THE MINISTRY OF EDUCATION AND SCIENCE OF THE REPUBLIC KAZAKHSTAN

Kazakh national research technical university named after K.I. Satpayev

Mining and metallurgical institute named after O.A. Baikonurov

Department of metallurgy and mineral processing

Balgimbayeva Ulpan Amankoskyzy

The study of the behavior of copper and lead in the mine contractile smelting semi-products and recycling materials of the lead production

MASTER THESIS

Specialty 6M070900 – Metallurgy

Almaty 2019

THE MINISTRY OF EDUCATION AND SCIENCE OF THE REPUBLIC
KAZAKHSTAN

Kazakh national research technical university named after K.I. Satpayev

Mining and metallurgical institute named after O.A. Baikonurov

UDC669.046.548

On the manuscript

Balgimbayeva Ulpan Amankoskyzy

MASTER THESIS

For an academic master's degree

Title of the thesis	The study of the behavior of copper and lead in the mine contractile smelting semi-products and recycling materials of the lead production
Direction of preparation	6M070900 – Metallurgy

Scientific supervisor:
candidate of technical sciences
associate professor
________ N.K. Dosmukhamedov
«_14_» ___05___ 2019

Reviewer:
candidate of technical sciences
technical director LLP «Arna Solution»
________ B.S. Rakhimbayev
«_16_» ___05___ 2019

Normcontrol:
PhD, lecturer
________ G.M. Koishina
«_27_» ___05___ 2019

ДОПУЩЕН К ЗАЩИТЕ
НАО «КазНИТУ им. К.И. Сатпаева»
Горно-металлургический
институт им. О.А. Байконурова

ADMITTED TO PROTECT
Head of the department
metallurgy and mineral processing ,
candidate of technical sciences
________ M.B. Barmenshinova
«_30_» ___05___ 2019

Almaty 2019

THE MINISTRY OF EDUCATION AND SCIENCE OF THE REPUBLIC
KAZAKHSTAN

Kazakh national research technical university named after K.I. Satpayev

Mining and metallurgical institute named after O.A. Baikonurov

6M070900 – Metallurgy

APPROVAL
Head of the department
metallurgyand mineral processing,
candidate of technical sciences
Barmenshinova M.B.
"20th" september 2018

TASK
for the implementation of the master's thesis

The master student *Balgimbayeva Ulpan Amankoskyzy*
Thesis: *The study of the behavior of copper and lead in the mine contractile smelting semi-products and recycling materials of the lead production.*
Approved *by the order of the Rector University № - 1039-m. from "20" september 2018.*
Deadline for completion of the thesis *"07" june 2019.*
Initial data for the master's thesis: *industrial data of LLP «Kazzinc», methods and planning of the experiment.*
List of issues to be developed for master's thesis:
a) study of the form of copper, lead, arsenic and antimony in the products of mine contractile smelting – slag and matte;
b) the causes and factors that affect the loss of copper and lead from slag;
c) comparative analysis of technological indicators;
d) distribution of non-ferrous metals between smelting products;
e) discussion of the research results and conclusions;
f)preparation of slides for the report.
List of graphic material on slides.
Recommended basic literature:
1 Dosmukhamedov N. K., Dauletbekov T. S., Egizekov M. G., etc.Copper production of Kazakhstan.Almaty. 2010. 472 p.
2 N.K. Dosmukhamedov, E.E. Zholdasbay, T.S. Dauletbakov, U.A. Balgimbayeva, M.B. Kurmanseitov, G.Zh. Moldabaeva. Ways of improving the technology of processing of semi-products and recycling materials of the lead production // VestnikKazNRTU – 2018. №5 (129) – P.106-112.

SCHEDULE
preparation of master's thesis

Name of sections, list of issues to be developed	Terms of submission to the supervisor	Notice
Introduction	07.02.2018	
Literary review. Current state of lead production	14.02.2018	
Theoretical features of physical-chemical processes occurring during the processing of semi-products and recycled materials for lead production	25.06.2018	
Investigation of the behavior of copper, lead and related metals-impurities in the conditions of mine contractile melting	03.10.2018	
Possibility of using the Vanyukov process to process semi-products and recycled materials for lead production	11.02.2019	
Conclusion	13.05.2019	

Signatures
consultants and normcontrol's on the completed master's thesis with indication of the related sections

The name of the sections	**Consultant,** N.P.S. (academic degree, title)	Date of signature	Signature
Normcontrol	G.M. Koishina PhD, lecturer	27.05.19	Koishina

Scientific supervisor:______________________ N.K. Dosmukhamedov

The task was taken to the execution of the student ________ U.A. Balgimbayeva

Date "20th" "september" 2018

ABSTRACT

The master thesis contains an explanatory note on 110 sheets, 37 figures, and 13 tables.

The aim of this work is to study the behavior of copper, lead and related metals – impurities-arsenic and antimony, in the mine contractile melting of semi-products and circulating materials of lead production.

The following tasks were solved over the course of work:

a) It was found that the proportion of copper oxide losses during melting prevails over sulfide losses is ~78 %. To reduce copper losses with slag, first of all, it is necessary to provide measures to reduce copper oxide losses.

b) It was found that the proportion of lead in the slag in the form of its sulfide is high enough (~50 % of its total content in the slag). This indicates incomplete recovery of lead sulfide and separation of matte and slag during smelting. The presence of dissolved form of lead in the form of metal in the matte (50 % of its total content in the slag) requires measures to reduce the proportion of lead dissolved in the form of metal in the matte. The high content of lead in matte (up to 25 %) and slag (up to 1.7 %) has a significant impact on the extraction of lead in lead bullion, which in mine contractile smelting is low and barely reaches 60 %.

The results of studies on the distribution of arsenic and antimony between smelting products showed that arsenic is distributed between matte and lead bullion. The transition of arsenic to lead is associated with the formation of copper intermetallic compounds. A significant part of antimony is concentrated in the lead, which reduces its extraction into gases. Extraction of arsenic and antimony into the gas during melting is 43 % and 41 %.

The results obtained show that in order to increase lead recovery in lead bullion, it is necessary to organize measures to reduce lead losses with matte, and, first of all, to minimize the proportion of lead dissolved in the matte in the form of metal, and then to influence the reduction of lead sulfide content in the matte.

АННОТАЦИЯ

Диссертационная работа содержит пояснительную записку на 110 листах, 37 рисунков и 13 таблиц.

Цель настоящей работы – изучение поведения меди, свинца и сопутствующих металлов-примесей – мышьяка и сурьмы, при шахтной сократительной плавке полупродуктов и оборотных материалов свинцового производства.

В работе решены следующие задачи:

а) Установлено, что доля оксидных потерь меди при плавке превалирует над сульфидными потерями и составляет ~78 %. Для снижения потерь меди со шлаками, в первую очередь, необходимо предусмотреть мероприятия по снижению оксидных потерь меди.

б) Установлено, что доля свинца в шлаке в форме его сульфида достаточно высока (~50 % от общего его содержания в шлаке). Это указывает на неполное восстановление сульфида свинца и разделение штейна и шлака при плавке. Наличие в штейнах растворенной формы свинца в виде металла (50 % от общего его содержания в шлаке) требует принятия мер, по снижению доли растворенного в виде металла свинца в штейнах. Высокое содержание свинца в штейне (до 25 %) и шлаке (до 1,7 %) оказывает существенное влияние на извлечение свинца в черновой свинец, которое при шахтной сократительной плавке находится на низком уровне и едва доходит до 60 %.

Результаты исследований по распределению мышьяка и сурьмы между продуктами плавки показано, что мышьяк распределяется между штейном и черновым свинцом. Переход мышьяка в черновой свинец связан с образованием интерметаллидов меди. Значительная часть сурьмы концентрируется в черновом свинце, что снижает его извлечение в газы. Извлечение мышьяка и сурьмы в газ при плавке составляет 43 % и 41 %.

Полученные в работе результаты показывают, что для повышения извлечения свинца в черновой свинец необходимо организовать мероприятия по снижению потерь свинца со штейном, причем, в первую очередь, минимизировать долю свинца, растворенного в штейне в виде металла, после чего влиять на снижение содержания сульфида свинца в штейне.

АҢДАТПА

Диссертациялық жұмыс 110 бет түсіндірме жазбадан, 37 суреттен және 13 кестеден тұрады.

Осы жұмыстың мақсаты – мыстың, қорғасынның және ілеспе металдардың – қоспалардың-мышьяк пен сурьманың, қорғасын өндірісінің жартылай өнімдері мен айналмалы материалдарын шахталық қысқарту кезіндегі өзгерістерін зерттеу.

Жұмыста келесі міндеттер қарастырылған:

а) Балқу кезінде мыс оксидті шығындардың үлесі сульфидті шығындардан асып түседі және ~78 % - ды құрайды. Мыстың шығынын азайту үшін, біріншіден мыстың оксидтік шығындарын азайту жөніндегі шараларды қарастыру қажет.

б) Шлактағы қорғасынның сульфид түріндегі үлесі жеткілікті жоғары (оның шлактағы жалпы құрамының 50 % - ы). Бұл қорғасын сульфидінің толық қалпына келтірілмеуін және балқыту кезінде штейн мен шлактың бөлінуін көрсетеді. Штейндерде металл түрінде (оның шлактағы жалпы құрамының 50 % - ы) ерітілген қорғасын формасының кездесуі, оның штейндегі металл түріндегі ерітілген қорғасынның үлесін азайту жөнінде шаралар қабылдауды талап етеді. Штейндегі (25 % - ға дейін) және шлактағы (1,7 % - ға дейін) қорғасын, қара қорғасынды алуға айтарлықтай әсер етеді, ол шахталық жиырылу кезінде төмен деңгей көрсетеді, яғни 60 % - ға дейін жетеді.

Мышьяктың және сурьманың балқыту өнімдері арасында таралуы бойынша зерттеу нәтижелері және мышьяктың штейн мен қара қорғасын арасында таралуы көрсетілген. Мышьяктың қара қорғасынға өтуі, мыстың интерметаллидтерінің пайда болуымен байланысты. Сурьманың едәуір бөлігі қара қорғасында шоғырланады, бұл оны газға шығуына ықпал етеді. Балқытуда мышьяк пен сурьманы газға шығару 43 %-ды және 41 %-ды құрайды.

Жұмыста алынған нәтижелер бойынша, қорғасынды қара қорғасын құрамына арттыру үшін, қорғасынның штейнмен жоғалуын төмендету қажет, және штейнде металл түрінде ерітілген қорғасынның үлесін азайту жөн, содан кейін штейндегі қорғасын сульфидінің мөлшерін төмендетуге ықпал ету қажет.

CONTENTS

INTRODUCTION

Current state. One of the main problems of lead enterprises of the Republic is the processing of lead intermediates and recycled materials. The use of modern processes (Q-S-L, Oxygen-weighted cyclone electrothermal process, etc.) to solve this problem is constrained by a number of objective reasons: the complexity of the composition of the polymetallic charge, from which it is necessary to extract the maximum of useful components, the insufficient calorific value of the processed materials and the need to use expensive coke in a number of technologies, the complexity of hardware design, etc. [1-4]. In addition, the analysis shows that there is no information in the publications on their use for processing a wide range of semi-products and circulating materials formed in the production of lead [5-7].

The growing demand of the world economy for non-ferrous metals makes it necessary to increase the raw material base of the lead industry at the expense of deposits whose ores are characterized by an increased content of copper, arsenic and antimony. Involvement in the processing of this type of raw material has led, especially for lead enterprises, to an increase in the yield of intermediates and recycled materials with a high content of arsenic, antimony and their toxic compounds. Today, none of the processes included in the overall technological chain of the main lead production is achieved sufficiently deep sublimation of arsenic and antimony into dust, which reduces their withdrawal from the main production and leads to a sharp accumulation in the main production. Existing technologies can no longer cope with their processing: the accumulation of arsenic, a significant increase in material costs, a decrease in technological indicators, an increase in the incidence of the population living in the immediate vicinity of metallurgical facilities.

Urgency: One of the solutions towards the creation of a specialized recycling of lead semi-products and recycling of materials is the existing technology of the mine contractile smelting (MCM) used at LLP "Kazzinc".

The main purpose of MCM is to extract the main non-ferrous metals into the target products: copper-in matte, lead-in rough metal, zinc-in slag. The current state of MCM technology does not ensure the achievement of high performance. Extraction of copper in matte is ~83%, zinc in slag-60%. Lead recovery in lead bullion barely reaches the level of 60%, due to its increased content in slag (up to 1.7 %) and matte (up to 30 %). Large losses of lead with matte entail significant losses of precious metals, which are irrevocable for the lead enterprise. The final products are characterized by a high content of impurities (As, Sb). The further processing of such matte into copper bullion in the traditional way of converting greatly complicates the process and leads to an increase in material and energy costs.

A significant consumption of expensive coke (up to 15% of the charge weight) and a large slag yield (up to 40 % of the loaded charge weight) in the smelting process make the technology highly costly and inefficient.

