Fe}*3} \quad (13)$$

$$G_{Fe_3O_4}=G_{Fe}^{Fe_3O_4}+G_{O_2}^{Fe_3O_4} \quad (14)$$

Also SiO_2, CaO and other:

$$G_{SiO_2}=G_{SiO_2}^{int.sl.} \quad (15)$$

$$G_{CaO}=G_{CaO}^{int.sl.} \quad (16)$$

$$G_{other}=G_{other}^{int.sl.} \quad (17)$$

The obtained calculation results are shown in table 3.

Appendix B

For the calculation, the following formula was used:

$$G_{Me}^{al.} = \frac{G_{Me}^{a/al.} * U_{Me}^{al.}}{100} \tag{18}$$

where $G_{\mathrm{Me}}^{\mathrm{Alloy}}$ – quantity of metal in alloys (kg);
$U_{Me}^{al.}$ – extraction of metals into an alloy (%);
$G_{Me}^{a/al.}$ – quantity of metal in the charge (kg).

So for Cu:

$$G_{Cu}^{al.} = \frac{G_{Cu}^{a/al.} * U_{Cu}^{al.}}{100} \tag{19}$$

Exactly the same calculations for Fe.
The contents according to the formula:

$$\% \text{ Me} = \frac{G_{Cu}^{alloy} * 100}{G_{alloy}} \tag{20}$$

$$G_{alloy} = G_{Fe}^{alloy} + G_{Cu}^{alloy} \tag{21}$$

Appendix C

The number of metals in the slag is found by the difference:

$$G_{\mathrm{Me}}^{slag}=G_{Me}^{charge}-G_{\mathrm{Me}}^{dust}-G_{\mathrm{Me}}^{alloy} \qquad (22)$$

where G_{Me}^{slag} - amount of metal in the slag (kg);
G_{Me}^{charge} - amount of metal in the initial charge (kg);
G_{Me}^{dust} - amount of metals in the dust;
G_{Me}^{alloy} - amount of metals in alloys.

$$G_{\mathrm{Me}}^{slag}=100-64{,}39-5{,}245=30{,}365 \qquad (23)$$

Slag is the oxide product, metals are converted into oxide compounds. These are such metals: →Pb→PbO; Cu →Cu_2O; Zn→ZnO; Fe→FeO; As→As_2O_5

$$G_{Pbo}=\frac{G_{Pb}^{slag}*(M_{Pb}+M_{O_2})}{M_{Pb}} \qquad (24)$$

where G_{PbO} - amount of PbO
G_{Pb}^{slag} -amount of Pb in the slag

$$G_{Pbo}=\frac{0{,}07*(207+32)}{207}=0{,}08 \qquad (25)$$

$$G_{Cu_2}O=\frac{G_{Cu}^{slag}*(M_{Cu}*2+M_{O_2})}{M_{Cu}*2} \qquad (26)$$

$$G_{Cu_2}O=\frac{0{,}023*(64*2+32)}{128}=0{,}028 \qquad (27)$$

$$G_{ZnO}=\frac{G_{Zn}^{slag}*(M_{Zn}+M_{O_2})}{M_{Zn}} \qquad (28)$$

$$G_{ZnO}=\frac{0{,}2*(65+32)}{65}=0{,}29 \qquad (29)$$

$$G_{FeO}=\frac{G_{Fe}^{slag}*(M_{Fe}*+M_{O_2})}{M_{Fe}} \qquad (30)$$

$$G_{FeO}=\frac{0{,}37*(56+32)}{56}=47{,}80 \qquad (31)$$

$$G_{As_2O_5}=\frac{G_{As}^{slag}*(M_{As}*2+M_{O_2}*5)}{M_{As}*2} \qquad (32)$$

$$G_{As_2O_5}=\frac{0{,}004*(75*2+32*5)}{75*2}=0{,}008 \qquad (33)$$

After that, by the difference we find O_2 in the slag. General formula:

$$G_{O_2}^{MeO}=G_{MeO}-G_{Me}^{slag} \quad (34)$$

where $G_{O_2}^{MeO}$-amount of O_2 in MeO.
G_{MeO}-amount of MeO (kg.)
G_{Me}^{slag}-amount Me in the slag(kg.)

All O_2 found by formula (34) are summed and subtracted from the number of O_2.

Appendix D

Find the amount of sulfur that passes into gases.

$$G_S^{gases}=G_S^{a.} \tag{35}$$

$$G_{SO_2}^{gases}=\frac{G_S^{gases}*M_S+M_{O_2}}{M_S}=1{,}12 \tag{36}$$

CO_2: CO = 1:2:

$$G_C^{CO}=2/3\quad G_c^{coal}=0{,}97 \tag{37}$$

$$G_C^{CO_2}=1/3\quad G_c^{coal}=0{,}49 \tag{38}$$

$$G_{CO}=\frac{G_C^{CO}}{M_c}*(M_C+M_{O_2})=2{,}27 \tag{39}$$

$$G_{CO_2}=\frac{G_C^{CO_2}*(M_C+M_{O_2}*2)}{M_C}=1{,}79 \tag{40}$$

Find O_2 which must be submitted to the oven for SO_2, CO and CO_2

$$G_{O_2}^{SO_2}=G_{SO_2}-G_S^{SO_2}=0{,}5 \tag{41}$$

$$G_{O_2}^{CO}=G_{CO}-G_C^{CO}=1{,}3 \tag{42}$$

$$G_{O_2}^{CO_2}=G_{CO_2}-G_C^{CO_2}=1{,}3 \tag{43}$$

$$G_{O_2}=G_{O_2}^{SO_2}+G_{O_2}^{CO}+G_{O_2}^{CO_2}=3{,}1 \tag{44}$$

Air is used as a blow, O_2→21 %:

$$G_{blow}=\frac{G_{O_2}*100}{21\ \%}=12{,}4 \tag{45}$$

Amount of N_2 in the blow:

$$G_{N_2}^{blow}=G_{blow}-G_{O_2}=9{,}28 \tag{52}$$