The process of MCM is accompanied by a large output of dust (up to 15 %

of the weight of the loaded charge). Dust get gas twice exceeds a similar indicator agglomeration firing. The dust obtained during melting is characterized by a high content of non-ferrous metals,%: Pb – 6.2; Cu – 4.41; Zn – 5.5. In this case, the extraction of arsenic in the dust is about 60%, and antimony – 50%.

The concentration of arsenic and antimony in the resulting liquid smelting products and the low transition to sublimates observed at the same time does not allow arsenic and antimony to be withdrawn with sufficient accuracy from the technological process. The circulation of the resultant materials in the main branch of the technological scheme leads to the accumulation of these impurities. The established patterns give special urgency and relevance to an additional study of the behavior of arsenic and antimony during the process of mine contractile smelting. This is important, both in terms of improving the technological indicators of the process, and conducting an assessment of their environmental impact.

Despite the current shortcomings, the existing technology of mine contractile smelting continues to be used as a necessary measure that to a certain extent resolves the issue of processing a large volume of the intermediate products obtained and recycled materials in the facility. The technological process, designed to recycle or at least minimize the output of intermediate formations, continues to aggravate environmental problems. This turns technology into one of the most dangerous and risky objects in the structure of lead production. The technology either requires improvement or the adoption of another, more optimal solution to process the obtained by-products and recycled materials.

The purpose of this work is to study the behavior of non-ferrous metals, arsenic and antimony during the mine contractile melting of intermediates and circulating materials of lead production.

The following tasks were solved over the course of work:

a) A comparative analysis of technological indicators was carried out based on the analysis of physicochemical characteristics of autogenous melts, widely introduced in lead production.

b) Metallurgical calculations of the mine contractile smelting process were carried out and a distribution of metals between the smelting products was established.

c) The forms for finding copper, lead, arsenic and antimony in the products of the mine contractile smelting - slags and mattes were studied.

d) The thermodynamics of the system copper-lead matte - slag - gas phase was investigated under controlled values of the partial pressure of oxygen and sulfur.

e) Identify the causes and factors that affect the loss of copper and lead from the slag.

Scientific novelty:

– In the study of thermodynamics of equilibrium of a complex multicomponent system copper-lead matte-slag – gas phase under controlled partial pressure of oxygen (P_{O_2}) and sulfur (P_{S_2}).

– In the study of the forms of non-ferrous metals, iron and arsenic in the products of mine contractile melting – copper-lead matte, slag.

– In determining the influence of the composition of matte on the equilibrium distribution of non-ferrous metals (Cu, Pb, Zn) and related impurity metals (As, Sb) between matte and slag.

Practical significance. On the basis of the conducted experimental researches the ways of processing and improvement of melting of semi-products and circulating materials of lead production are shown. The proposed solutions allow to predict the content of copper and lead in the slag depending on the composition of matte, slag and partial pressure of oxygen, sulfur. The obtained results can be used in the development of new effective technologies for the processing of complex composition of copper, lead containing substandard intermediates and recycled materials of lead production.

Methodological basis. The main methodological principle used in the work is the thermodynamic approach, which is based on the idea of achieving thermodynamic equilibrium (or close to it) between the products of melting, which allows to establish the behavior of the main and related metals during melting to use the laws of chemical thermodynamics.

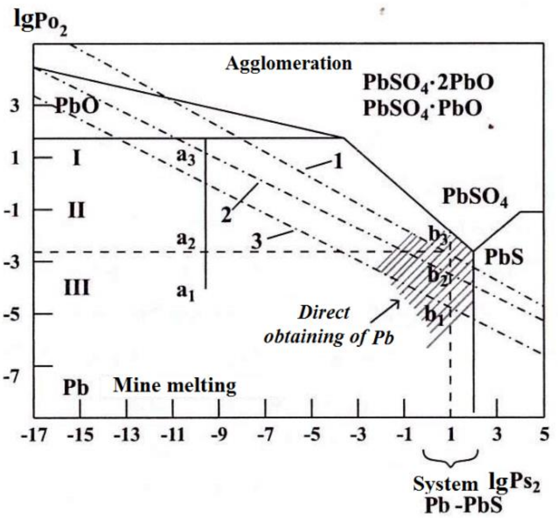
Physicochemical studies, laboratory experiments, analysis and processing of the results are widely used in the work. Methods of analysis: chemical, x-ray phase and thermal.

1 Literary review. Current state of lead production

1.1 Autogenous processes for the direct production of lead from sulfide lead raw materials

Due to a number of objective reasons related to the physical and chemical properties of lead and its compounds, the introduction of autogenous processes in the production of lead is significantly lagged behind in comparison with their use in the production of copper [8-10]. However, a sufficient number of direct lead production processes from primary lead sulfide concentrate have been developed [11-13]. Hardware design of the processes implemented in the industry, allows you to use them for processing of various types and types of raw materials. Lead production in the world practice going in the direction of development of two variants: smelting to matte, which is characteristic for a complex thermodynamic system matte – slag – lead bullion and slag – lead bullion. The choice of the processing scheme depends on the specific conditions and is determined by the technological capabilities of each individual enterprise. With a low content of lead in sulfide raw materials and an increased content of copper in it, it is preferable to conduct melting on matte. However, the experience of lead plants shows that most of them work under the second scheme – with the production of lead bullion and lead-rich slag, which requires further recovery operations to extract lead.

The chart analysis of phase associations of the system Pb – S – O in the coordinates Lg P_{O_2} and Lg P_{S_2} characteristic of autogenous melting of lead, shows the presence of only a small, narrow area of direct obtaining of lead (Figure 1.1) [14].



in the diagram of Pb – S – O at T=1473 K: I – C_{PbO}=1; II – C_{PbO}=0.1; III – C_{PbO}=0.05; $1 - P_{SO_2} = 1$; $2 - P_{SO_2} = 0.1$; $P_{SO_2} = 0.01(P_{O_2}, P_{S_2}, P_a)$. The shaded area is the direct production of lead

Figure 1.1 - Schematic representation of different processes

The diagram is based on calculated data, taking into account the results of experiments to determine the activity of lead in the slag. Inclined lines correspond to the equilibrium reaction

$$SO_2 = ½S_2 + O_2. \tag{1.1}$$

The dissociation reaction depends on and P_{O_2}. In the system, P_{O_2} = 0.1 atm. corresponds to air blowing, P_{O_2} = 1.0 atm - to oxygen blowing. The direction of the traditional process: Agglomeration - mine smelting - is characterized in the diagram by a thick line from point b_1 to points a_1, a_3. In the transition from a_1 to a_3, in a wide range, the equilibrium constant of the reaction

$$(PbO) + CO = [Pb] + CO_2 \tag{1.2}$$

does not depend on P_{S_2}, as can be seen in Figure 1.1. If we take into account the difference in the activities of the components in the system or the PbO concentration in the slag, then the lines limiting the stability of metallic Pb and slag will go down to the lower values of P_{O_2}. This means that by reducing the P_{O_2} system (reducing the concentration of Fe_3O_4 in the slag at a constant of P_{S_2}), we get poorer slags (points a_1, a_2, a_3). Up to 4.5 % sulfur dissolves in metallic lead at a temperature of 1000°C. The total reaction of obtaining lead from sulfide concentrates can be written as follows:

$$PbS + O_2 = Pb + SO_2. \tag{1.3}$$

On the potential diagram, the area of possibility for obtaining Pb for the given values of P_{O_2} and P_{S_2} is shaded. If we take the P_{SO_2} system as constant, then it is obvious that with direct lead smelting using autogenous methods there are two possible ways to solve the problem: a) to obtain lead with a high sulfur content (point b_2 in Figure 1.1) and a relatively low concentration of PbO in the slag; b) to obtain relatively pure sulfur in lead, but at the same time have rich slags (point b_3 in Figure 1.1). It is along these two paths that the development of autogenous smelting of lead concentrates takes place.

Theoretically, the best way to process lead concentrates is to obtain metallic lead due to the oxidation for a portion of lead sulfide to oxide with further interaction of the latter with PbS. However, the resulting lead will contain too much sulfur and, therefore, will require additional processing. In addition, a similar process will be characterized by high vapor pressure and a high degree of dust recirculation.

The theoretical features described above, despite the differences in hardware design, are reflected in all the implemented autogenous processes. The widely developed autogenous processes include: TBRC developed in Sweden; Outocumpu process developed in Finland; the QSL process from the company Lurgi and the oxygen-weighted cyclone electrothermal process developed in the former USSR [15].

Table 1.1 shows the compositions of the resulting smelting products during the processing of sulfide raw materials, in the TBRC process.

Table 1.1 - The compositions of the products of smelting process TBRC

Components	Melting products			
	Slag		Matte, % (by weight)	Lead bullion, % (by weight)
	to depletion, %	after the unification %		
Cu	7.5	1.1	53.1	-
Ni	1.0	0.17	2.8	-
Zn	9.7	8.6	2.0	-
Pb	11.3	7.7	11.7	-
Sb	0.09	0.11	0.08	-
Fe	~ 40	~ 40	-	-
Fe_3O_4	~ 26	~ 12	-	-
Cu	-	< 0.1	-	-
Pb	35	1.0	-	97
Sn	1.3	0.8	-	S<0.5 %
Fe	~ 22	22	-	-
SiO_2	~ 33	33	-	-
CaO	~ 20	20	-	-
MgO	~ 1.5	1.5	-	-
Zn	16	22	-	-
Na_2O	~ 3.5	3.5	-	-

Outokumpu (Finland) has developed and patented the process of Suspended Smelting (IP) of lead concentrates. The essence of the process is as follows. A mixture of dry concentrate (humidity up to 0.3 %), fluxes and recycled dust is melted in a suspended state at a temperature of 1300–1400ºC in the presence of oxygen-enriched air or pure oxygen. Exothermic reactions eliminate the need for additional fuel.

The molten particles are separated from the gas flow in the furnace sump to form a slag layer and a metal layer containing lead and precious metals.

Slag and metallized layers are continuously sent together to the electric furnace (a variant of the process is the release of lead separately from the slag). In the electric furnace coal dust is injected into the slag layer (as a reducing agent). The depleted slag is continuously removed through the upper drain. Lead bullion is also continuously pumped through the siphon and sent for refining. The gases of the VP furnace pass through a two-section heat recovery boiler with forced circulation, where they are cooled to a temperature of 350ºC.

During processing, t/h: 17 concentrate, 0.4 silicate flux, 2 circulating dust-in the melting process, 12 tons of lead bullion, 3 tons of slag and 2450 m^3/h of gas containing, %: 90 SO_2, 3 H_2O, 7 N_2. Gas temperature 1200°C. Melting is carried out on the blast of 95 % oxygen, its flow rate is 2160 m^3/h, the temperature is 25°C. When depleted in the electric furnace 3 t/h slag consumption of coal is 0.2 t/h, while receiving 0,8 t/h Pb bullion, 1.9 t/h slag and 450 m^3/h of waste gas containing,%: 80 CO, 2.7 CO_2, 6.3 N_2, 0.3 H_2O, 10.7 N_2.

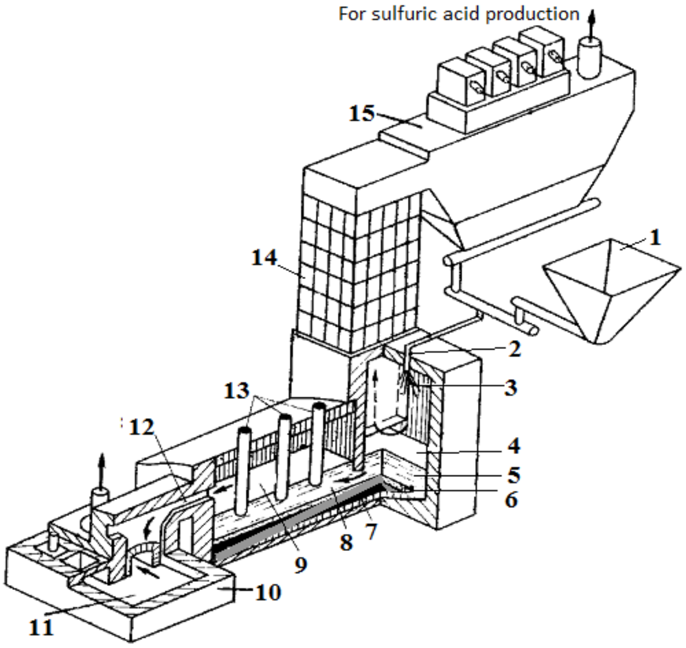
Total lead recovery is 97-99%.

Table 1.2 shows the comparative indicators of the conventional process of processing of lead concentrates (agglomeration – mine smelting) and the process "Outokumpu", the data of which are obtained on the basis of semi-industrial tests.

Table 1.2 - Comparative analysis of indicators of different processes

Shared data	Aglomeration – mine melting	Outokumpu
Content in concentrate:		
Pb	74	75
Zn	2.3	1.8
S	15.7	15.2
Capacity by lead bullion t/day	300–500	420
The extraction of Pb, %	96	98.7
The Pb content in the slag, %	2–4	2
Energy intensity and reagents		
Fuel consumption, kJ/t Pb	7.7	–
The consumption of O_2, kg/t Pb	0	164
Consumption of electric energy (including heat, the impoverishment of the slag production O_2 and sulfuric acid), kV/t Pb	185	241
Consumption of carbon electrodes, kg / t	0	1.0
Oxidation stage		
Type of reactor	Sintering machine	Furnace VP
V exhaust gases, m^3/t Pb	2400	180
The contents of SO_2, %	5.5	85
Reduction step		
Type of reactor	Mine furnace	Electric furnace (for slag)
V exhaust gases, m^3/t Pb	2000–3000	60
CO_2 content, %	0.1-0.2	0.3

American experts argue that the most promising of the pyrometallurgical methods of direct production of lead, developed in the USSR, is the process of oxygen-weighted cyclone electrothermal melting process (figure 1.2).



1- hopper for charge; 2-burner; 3-torch; 4-melting chamber; 5-slag; 6-matte; 7- lead bullion; 8-siphon; 9-electric furnace; 10-capacitor; 11-rough zinc; 12-flue gas; 13-electrodes; 14 - cooling tower for gases; 15 - electric filter EMU-7

Figure 1.2 - Diagram of the installation of the oxygen-weighted cyclone electrothermal process

The process of processing sulfide concentrates of heavy non-ferrous metals (in particular, lead-zinc) is based on a rational combination of the use of oxygen, electricity, the principles of cyclone and suspended melting. The process of roasting - smelting, the separation of the phases, the improvement of processing, the condensation of molten zinc flow in one unit.

Process the oxygen-weighted cyclone electrothermal process worked in several variants, differing in the form of products obtained, in which the zinc is extracted. Zinc can be transferred to rough metal, oxidized sublimates or in the slag, and then removing his fuming or rolling process in existing plants. The choice of an option should be tailored to specific conditions.

The oxygen-weighted cyclone electrothermal process, compared with other processes, has the following main advantages: the ability to extract 90-97.5 % lead and high (up to 78 %) zinc recovery in the processing of lead-poor concentrates containing from 12 to 65 % lead; relatively low investment; small size of the equipment used and smaller production areas; lower costs of intra-workshop transport; improved working conditions due to low emissions of harmful gases; the possibility of high automation.

The use of oxygen-weighted cyclone electrothermal process technology for the processing of collective copper-lead-zinc concentrates provides greater economic efficiency than reflective melting, suspended melting and electric melting.

Ausmelt technology, which offers low cost of production, high intensity of the smelting system to produce lead bullion and slag, is widely used. The technology does not require grinding or drying of the supplied materials [12].

The reactor of the installation is a vertical cylinder, the main design feature of which is the system of injection air supply through a vertical lance lowered from the top of the stove into the molten slag located at the bottom (figure 1.3).

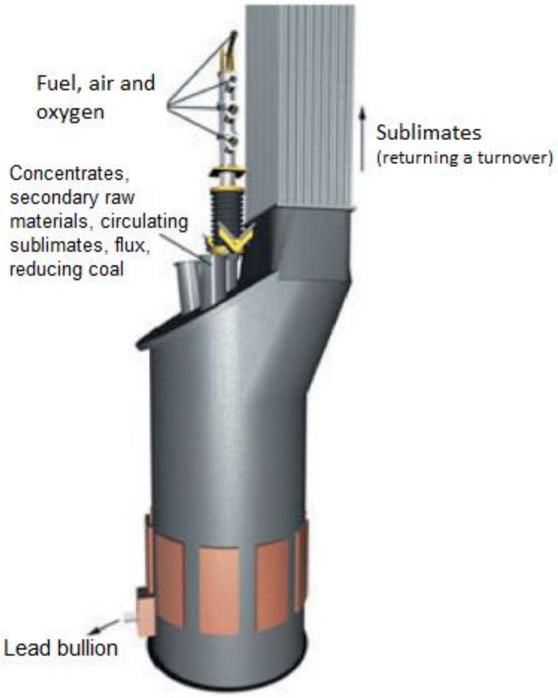


Figure 1.3 - General view of Ausmelt melting furnace

Loading of materials is carried out from the top of the furnace. Oxidation of sulfides occurs due to their interaction with air and oxygen injected from the bottom of the lance and creating a high-intensity vortex chamber. The exhaust gases from the furnace pass through the exhaust boiler for cooling and steam generation. Further, the cooled gases are directed to an electrostatic filter to remove dust, and then used in the process. Pre-frozen, on the outer surface of the lance, a layer of slag prevents the lance from the effects of the melt, increasing its service life.

The main disadvantages of the process include the complexity of the operation of lances (sufficiently large size, complexity of installation, maintenance of high pressure, etc.). When the lance fails, the technology is experiencing some difficulties, up to the stop. No favorable conditions are created for the separation of smelting products. The possibility of melt reoxidation is not excluded.

Slags are characterized by a high content of copper and lead, which requires additional depletion operation. In addition, further refining of lead bullion, increases the output of the slurry.

A common characteristic feature of all new varieties of autogenous melting processes (melting in suspended state, cyclone process, melting in melts) is the maximum use of own energy resources of sulfide raw materials due to exothermic reactions of sulfide oxidation and slag formation.

Autogenous processes have significant advantages over all other applied and developed processes of processing of lead concentrate in terms of reducing energy consumption, saving capital and operating costs for environmental protection while increasing the complexity of the use of raw materials.

The advantage of these autogenous processes is the combination of firing and melting of lead concentrates in one unit with the production of metal lead. However, these alternative technologies are limited by the composition of the processed raw materials: the introduction of sulfate oxidized lead containing materials (cakes, dusts, slurries) is strictly limited. The disadvantages of these processes is that they are accompanied by the formation of sufficiently hot gases (880–1300°C) and a large dust removal (15-25 % of the weight of the charge).The results of theoretical studies are fully supported by the development of various processes of lead production. These circum stances are proof that the production of lead is still the classical scheme of agglomeration – mine smelting recovery will remain dominant.

1.2 Mine recovery smelting of lead sinter

The pyrometallurgical method, classic for lead technology, consists of the following stages: sintering firing of lead charge, sinter smelting, refining of black lead (figure 1.4). This method is applicable for the production of lead from concentrates and industrial products of almost any composition – rich and poor, clean and heavily contaminated with various metals and waste rock components.

This exceptional position of lead smelting in modern metallurgy is explained by the simplicity and cheapness of the method.

The main method of processing lead-containing raw materials is a two-stage technology (figure 1.4), according to which the sulfide lead concentrate is first subjected to oxidative firing to convert PbS into a PbO form and obtain a sintered firing product (agglomerate). Then the charge, consisting of a mixture of agglomerate and coke, is melted in a mine furnace, where lead oxide is reduced to the metal by reactions:

$$PbO + C = Pb + CO - 107.7\ kJ \qquad (1.4)$$

$$PbO + CO = Pb + CO_2 + 65.9\ kJ \qquad (1.5)$$

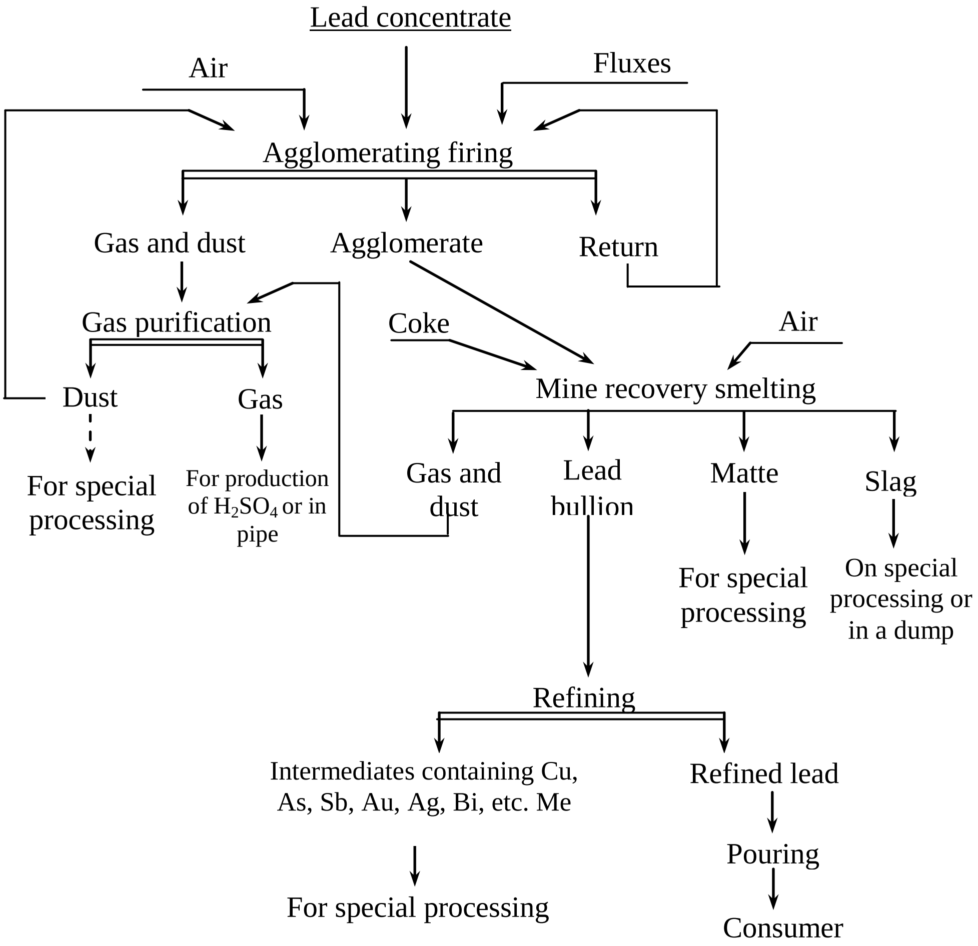


Figure 1.4 - The technological scheme of processing of lead sulfide concentrates, using reduction smelting mine

The main product of this process is lead bullion, which is then sent for refining.

Mine smelting of lead agglomerate. Mine smelting is the second stage in the processing of sulfide lead concentrates by two-stage technology. The charge of the mine furnace consists of lead agglomerate, coke and other materials (circulating intermediates, additional fluxes, iron scrap). The purpose of melting-as fully as possible to extract lead from the charge in the form of rough metal, which also concentrates gold and silver; slag waste rock and transfer to slag as much zinc present in the charge. Often, when melting, another liquid product is obtained-matte, which also passes part of the metals.

Slag and matte are released from the furnace through the annulus, located in the end wall of the furnace and in the recess of the end caisson slightly above the level of lead in the furnace. The release of slag and matte from the furnace can be carried out continuously through the device with a hydraulic seal or periodically. The separation of slag and matte into independent products is carried out either in a mobile settling furnace or in a stationary electrically heated sump.The main chemical processes in the smelting of lead sinter are recovery, deposition, sulfidation and combustion of carbon solid fuels. The combustion processes of carbon fuel have a very large impact on the operation of the mine furnace. Coke is used as a reducing agent and fuel for mine smelting, which is due to its following properties, favorable for use in mine furnaces:

a) sufficiently high calorific value (26000-32000 kJ/kg);
b) good mechanical and thermal strength;
c) relatively high ignition temperature (600-750°C);
d) required porosity – 49-53 %;
e) required particle size distribution.

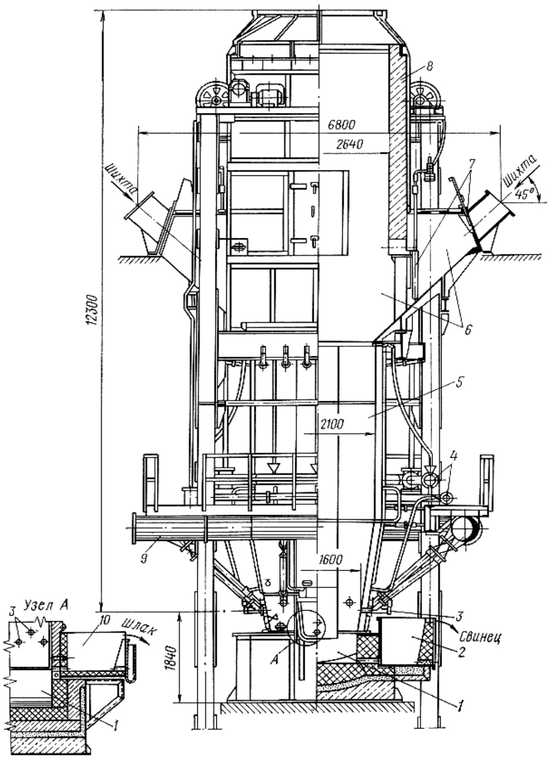
The modern minefurnace is shown in figure 1.5.

The main advantages of lead reduction smelting over other lead production methods are the following:

- low requirements for processed raw materials;
- high specific productivity of the mine furnaces;
- high direct lead extraction of the base metal constituting average 92 %, and some of the advanced foreign factories – "Port Pirie" (Australia), "Noyelles – Godault" (France), etc. – 98 %);
- high thermal efficiency;
- low energy intensity;
- high complexity of the use of raw materials, provided in combination with other methods;
- extensive possibilities of process intensification through the application of oxygen and natural gas.

Despite the high technological performance (specific propellant, high lead recovery) and continuous improvement, mine remediation smelting has some disadvantages:

- high consumption of coke (up to 17% of the charge weight);
- large dust removal (6-8%) due to significant gas yield;
- weak regulation of the thermal regime and recovery capacity of the oven.



1 – mine furnace; 2 – siphon for the production of lead bullion; 3 – lance; 4- water cooling system manifolds; 5-mine furnace;6 – the furnace top; 7 – loading gate; 8 – the tent of the furnace top; 9 – collector for the supply of the blast; 10 – siphon for the release of slag

Figure 1.5 - Cross section of the mine furnace

1.3 Products, semi-products, recycled materials of lead production and methods for their processing

In addition to marketable products resulting from the processing of non-ferrous metal ores, non-ferrous metallurgy enterprises receive numerous semi-products, recyclable materials and metallurgical production waste. These include slags, mattes, dust, gases, agglomerates and dust, cakes, slimes, solutions, etc. Below we consider the general characteristics of the main products and the most important semi-products of metallurgical technology, which are obtained when processing lead-containing materials.

Lead bullion. Lead bullion contains from 93 to 98 % of the base metal. Impurities contained in the lead bullion are contained in the percent range: 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, silver (1-5 kg/t), gold (1-30 g/t), slag-forming components (0.3-0.8 %) and sulfur (from 0.1- 0.3 %) at mine smelting up to 3-5 % at autogenous methods.

Lead bullion's composition does not meet standard requirements; in terms of its physical-chemical characteristics, it is not suitable for any consumer industry.

Processing method. The purification of impurities from lead bullion is carried out by one of two methods: pyrometallurgical (using periodic or continuous technological processes) used at all plants in Russia and the CIS and most foreign enterprises, and electrolytic (essentially combined fire copper extraction and subsequent electrolytic refining in aqueous solutions). Electrolytic refining of lead from smelts has not gone beyond the stage of pilot testing.

Lead refining is a very complicated and expensive process, based on the use of fairly fine chemical technology. In the process of refining lead bullion, a number of operations are carried out, the order of implementation depends on the physical-chemical properties of impurities and the compounds formed. The most rational scheme for refining lead bullion includes the following operations [16]:

- copper extraction;
- desalination;
- alkaline refining (lead softening);
- silver extraction;
- zinc extraction;
- bismuth extraction;
- high-quality refining.

Mattes. Lead production mattes are characterized by high lead content and are an intermediate metal-containing product.

Matte melts have a very low viscosity. At melting temperatures (1200 – 1300°C) their viscosity does not exceed $5 \cdot 10^3 \text{Pa} \cdot \text{s}$. Matte viscosity decreases with increasing temperature, as well as sulfur and iron content. Very poor mattes are so fluid that they easily penetrate into the smallest pores and cracks of the lining.

The density of the molten matte increases with increasing copper content from 4.000 to 5.700 kg/m^3. With high metalization of mattes, their density can reach high values (up to 7 t/m^3).

Pricessing of copper-lead matte. There are three ways of processing copper-lead matte:

a) Matte, granulated or crushed to 6-8 mm, is mixed with quartz and agglomerated to a content of 4-5 % sulfide sulfur in the agglomerate. Then the sinter is melted in a mine furnace to produce recycled slag, lead bullion and copper-rich matte. The latter is leached with a solution of sulfuric acid to obtain copper sulfate ($CuSO_4 \times 7H_2O$) from solutions.

Most often, concentration smelting (contractile) in the mine or electric furnaces is used for the enrichment of matte for copper. When smelting matte in a mine furnace with a coke consumption of 11–13 % and with the addition of 2-3 % limestone, lead bullion, copper-rich matte and recycled slag are obtained. Matte enrichment can be carried out in electric furnaces with the addition of a magnetic fraction obtained in clinker kilns, while iron displaces lead from its sulfide.

b) The second method of copper – lead matte processing consists in blowing out the matte with air, which is carried out in a converter with the use of an acid flux - quartz additive or without it.

c) In the first case, the process proceeds according to the usual scheme adopted in copper metallurgy, namely: matte purging is carried out in the main converter of a horizontal type. To slag iron present in the matte, which oxidizes to nitrous and trioxide when matte is blown, some amount of an acidic flux — quartz is formed in the converter, forming a monosilicate compound ($2FeO \cdot SiO_2$) with ferrous oxide.

d) In addition to the method of blowing copper-lead matte described, a second method can be used, in which there is no supply of acid flux to the converter. In this method, the copper-lead matte is also purged in the main converter of a horizontal or vertical type. Liquid copper – lead matte is poured into the converter and is blown with air without feeding quartz into the converter. When purging, the formed lead oxides mostly evaporate (about 90%). Part of the zinc also evaporates. The main part of the zinc goes into slag in the form of zinc ferrites, which greatly increase the viscosity of slags. Iron sulfide is oxidized to FeO and Fe_2O_3 and form $xFeO \cdot yFe_2O_3$ type compounds.

As a result of copper-lead matte blowing in the converter, viscous ferrite slags with copper and metallic copper sulphides entangled in them are formed. Almost all of the lead passes into the gas phase (the task of this method is the distillation of lead).

This process has the following advantages:

- the slags obtained do not require processing to extract lead;
- it is not required to introduce lime into the ducts to neutralize sulfuric anhydride, this process occurs due to volatile Pb and Zn oxides.

The main disadvantages include:

- limited application, since it is required to have copper at the same time as the lead plant in order to process the viscous mass;
- the slag obtained during the processing of copper matte together with the ferrite mass, possesses significant viscosity due to the insufficient destruction of magnetite in it - Fe_3O_4.

e) In order to remove lead from the copper lead matte based on the volatility of lead sulfide and metallic lead, copper lead matte is evacuated in a medium vacuum. Reducing the external pressure reduces the boiling point of substances and increases the rate of distillation.

The evacuation of matte at a temperature of 1200-1250°C allows you to give off about 95 % of lead. The condensate contains 88-90 % Pb and consists of a mixture of lead sulfide and metallic lead. The process has been tested at SHSZ in semi-continuous devices with a productivity of 10-15 t/m^2 per day.

Metallurgical slags. Slags are the second mandatory product of most metallurgical smelting. They are formed by the slagging of waste rock and fluxes and consist mainly of oxides. In addition to slag-forming components, real factory slags necessarily contain a certain amount of recoverable metals.

With a relatively low content of valuable components, the resulting slags are a waste product, i.e. waste from metallurgical production. However, slags can only conditionally be considered waste. With the development of metallurgical technology, they can again become a valuable raw material for the production of a number of non-ferrous metals, as well as iron and other valuable components.

In certain types of metallurgical smelting, and especially in refining processes, slags are very rich. Such slags require mandatory depletion. They are often used as recycled materials, or subjected to special processing.

To obtain slags of optimal composition, quartzite and limestone are most often used as fluxes in non-ferrous metallurgy. Instead of the usual quartz rock, gold-bearing quartz ores are often used, since while smelting, precious metals are extracted from them into matte or draft metal.

Processing of lead slags. To extract zinc, lead from slags, the following processes are used [5]:

a) Fusing (gas process), in which zinc and lead are transferred to the gas phase from liquid slag by blowing the latter with an air-dust mixture or converted natural gas. This is the main method for slag processing;

b) Rolling. This process is used to process solid zinc-containing materials. In this process, zinc and lead are also transferred to the gas phase by heating the zinc-containing material in a mixture with fine toxic or coal in a tube furnace with a diameter of 2.5-4.5 and a length of 30-90 m and inclined by 3-5°. The best varieties of sublimates of zinc oxides are sent to the paint industry. Impurity-contaminated oxides are processed at a zinc plant to produce zinc and residues, which are again sent to lead production;

c) Electrothermal process. In an electric furnace, due to heating due to electricity, coke consumption is minimized for reduction reactions (4-5 %). At the same time, the partial pressure of zinc vapor in the gas phase approaches the theoretical one and, when the gas is cooled, favorable conditions arise for the condensation of zinc in the form of a metal. Zinc vapors were condensed in a liquid condenser irrigated with liquid zinc. The sublimation of zinc was 85 %, of which about 83 % is condensed into liquid metal. Electricity consumption amounted to 1200 kWh per ton of zinc.

Gases and dusts. Most pyrometallurgical processes are characterized by the formation of significant amounts of gases and dusts. As a rule, these two products are removed from the furnace together.

Waste metallurgical gases can be classified into process gases, which are formed due to chemical reactions, and furnace gases, which are products of fuel combustion. The composition and amount of waste gases are fully determined by the type of raw material being processed and the type of metallurgical process used.

In most cases, the exhaust gases leave the metallurgical unit heated to 800-1300°C or more.

All dust generated during metallurgical processes is subject to capture. At the same time, two main objectives are pursued:

a) The use of valuable components, passed in the dust;

b) The prevention of environmental pollution.

Processing of dusts and sublimates of lead production. Currently, most plants use the process of complex processing of dusts, based on the granulation of dusts with strong sulfuric acid, followed by heat treatment of the obtained granules at a temperature of 300-350 °C in fluidized bed reactors. At the same time, 85-90 % of arsenic, chlorine, fluorine and 60-90 % of selenium are distilled; and non-ferrous metals and some rare sulfates and when leaching the sulfate product goes into solution. Leaching is at a ratio of W:T = 3 and a temperature of 70-80 °C, the residual acidity is 10-15 g/l.

98 % of lead is transferred to the cake, which is sent as a working material to lead production.

Copper slurries and methods for their processing. Dry slips, as a rule, are processed separately, while copper is extracted into matte and speiss and removed from lead production, and lead is returned to the main cycle.

There are various schemes for processing slips - in small mine kilns, in reflective and short drum rotary kilns, electric furnaces (sodium sulfate smelting) using various reagents.

1.4 Selection and justification for the direction of scientific research

The intensive development of the international market economy observed in recent years leaves a growing imprint and has a significant impact on all sectors of a country's economy, including the mining and smelting industry. In this context, the need for an analysis and assessment of the overall state of the lead industry is particularly enhanced. Solving the issues regarding the processing of semi-products and recycled materials for lead production, increasing the extraction of copper and lead from them, as well as improving the quality of the target products obtained, associated with an increase in the growth of their volumes, have become top priorities.

The solution of the problem is complicated by the fact that associated substandard semi-products are characterized by complex chemical and phase composition. The presence of significant concentrations of metals in them-impurities (As, Sb, Cd, etc.) have a significant negative impact not only on the environment, but also significantly affect the distribution of base metals between the melting products in the direction of deterioration, reducing the quality of the final products. Thus, the results of our earlier studies [17, 18] on the distribution of metals in the processing of semi-products and circulating materials of lead production in the conditions of mine contractile smelting LLP "Kazzinc" show that the extraction of copper and lead in the target products remain at a low level and are ~80-85 % and 45-55 %, respectively. Due to the lack of alternatives, the current technology remains as a necessary measure of the processing of these intermediate products and recycling materials.

It is obvious that to develop a new technology it is necessary to have a reliable theoretical and practical material. However, as the analysis shows, in the technical literature there are practically no data on the study of thermodynamics of complex sulfide systems describing the compositions of industrial products and circulating materials, the equilibrium of the copper-lead matte – slag – gas phase system is poorly studied, there are no data on the compositions of sulfide polymetallic materials. The coverage of such theoretically important issues as the mechanism of copper and lead transition from polymetallic copper-lead matte to slag seems insufficient. There is no data on the study of the forms of finding metals in smelting products in the processing of complex composition of copper, lead containing raw materials. All these gaps and their solution formed the scientific basis and direction of research of this work.

In this perspective, it seems natural question: Why not use high-performance autogenous processes for the processing of these materials? The use of autogenous melting could be one of the most important ways to address this issue and a significant reserve for improving technological indicators of production. The main reason for inhibiting the introduction of autogenous processes is the practical absence in the scientific literature of experimental results on equilibrium in a complex system Fe – S – O – Me (where: Me – Cu, Pb, Zn). At the present time remains controversial also the mechanism of oxidation of sulfides. Nevertheless, a sufficiently complete study of iron sulfide oxidation, which determines the first stage of autogenous processes and conversion of any matte, allows us to carry out a qualitative and quantitative assessment of the use of autogenous melting for processing the initial charge, consisting of semi-products and circulating materials of lead-zinc production.

In this work, from the general theoretical and technological positions, the possibility of using the Vanyukov process for the processing of copper slurry together with poor copper-lead matte obtained in the mine reduction melting of lead agglomerate is considered.

2 Theoretical features of physical-chemical processes occurring during the processing of semi-products and recycled materials for lead production

2.1 Thermodynamics for the equilibrium of the system metal (lead) – matte

The processing of polymetallic lead concentrates or agglomerates containing a significant amount of copper provides for smelting on a matte, with the concentration of the main amount of copper, a part of lead and zinc in them. Obviously, the presence of a complex copper-lead matte in contact with the slag will significantly affect the total loss of copper and lead with the slag.

In reality, the process of transition of valuable metals from complex matte to slag is a complex mechanism. In this case, when it is impossible to determine the dissolution of metals in slags using exchange reactions, it is convenient to use the calculations of the coefficient of distribution of metals between the smelting products. This approach is often used in metallurgical practice due to the complex nature of the smelting products involved in the process. The determination of the distribution coefficient of metals between the products of smelting allows us to give an overall assessment of one or another dissolution mechanism that prevails under specific conditions. Therefore, the issues of losing valuable metals with slag, the definition of the mechanism of their transition into the slag are given the most attention.

The results of studies in the distribution of copper and lead in the system of copper-lead matte – slag – gas phase are provided in [19]. When studying this system, the authors used the following methods: melting in twin crucibles; filling the matte powder onto the surface of the liquid slag; and pouring the liquid matte under the molten slag. The use of various techniques allowed the authors to obtain reliable experimental data on the determination of the content of dissolved metals in slags. In the process of research, the authors studied the influence of a number of factors: composition of slag and matte, the influence of the gas phase and temperature on the distribution of metals between the smelting products.

In the studies, industrial copper-lead mattes from CC STSK (now LLP Kazzinc) were used, which brought into contact with multicomponent slags that are in composition for industrial slags. It has been established that in order to quantify the solubility of metals, in the cases considered, it is most expedient to use the coefficient of distribution of metals. The authors of [19] suggested that the transition of lead into slag is mainly determined by the joint transition of lead cations and sulfur anions into the slag. In the case of copper, the values of the product of solubility of such constancy are not preserved.

It is shown that an increase in carbon dioxide content in the gas phase of more than 25 % leads to a sharp increase in lead solubility in slags. The authors concluded that, under oxidative conditions of the environment, along with the oxidation of lead by carbon dioxide, some other forces come into play that regulate the dissolution of lead in the slag. To explain this phenomenon, the authors analyzed the reaction's equilibrium:

$$Pb + Fe_3O_4 \leftrightarrow PbO + 3FeO. \qquad (2.1)$$

The reaction's equilibrium constant was calculated by the expression:

$$K_{(2.37)} = (a\,Pb^{2+}) \cdot (a^3_{FeO})/(a_{Fe_3O_4}) \qquad (2.2)$$

As a result of the calculations, the direct dependence of the lead dissolved in the slag at the ratio of $(a^3_{FeO})/(a_{Fe_3O_4})$ and the magnetite activity in the slag was established. The resulting pattern is of fundamental importance for practice.

In metallurgical practice, which is especially typical for reducing mine lead smelting, converter furnace slag containing magnetite is often added to the initial charge. The introduction of “solid” oxygen in the slag composition into the melt increases the degree of the system's oxidation, which leads to a sharp increase in the transition of valuable metal cations into slag.

The tendency to complicate the composition of the feedstock, the components of the mixture and the resulting products of the bottoms requires clarification of available results and additional research. In particular, in the scientific literature there is no data on the forms of non-ferrous metals in real slags and mattes. The behavior of related impurities in smelting processes has not been studied, their influence on the distribution of base metals among the smelting products has not been determined.

2.2 Losses of non-ferrous metals with slags

Rich slags, the loss of metals with which are becoming more and more tangible for production, began to either be sent to circulation, or depleted in special electrically heated sedimentation tanks. However, the measures taken do not give a positive effect.

Usually with slags, a significant part of the metals is lost in the form of a thin mechanical suspension. The formation of a mechanical suspension of valuable metals in the slag occurs [19, 20]:

a) Due to the low concentration and fine impregnation of valuable components in the initial mixture mainly during the course of processes in dilute solutions;

b) Due to changes in the redox potential of metallurgical systems during the process and as a result of different rates of oxidation and reduction reactions in the melts;

c) As a result of wetting and spreading of liquid sulfides and metals with lower melting points across the solid mixture;

d) During sublimation followed by condensation in the form of thin films of valuable volatile components;

e) As a result of an abrupt change in temperature when solid sulfides of the charge enter the liquid slag. Sudden changes in temperature, leading to a decrease in solubility, can also be the cause of precipitation of a thin suspension from the melt.

The listed reasons quite fully show the mechanism for the formation of mechanical losses of metals. The exclusion of these factors allows us to obtain them during the smelting slags, without hardly any finely dispersed metals.

One of the conditions for reducing the mechanical losses of metals with slags is the creation of conditions for their consolidation and sedimentation. To increase the rate of coalescence of particles, slag mixing is effective in the presence of a recovery phase.

The dynamics of mechanical suspension in the slag is significantly affected by the viscosity and surface properties of the slag, the action of which is mutually opposite. The increase in viscosity slows down the sedimentation of the suspension, while the growth of interphase tension in the slag – suspension system promotes the consolidation of the suspension and accelerates its release. The viscosity should first be determined by the nature and composition of the melt, as well as its temperature.

Based on the nature of the slag melts [21], it follows that the viscosity of a fluid depends on the probability of a particle moving from one position to another. The easier this transition is, the lower the viscosity. With increasing temperature due to the increase in the number of particles with the necessary energy supply for such transitions, the viscosity decreases.

As the temperature rises, the number of broken Si – O bonds increases, as a result of which the activation energy of the viscous flow of SiO_2 decreases. When MeO is added to SiO_2, the Si – O – Si bonds break and are replaced by Si – O – Me. The appearance of O-Me non-directional heteropolar bonds, whose energy slightly varies with distance, loosens the three-dimensional SiO_2 network, facilitates the movement of particles and reduces the activation energy of viscous flow. The drop in activation energy slows sharply when a certain MeO content is reached. From this moment on, the three-dimensional SiO_2 grid breaks into separate pieces — complex anions.

Minimal amounts of metals in slags in the dissolved form should be expected in the conditions of equilibrium of the matte – slag system. However, in practice most metallurgical systems are far from equilibrium. In this case, the final content of dissolved metals in the slags is determined by the composition of the smelting products and the conditions of the process.

In metallurgical practice, which is especially typical for reducing mine lead smelting, converter furnace slag containing magnetite is often added to the initial charge. The introduction of “solid” oxygen in the slag composition into the melt increases the degree of the system's oxidation, which leads to a sharp increase in the transition of valuable metal cations into slag.

According to A.V. Vanyukov [19, 20], even a small increase in the oxygen concentration in the gas phase (up to 0.05 %) significantly increases the amount of dissolved metals in the slag. An increase in the oxygen content in the gas phase shifts the $Fe^{2+} \leftrightarrow Fe^{3+}$ equilibrium toward trivalent iron. In this case, there is an additional possibility of transition of non-ferrous metals into slag, due to the reactions of interaction of copper and lead sulfides with magnetite.

The number of Fe^{2+} and Fe^{3+} positions in the slag, and the change in their ratio has a significant impact on the distribution of metals between the slag and the matte and the shape of the metals. For practice, a very important criterion for assessing the mechanical loss of metals in the slag is the concentration of sulfur in the latter.

The analysis shows that under a reducing atmosphere in equilibrium conditions, the mechanism of transition of copper and lead from matte to slag is determined by the flow of a number of reactions: exchange - between the sulfides of valuable metals and iron oxide; the joint transition into the slag cations of lead and sulfur anions and the reaction of interaction of copper and lead sulfides with magnetite.

The tendency to complicate the composition of the feedstock, the components of the mixture and the resulting products of the bottoms requires clarification of available results and additional research. In particular, in the scientific literature there is no data on the forms of non-ferrous metals in real slags and mattes. The behavior of related impurities in smelting processes has not been studied, their influence on the distribution of base metals among the smelting products has not been determined.

3 Technology for processing of lead semi-products and recycled materials at LLP Kazzinc

3.1 General technological scheme for processing of semi-products and recycled materials

The existing technological scheme for processing of industrial products and recycled materials is presented in Figure 3.1.

A characteristic feature of the technology is the output and organization of self-processing in the mine furnace of almost all the revolutions of lead production - poor in copper, matte mine recovery smelting, copper slurries, slag crusts, second alkali melts, converter slags and other materials containing lead.

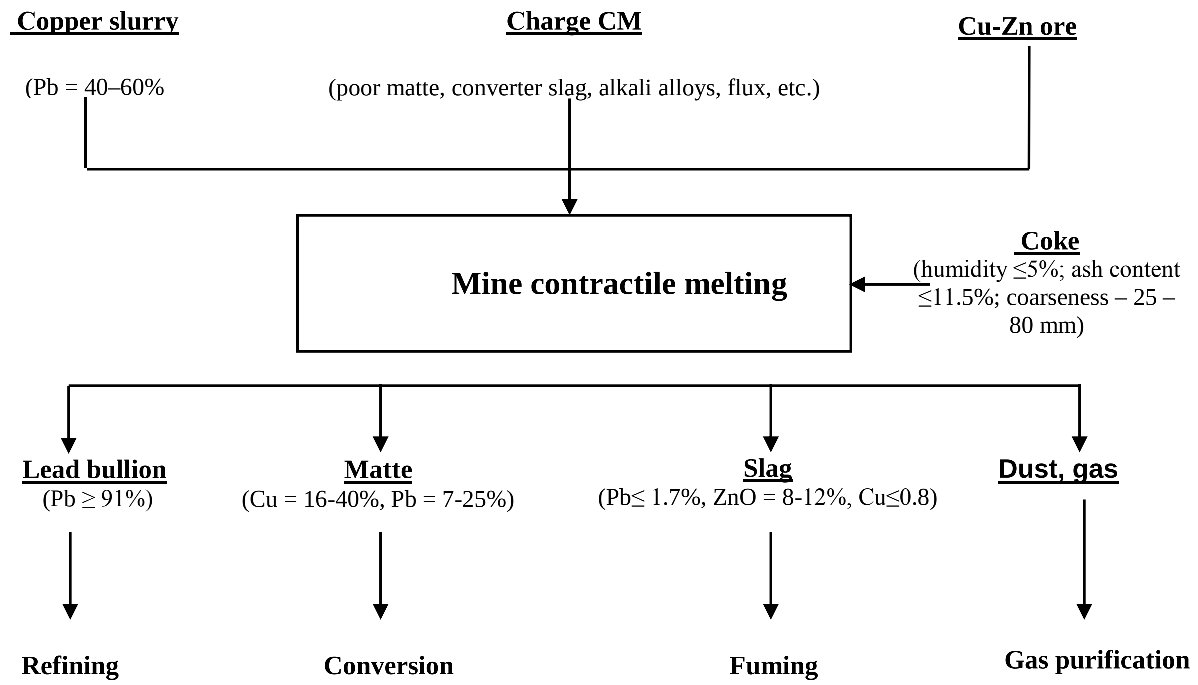


Figure 3.1 – Schematic diagram of the mine contractile melting

On lead production according to the technology, three existing mine furnaces are provided. On one of them, the classical smelting sinter is carried out, on the second - contractile smelting - with withdrawal of industrial products and recycled materials for separate processing. The third furnace is either in repair or in reserve.

3.2 Theory and practice of mine contractile smelting

Mine recovery lead smelting is carried out in a weakly reducing atmosphere, providing selective recovery metals at equilibrium oxygen pressures $P_{O_2} = 10^{-8} \div 10^{-7}$ atm.

High-quality coke is both a fuel and a reducing agent. Coke should have a developed surface, low ash content (7.5 ÷ 8 % ash) and high reactivity. Coke porosity is usually 37–57.5 %. Coke consumption depends on its quality, ash content in it, as well as on the physical-chemical properties of the charge (heat consumption and reducing ability), slag composition, rate and nature of smelting.

By the nature of the process and the resulting products, the smelting of the mine can be non-matte and polymetallic matte. The formation of matte contributes to an increase in the equilibrium pressure of oxygen up to $10^{-6} – 10^{-5}$ Pa, caused by a violation of the melting mode while reducing the reducing agent: oxygen ratio. Lead smelting matte contains sulfides of iron, lead, copper, zinc and silver, as well as metallic silver and gold. In the future, matte is sent to convert.

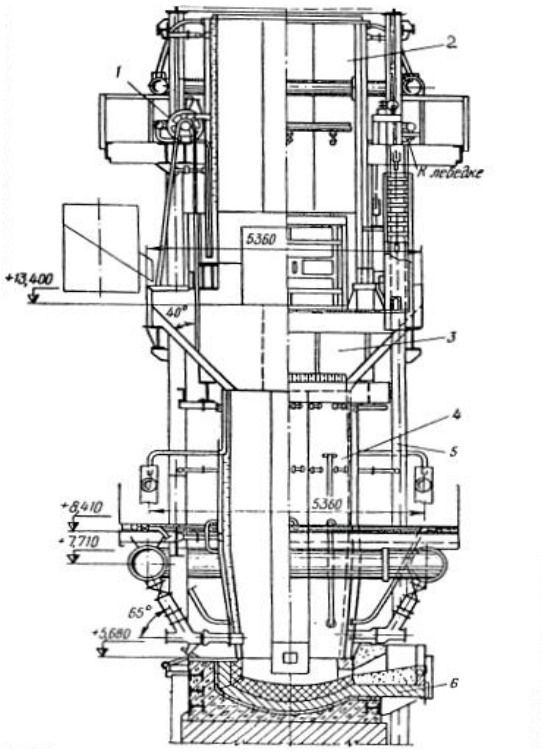
The charge smelting is carried out on a mine furnace with evaporative cooling of caissons, a schematic image of which is shown in Figure 3.2

The furnace operates in continuous mode and under discharging. The discharge in the furnace flue is 10–20 mm of water. Art. The volume of exhaust gases is about 300.000 m^3/h. The temperature of the exhaust gases does not exceed 750°C. The furnace's air mode is controlled by the readings of the manometer and gas analyzer (the oxygen content in the blast is 30 %). The furnace is equipped with a system for signaling the pressure drop in the blast, the temperature of the exhaust gases and the water level in the separator tank. Purified water is used for cooling to produce process steam in an evaporator unit.

The mine furnace is installed directly on the furnace hearth. The kiln mine consists of two rows of caissons: the first row is attached to the sides of the hearth; the second, resting on a rigid ring, is mounted around the furnace.

For the loading of coke and lead materials, a top plate is provided, which is mounted on water cooled beams.

The separation of the liquid products of smelting takes place in the furnace sumps. Electrothermal furnaces with a volume of 12–16 m^3 and a capacity of 1.200–2.500 kW are used as settling tanks. Three electrodes with a diameter of 550 mm are placed along the long axis of the furnace. The distance between the electrodes is 1.800 mm. The furnace is lined with refractory bricks.



1 - loading winch; 2-tent; 3-column; 4-mine; 5-column; 6-horn

Figure 3.2 – Cross-section of the mine furnace

The inside of the furnace is made of magnesite brick, and the outside of fireclay. The laying is concluded in a steel casing, 12 mm thick. The arch of the furnace is arched, 360 mm thick. The thickness of the bottom of the sump is 640 mm, and has the shape of the invert. The hearth is lined with various refractory materials. The top layer is made of magnesite brick, the middle layer is made of fireclay, and the bottom layer is made of refractory concrete.

The level of the melt is maintained in the range of 1.000-1.200 mm. Loading products smelting mine contractile furnace is made through the hole in the vault of the sump pump.

Workers holes for the release of smelting products - lead, matte and slag - are located in the end part of the sump. An emergency bore hole is provided for slag production above the main slag pit of the settling tank, which is used in case of overflow of the settling tank with smelt.

Thus, the water consumption for cooling the caissons was reduced by about 15 times, the steam produced under an overpressure of 4-5 atm, is fully used for the needs of the complex.

The mine furnace consists of a forge, a mine, a top furnace and an electrically heated settler. The hearth is located on the foundation. The hearth walls are laid out of refractory chrome-magnesite brick, 600-800 mm thick. The laying is enclosed in a tight steel welded casing and is tightened with metal rods. The height of the furnace is 5.5 m. The length and width of the forge corresponds to the dimensions of the furnace in the area of the lance, the depth of which is 0.5-0.8 m.

The hearth is constantly filled with lead, matte and slag. The depth of the hearth is chosen based on the copper content in the initial mixture - the more copper, the smaller the depth of the hearth.

Lead bullion continuously released through a siphon. The lead level in the receiver is 100-200 mm above the level in the furnace. Due to the pressure difference of the air blown into the furnace and the weight (pressure) of the slag and matte. The advantage of the siphon release is the ability to control the level and temperature of the melting products in the furnace, as well as preventing the formation of the hearth.

To prevent the overgrowth of the hearth on the bottom, some layer of metal is retained. Slag and matte are released from the hearth through a special hole in the outlet caisson, which is usually installed in the end wall of the furnace. The hole for the release of slag from the furnace and matte is located slightly below the lance axis.

Coke is loaded into the furnace in layers with agglomerate. Through the lances, compressed air is supplied to the focus of the furnace consisting of red-hot coke to create the required intensity of coke combustion, the thermal mode of smelting and the creation of a gas atmosphere. Furnace gases passing through the thickness of the mixture, heat it and participate in the reduction of oxidized compounds of lead and other metals. The temperature at the focal point of the furnace reaches 1500°C, at the exit from the furnace (in the top) - 200 ÷ 400°C. As the coke burns out and lead and slag are formed, the charge column (4–6 m) slowly (1 m/h) goes down and it is replenished with successive loads of sinter and coke (eaves).

During smelting, coke reaches the lance area and forms a constant layer there. Before the melting site, the sinter should fall sufficiently to maintain sufficient porosity and heat resistance. At a temperature of 750°C, there is a noticeable reduction of lead from the agglomerate. Mine lead smelting progress is determined by the behavior and state of the sinter in the furnace up to 850–900°C. The recovery process of lead sinter is intensified at 900–1000°C.

Hard-to-reduce oxides (alumina, silica, calcium oxide, iron oxide, zinc oxide) alloy and form slag. Lead recovery and melting occurs more intensively when melting more porous agglomerate due to lower diffusion resistance of the charge. The sinter melting zone is determined not by the coke consumption, but by the composition and physical, chemical properties of the slag. The main product that determines the temperature in the furnace is superheated slag, which does not have a specific melting point. The slag melts in the temperature range from the beginning of the softening of the agglomerate to its fluidity.

The main condition for the effective operation of lead smelting mine furnaces is the concentration of the focus on coke combustion, which is determined by the conditions of smelting, the furnace design, and physical-chemical properties of the sinter, such as heat resistance, softening, reducibility, porosity, structure, etc.

The composition of the gas atmosphere in the mine furnace is formed by the combustion of coke. Coke carbon is oxidized to CO_2 by oxygen at the focal point of the furnace near the lance along the reaction:

$$C + O_2 = CO_2 + 393.5\ \text{kJ}. \tag{3.1}$$

Heating and melting of the components of the charge, as well as the thermal conditions of the smelting of the mine are provided by the heat generated by this reaction. The temperature here reaches 1400-1500°C. Carbon dioxide rises up with furnace gases heated to 1400–1500°C, and interacts with an excess of hot coke to form carbon monoxide:

$$C + CO_2 = 2CO - 172.4\ \text{kJ}. \tag{3.2}$$

In the mine furnace, in the smelting conditions (at Σ_P= 25-50 kPa) there is a significant amount of CO required for the reduction of metal oxides. At the focal point of the furnace, the reduction of oxides by solid carbon (coke) proceeds quite intensively:

$$MeO + C = Me + CO \tag{3.3}$$

However, the direct reduction of lead oxides with solid carbon has a local and small value, since the contact surface between solid carbon and metal oxides in the upper horizons of the furnace is insignificant. The dominant role in the smelting process belongs to the gaseous reducing agent formed during the smelting - carbon oxide.

$$MeO + CO = Me + CO_2. \tag{3.4}$$

Hot liquid lead dissolves easily reconstitutable impurities: copper, arsenic, antimony, tin, bismuth, silver, gold, as well as some amount of lead sulfide.

Liquid smelting products – lead bullion and slag flow down, pass the focus of the furnace and are collected in an internal furnace located in the lower part of the furnace. After settling and stratification according to density, lead bullion and slag are released from the furnace as they accumulate.

Lead and matte are released from the sedimentation tank through bore-holes as they accumulate.

Lead bullion is sent for further refining. A significant concentration of arsenic and antimony (1.8 and 3.0 %, respectively), as well as copper in it, reduces the quality of produced industrial products and recycled materials, increases the operating costs of further operations. The output of copper slips increases, and the quality of lead bullion deteriorates.

Slags containing 15–18 % zinc are sent for fusing to extract zinc from them. Extraction of zinc in sublimates barely reaches 80 %. When fusing, it is not possible to achieve a sufficiently complete depletion of slags and non-ferrous metals, which does not allow the use of the latter for their intended purpose. Slags continue to accumulate, occupying large areas.

Gases, after cleaning from dust are utilized, and dust is sent to the initial stage - agglomeration.

The output of copper-lead matte is 80-110 tons per day, which is further processed by converting to produce blister copper. Every month, on average, they process up to 3.000 tons of matte. Converter dust is sent to the chemical-metallurgical department for further processing. Gases from mine contractile smelting and conversion, after cleaning from dust, are sent to be recycled [12].

The implementation of independent, separate processing of almost all industrial products and recycled materials in a single unit, and the organization of the production of blister copper at the lead enterprise makes the existing technological scheme the most complete.

3.3 Characteristics of raw materials and smelting products

The initial charge of mine contractile smelting is a complex mixture of different materials conglomerate.

Data on the chemical composition of the products that form the basis of the charge of mine contractile melting are given in Table 3.1.

Table 3.1 - Compositions of products of charge of mine contractile melting

Name of produce	Metal content, % (wt.)							
	Cu	Pb	Zn	Fe	S	SiO_2	As	Sb
Copper-zinc ore	2.72	0.37	3.35	26.82	31.48	14.70	–	–
Flux ore	–	0.62	–	–	–	74.80	–	–
Converter slag	3.83	33.50	4.54	10.60	–	15.70	2.30	0.94
Alkaline floats	0.03	23.44	9.30	–	–	–	0.37	0.53
Poor matte	20.80	19.50	11.40	16.70	11.10	–	1.10	0.56
Copper slurry	19.00	30.30	4.00	–	9.29	–	3.87	1.40

Copper-zinc and flux ores contain precious metals in their composition.

High lead content in converter slags attracts attention - up to 35 % Looking ahead, we note that this distribution of lead during conversion largely influences the distribution of other metals between conversion products. A significant amount of arsenic and antimony is concentrated in the converted slag. The arsenic content in them reaches the level of 2.5 %, and antimony – up to 1.5 %.

Alkaline water is also characterized by a high lead content. The amount of arsenic and antimony in them does not exceed 1.0 %. Alkaline smelts also contain by percent: 2.35 cadmium, 7.6 thallium, and 0.023 tellurium.

Copper-poor mattes are obtained from mine ore smelting as a result of the processing of lead sulfide concentrate with a high copper content. The output of such mattes ranges from 10 to 25 tons per day. Their average monthly output is about 550 tons. Despite the equal values of the ratio of copper to lead in mattes (1.0-1.5), the content of base metals in mattes is almost twice as high, reaching a level of 23 %, for copper and lead. Despite these positive developments, the quality of the mattes leaves much to be desired, due to the increased concentrations of arsenic and antimony in them. The sum of these metals in mattes is 1.5 %.

The output of copper slurries is in direct proportion to the concentration of copper in lead bullion, which varies from 2.0 to 5.0 %.

In copper slurries, compared with the other components of the charge, the concentrations of arsenic and antimony are maximum (see Table 3.1).

The structure of the initial charge of mine contractile smelting in practice is presented in the form of Figure 3.3 - as the sum of converter slag, copper slips and the mixture of contractile smelting (CM).

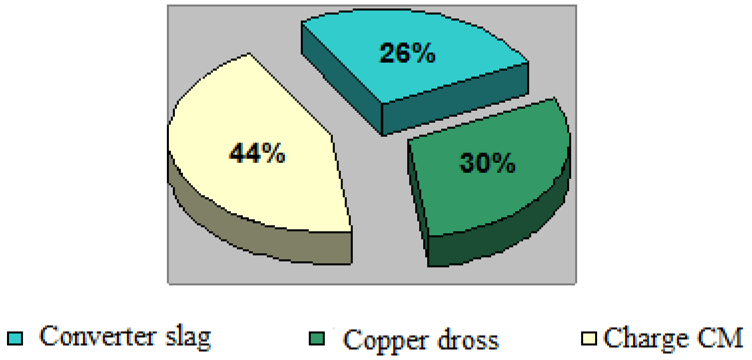


Figure 3.3 – Structure of the initial charge composition mine contractile melting

Such a representation of the structure of the initial charge is very conditional and leads to significant errors in the process of carrying out metallurgical calculations. The structure of the charge of the joint venture is highly complicated and includes a mixture of the following products - poor copper-lead mattes obtained after the mine smelting reduction of sinter, copper-zinc and flux ore, as well as a small amount of alkaline melts, cakes and other recycled materials for lead production.

The whole range of issues relating to the technological essence of the process ultimately manifests itself in a detailed, element-by-element material balance of the process, in which all the raw materials and the resulting smelting products must be presented. Therefore, the representation of the structure of the initial charge in the form of Figure 3.3 will lead to significant errors in the calculation of the average composition of the initial charge and the material balance of the process. The most correct and correct is to show the structure of the initial charge in expanded form, as shown in Figure 3.4.

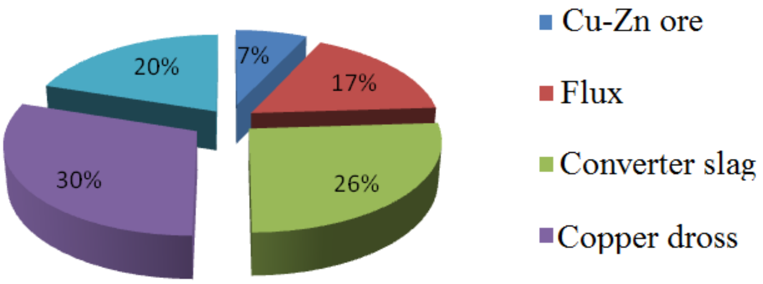


Figure 3.4 – Structure of the initial charge mine contractile melting

It is established that 90 % of copper, of its total amount in the charge, is deposited with the charge of the joint venture and copper slips. The total proportion of lead and zinc introduced with these products is 70 and 75 %, respectively.

The share of lead in the charge of the joint venture is 41.2 % of its total amount. Copper slurries contain 30 % lead. The share of zinc applied with the charge of the joint venture is high – 50 % of its total amount in the entire charge The amount of zinc entering the mixture with copper slurries is two orders of magnitude lower and amounts to ~ 25 %.

The bulk of arsenic and antimony is deposited with copper slips — 46.2 and 53.8 %, respectively. The amount of arsenic introduced with the charge of the joint venture is two times more than antimony and makes up ~ 30 % of the total amount in the charge.

The proportion of copper introduced with the converter slag in the total charge is minimal – 8.5 %. With the converter slag, almost the same amount of lead and zinc is applied as with copper slurries – 28.8 and 25 %, respectively. The share of arsenic and antimony with converter slag is also quite high – 23.9 and 30.8 % of the total amount in the initial charge.

Analysis of the composition of the initial mixture of mine contractile melting shows that up to 70 % of arsenic and antimony, of their total content in the initial mixture, is made with copper slurries and converter slag. At the same time, if the processing of copper slips containing high levels of copper and lead seems to be quite justified, then the involvement in the processing of converter slag with a deliberately low copper content, with the aim of its recovery, is not entirely appropriate. In the latter case, more impurities are introduced into the initial mixture of contractile melting than of copper.

Additionally, magnetite (up to 25 %) is introduced into the process, which has a significant downward effect on the distribution of metals between the smelting products and on the quality of the target products. The withdrawal of the converter slag from the composition of the charge, and its simultaneous adjustment, will improve the technical and economic indicators of the mine contractile melting process. In this case, one can expect an optimal distribution of base metals and impurities between the smelting products.

From the results obtained, it follows that a significant amount of impurity metals is introduced into the process with copper slurry and converter slag. The increase of technological indicators of the process requires the organization of additional measures aimed at reducing the content of non-ferrous metals in slag and deeper sublimation of arsenic and antimony into dust.

The question of impoverishment of slag on non-ferrous metals devoted a significant amount of work. The choice of method should be determined based on the conditions of a particular process, and dictated by the economic and environmental feasibility of the decision.

In this work, it is proposed to improve the existing technology of mine contractile melting by changing the composition of the initial charge by adjusting the consumption of copper-zinc ore.

The proposed solution, in our opinion, has a number of fundamental technological advantages. First, the organization of direct processing of the optimal consumption of copper-zinc ore will increase the complexity of its use and provide high extraction of non – ferrous metals in the target products: copper – in matte, zinc – in slag, lead-in lead bullion. Secondly, optimization of copper-zinc ore consumption will significantly affect the reduction of the amount of waste rock and iron introduced into the process. This will significantly reduce the consumption of silica flux. The measures taken together will significantly reduce the slag yield. Simultaneous use of high-sulphur copper-zinc ore as sulfidization for the depletion of converter slag non-ferrous metals, arsenic and antimony will ensure an optimal distribution of non-ferrous metals and impurities between the melting products, which will significantly improve the formation of the phases, their separation and the quality of the final products.

Improving the process of mine contractile melting requires research, first of all, the behavior of non-ferrous metals, arsenic and antimony in the processing of semi-products, recycled materials in conjunction with copper-zinc ore. The thermodynamic evaluation of the interaction reactions between the components of converter slag and copper-zinc ore is of fundamental importance.

4 Experimental part. Investigation of the behavior of copper, lead and related metals-impurities in the conditions of mine contractile melting

4.1 Forms of copper and lead in the smelting products

In this section, the forms for finding non-ferrous and related metals in the mine contractile smelting products of copper-containing lead semi-products and recycled materials, which are of fundamental importance for identifying the causes and factors affecting the loss of copper, lead from slags and low lead extraction in lead bullion, are investigated.

Studies of the form of metals in solid samples of industrial matte and slag mine contractile melting was carried out using x-ray phase analysis and mineralogical studies.

Elemental analysis of the samples was performed on a mass spectrometer with inductively coupled plasma Agilent 7700 Series ICP-MS (USA).

The study of the forms of metal detection was carried out using an automated x-ray diffractometer DRONE – 3 with Sika radiation, β-filter. Conditions of diffractograms shooting: U=35 kV; I=20 mA; shooting θ-2θ; detector 2 deg/min. x-ray Phase analysis on a semi-quantitative basis is performed on diffractograms of powder samples of slags and matte using the method of equal weightings and artificial mixtures. Quantitative ratios of crystal phases were determined. Interpretation of diffractograms was carried out using data from ICDD card index: powder diffractometric data base PDF2 (Powder Diffraction File) and diffractograms of minerals pure from impurities. For the main phases, the content was calculated.

Mineralogical studies of the surface structure of solid samples of matte and slag were carried out using a microscope Neofot (Carl Zeiss AG, Germany).

The results of elemental analysis of the compositions of the studied samples of matte and slag are given in table 4.1 (sample array).

It is seen that the content of copper in the matte varies from 25 to 42 % (by weight), lead - from 19 to 30 % (by weight). There is a high content of arsenic and antimony in the matte, which range from 1.5 % to 5 % and from 0.8 % to 2.5 % (wt.), respectively.

The compositions of the resulting slag in the mine contractile melting, the main components are constant and contain % (wt.): CaO-17; FeO-25; FeO/SiO_2 ratio maintained at 1.0-1.2. The content of zinc oxide in the slag varies slightly and is at ~10-12 % (wt.). The content of copper, lead and arsenic in slag varies within, % (wt.): copper - 0.38 ÷ 0.6; lead - 0.58 ÷ 1.4; arsenic - 0.12 ÷ 0.2. Fluctuations in the content of antimony in the slag is negligible – in the range of 0.12 ÷ 0.14 % (mass.) and practically constant.

An interesting fact is that as a result of the analysis of traditional dependences of the type (Me) = f [Me], for copper, a close correlation could not be established, while for lead, a similar dependence accurately describes the direct dependence of the lead content in the slag on its content in the matte within a small spread (figure 4.1).

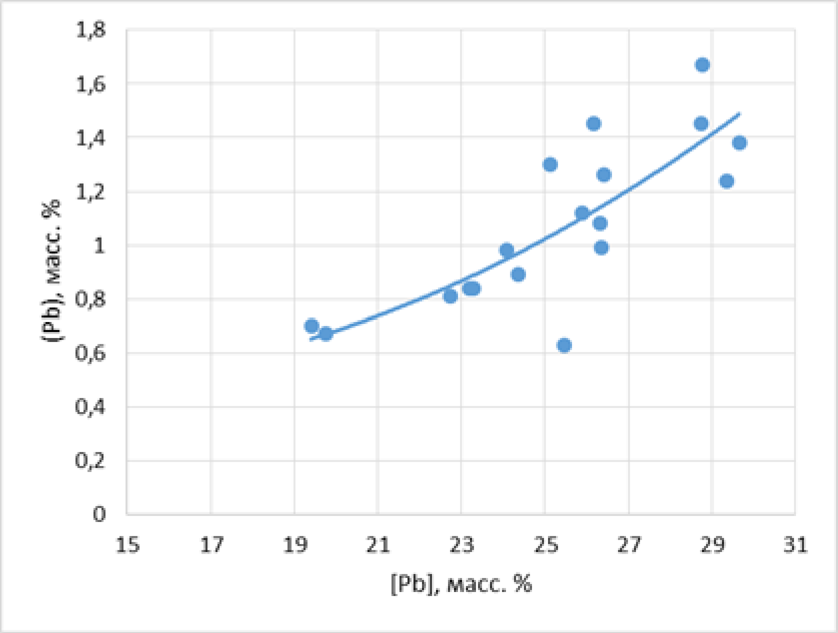


Figure 4.1 – The dependence of the lead content in the slag from its content in the matte

Table 4.1 –Results of elemental analysis of compositions of industrial samples of matte and slag

№	Matte composition, % (wt.)					Slag composition, % (wt.)						
	[Cu]	[Pb]	[Zn]	[Fe]	[As]	(Cu)	(Pb)	(ZnO)	(SiO_2)	(Fe_{total})	(CaO)	(As)
1	38.66	26.33	4.2	7.63	4.38	0.5	1.08	11.54	24.2	20.7	20.7	0.19
2	42.55	29.34	4.24	8.94	4.77	0.47	1.24	11.72	26.49	21.18	19.7	0.17
3	44.25	24.36	4.73	9.49	4.39	0.52	0.89	10.7	25.67	19.72	21.47	0.16
4	37.19	26.16	4.33	8.29	4.19	0.49	1.45	11.64	25.31	20.5	18.69	0.23
5	40.52	28.74	3.24	5.96	4.98	0.52	1.45	10.42	24.69	21.5	19.85	0.25
6	42.41	29.66	2.96	5.62	5.94	0.53	1.38	11.52	25.78	20.9	18.08	0.23
7	39.92	26.42	4.13	8.88	3.91	0.54	1.26	17.3	21.83	22.2	18.91	0.1
8	39.28	25.11	4.76	12.93	3.29	0.42	1.3	9.94	25.15	24.25	15.0	No
9	37.51	25.47	5.25	13.17	2.88	0.53	0.63	8.54	25.51	22.22	21.02	No
10	38.76	23.29	6.07	12.43	3.06	0.45	0.84	No	26.74	21.2	19.92	0.13
11	40.53	24.09	4.95	9.96	3.22	0.51	0.98	No	23.85	22.73	16.87	0.11
12	35.80	28.76	4.24	7.87	4.02	0.52	1.67	No	25.6	22.47	16.61	0.24
13	36.54	25.9	4.12	9.05	3.94	0.46	1.12	No	27.08	21.36	18.54	0.15
14	37.95	19.42	6.75	13.71	3.02	0.34	0.7	No	27.77	20.7	17.48	0.12
15	34.73	19.76	6.84	12.8	2.8	0.35	0.67	No	26.19	20.93	19.17	0.21
16	37.95	26.36	5.07	10.78	3.35	0.45	0.99	10.44	24.57	23.12	17.83	0.12
17	39.82	23.18	5.13	11.58	2.8	0.49	0.84	9.97	26.53	22.41	18.22	0.11
18	38.07	22.74	5.23	12.24	2.83	0.47	0.81	10.76	26.0	23.05	17.51	0.09

In our opinion, the established laws do not allow one to unambiguously interpret the mechanism for copper and lead transition into slag based on general theoretical considerations, as was customary in [19], but require more detailed studies to clarify this mechanism.

The significant variation in industrial data and the weak link between the copper content in the slag and its content in the matte indicates that copper in the matte is present not only in the sulfide form, but also in other forms. Apparently, this can be attributed to other metals present in the resulting mattes and slags.

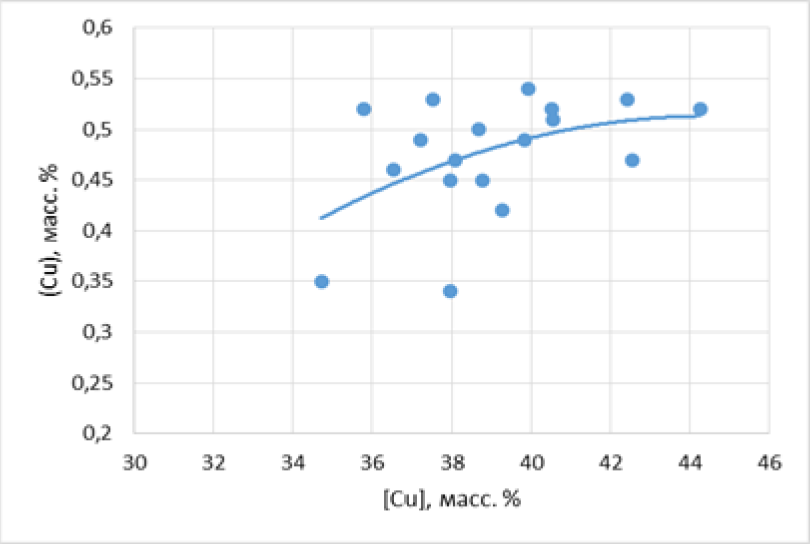


Figure 4.2 - Dependence of copper content in slag on its content in matte

In the case of copper, when constructing the dependence (Cu) = f [Cu], it is necessary to take into account not the total copper content in the matte, but only its share associated with the sulfide.

Figure 4.3 shows the diffraction patterns characteristic of powder samples of slags and mattes, obtained as a result of x-ray phase analysis method.

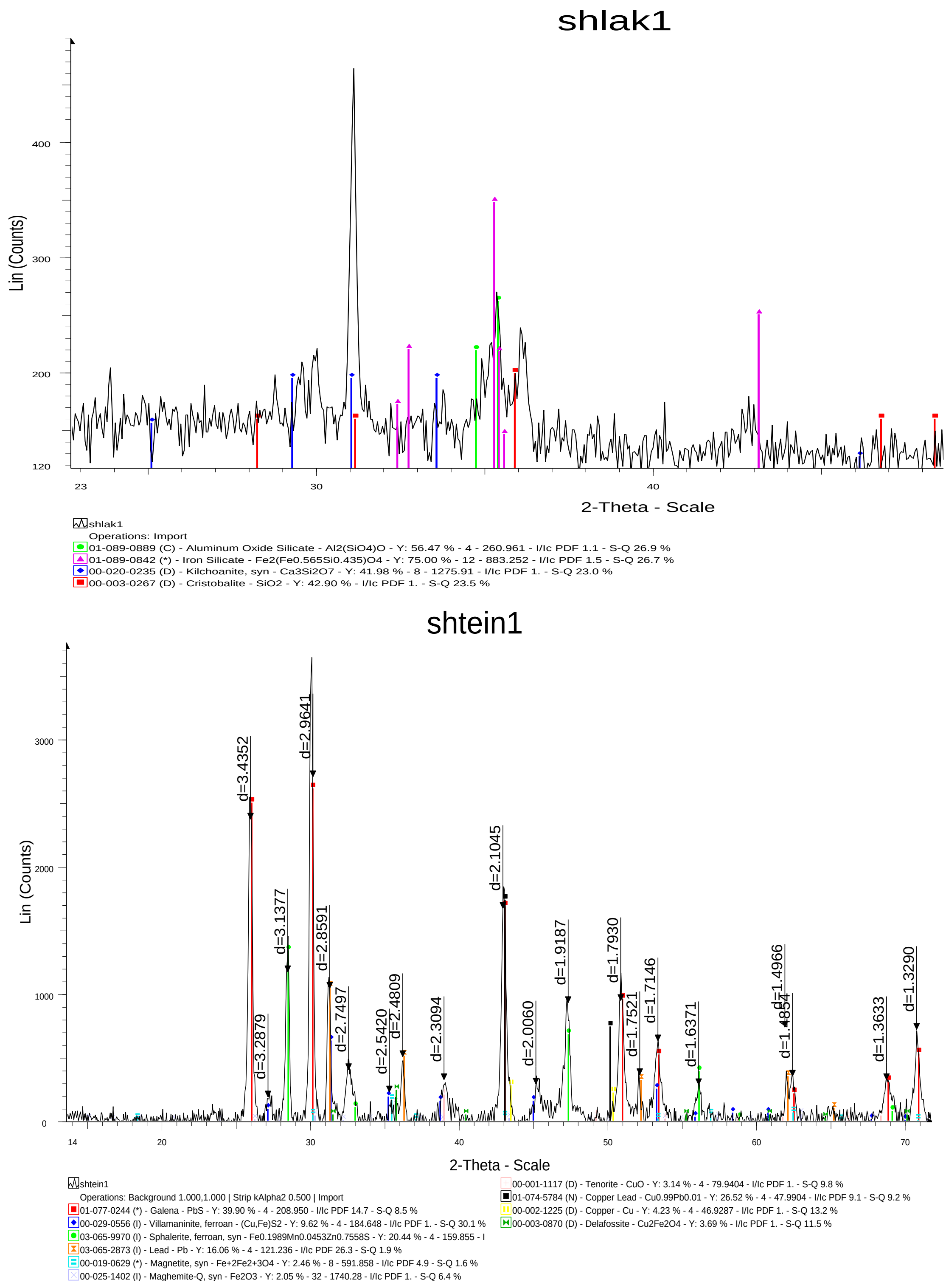


Figure 4.3 - Diffractograms of powder samples of slag and matte

The results of semi-quantitative x-ray phase analysis of slag and matte are shown in Table 4.2 and 4.3, respectively.

Table 4.2 - Results of semi-quantitative phase slag analysis

Name	Formula	Concentration, %
Olivine	$(Mg,Fe)_2(SiO_4)$	20.4
Fayalite	$Fe_2(SiO_4)$	20.0
The pyroxene (hedenbergite 1)	$CaFe(Si_2O_6)$	18.6
The pyroxene (hedenbergite 2)	$CaFe(Si_2O_6)$	14.5
Pyroxene (petedunnite)	$CaZnSi_2O_6$	12.1
Magnetite	Fe_3O_4	6.8
Cu,Zn,Fe Oxide	$Cu_{0.5}Zn_{0.5}Fe_2O_4$	5.6
Galena	PbS	1.9

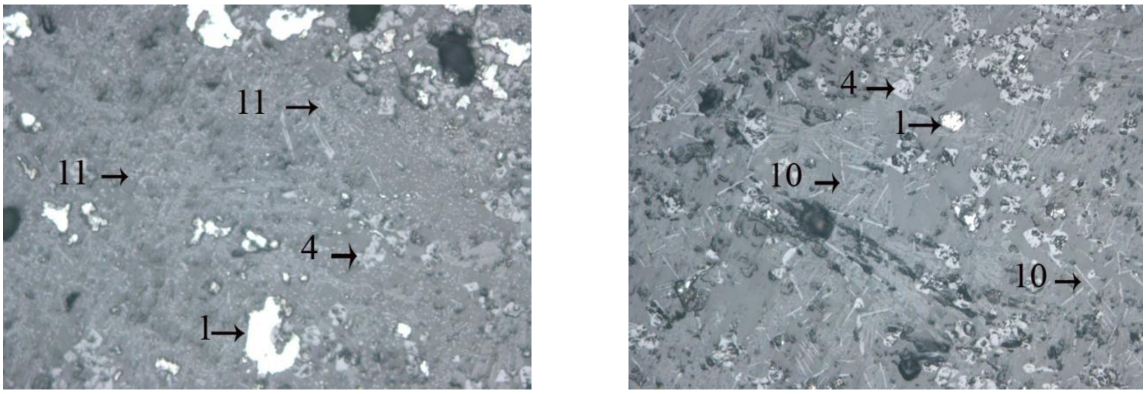
Table 4.3 - Results of semi-quantitative phase slag analysis

Name	Formula	Concentration, %
Chalcocite	Cu_2S	38.9
Galena	PbS	13.7
Sphalerite	ZnS	6.3
Iron sulfide	FeS	7.2
Delafossite	$CuFeO_2$	1.8
Magnetite	Fe_3O_4	6.3
Fayalite	Fe_2SiO_4	3.8
Metal lead	Pb	12.2
Metal phase	(Cu,Fe,As,Sb)	9.8

Figure 4.4 shows fragments of micrographs of solid slag samples

Slag based on fayalite (Fe_2SiO_4). Magnetite (Fe_3O_4) was found on the background of fayalite and non-bound cristobalite (SiO_2) in the form of splices of small grains. Also visible are clusters of delafossite ($CuFeO_2$) in the form of thin needles and small drop-shaped wustite grains (FeO). The inclusions of helenite $Ca_2AlSiAlO_7$) and a small amount of brown-red-brown spinels ((Fe, Ca) (Fe, Al, Zn)$_2$O$_4$) were established.

In the slag there are small inclusions of metallic lead and galena (PbS). On the microsection of samples, inclusions of white color with high reflectivity, characteristic of metal compounds, presumably, an alloy of copper and iron with arsenic and antimony (Me_3As, Me_3Sb, where Me – Cu, Fe) are pronounced. In slags, copper is mainly represented in oxide form. The proportion of the sulfide form of copper varies from 30 % to 38 %.



Increase - X300.1 - alloy of copper, iron with arsenic and antimony; 4 - magnetite (Fe_3O_4); 10 - delafossite $CuFeO_2$;11 – wustite (FeO)

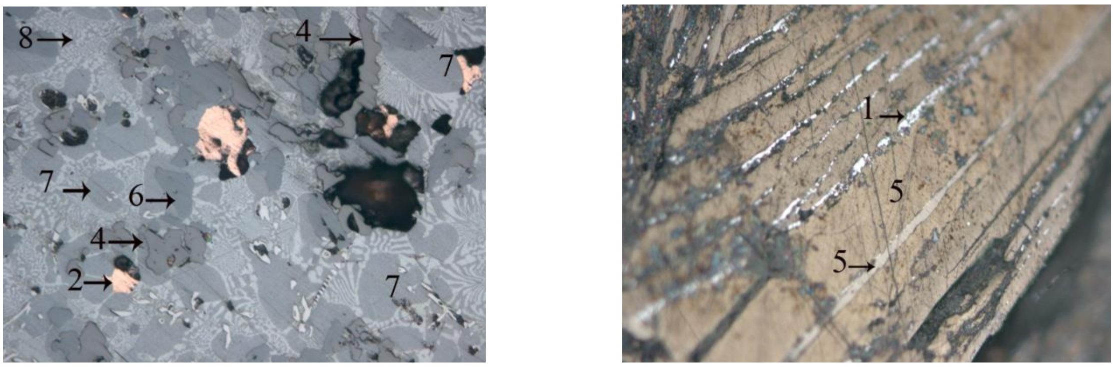
Figure 4.4 - Microstructure of the slag.

Lead in the slag is found in oxide (PbO), metal (Pb_{Me}), and sulfide (PbS) forms. The results obtained are in good agreement with the data of [7].

It was established that the share of the sulfide component of lead is ~ 50 % of its total content in the slag. This testifies to the fact that in the mine contractile melting there is no significant redistribution of lead forms between matte and slag. Therefore, to minimize the lead content in the slag during mine contractile smelting, it is necessary to provide measures aimed at reducing the dissolved (PbO, Pb_{Me}) and mechanical losses of lead (PbS) in matte.

The minor elements - arsenic and antimony in the slags, for the most part, are in oxide form. Antimony is partially detected in metallic form (Sb°). The results obtained are consistent with the data of [8-11].

The structure of copper-lead mattes looks somewhat more complicated (Figure 4.5).



1- alloy of copper, iron with arsenic and antimony; 2 - metal copper; 4 - magnetite (Fe_3O_4); 5 - iron-copper sulfides; 6 - sphalerite ZnS; 7 - plattnerite PbO_2; 8 - galena PbS.

Figure 4.5 - Matte microstructure. Increase - X300.

In all the matte samples examined, copper was mainly found in sulfide

(Cu_2S) form. Copper compounds with arsenic (Cu_3As) and copper with antimony (Cu_3Sb) with pronounced outlines in insignificant amounts were found. Small inclusions of copper are presented in the form of ferrites. Also compounds of arsenic and antimony with iron were found. It is characteristic that the proportions of the established various forms of copper in all matte samples are approximately equal and are at the level of: in the form of sulfide – 80 %, in the metallic form (the fraction of intermetallic compounds) ~ 15 % and in the form of copper ferrites – about 5 % of the total copper content in the mattes. Lead in mattes is represented by two forms - sulfide (PbS) and dissolved form, represented as PbO and Pb_{Me}. The proportions of the dissolved and sulfide forms of lead are approximately equal. The established forms of finding copper and lead in the products of mine contractile smelting are of fundamental importance for determining the quantitative relations of oxide and sulfide losses of metals with slag. Taking into account that the loss of copper and lead with slag and matte determine the peculiarities of the distribution of noble metals between the products of smelting, the results obtained take on special significance for practice.

The results allow us to draw a number of important conclusions for practice:

a) In the conditions of mine contractile melting, low extraction of copper in the matte is due to an increase in the total loss of copper with slag. It was found that the proportion of copper oxide losses during melting prevails over sulfide losses and is ~78 %. Therefore, in order to reduce copper losses with slag, first of all, it is necessary to provide measures to reduce copper oxide losses.

b) The high percentage of lead in the slag in the form of its sulfide (~50 %) indicates a lack of complete recovery of lead sulfide and separation of matte and slag during melting. The presence of dissolved form of lead in the form of metal in slags requires measures to reduce the solubility of lead in the matte.

c) Significant losses of lead with matte (up to 25 %) have a significant impact on the reduction of its extraction in lead and loss of precious metals, both with matte and slag. The study of this issue is of great interest for practice.

4.2 Thermodynamic calculations for the input mixture: Cu – Pb – Zn – As – Sb – Fe – S – O - SiO_2

The thermodynamics of the high temperature treatment of multicomponent mixtures Cu – Pb – Zn – As – Sb – Fe – S – O - SiO_2 has not been studied, although thermodynamic calculations in the absence of lead are available [26-28]. Standard values for pure substances were used [29-31]. The results of x-ray fluorescence measurements of converter slag and Cu-Zn ore and mineralogical studies on the form of the metals in converter slag [32] were used to calculate the thermodynamic properties. Arsenic and antimony in the slag are mainly found in the pentavalent form: As^{5+}, Sb^{5+} or As_2O_5 and Sb_2O_5 [33,34]. The Gibbs free energy (ΔG) at 1073–1573 K for three groups of reactions is shown in table 4.4.

Table 4.4 – Calculated Gibbs free energy (ΔG) for high temperature treatment of the metal mixture: $Cu-Pb-Zn-As-Sb-Fe-S-O-SiO_2$

		Gibbs free energy ΔG°_T (kJ/mol)				
		Temperature (K)				
First group	Reactions	1073	1273	1473	1573	ΔG°_T (kJ/mol)
1	$2CuFeS_2=Cu_2S+2FeS+0.5S_2$	-22	-83	-147	-180	$\Delta G^\circ_T=138.9-0.353T$
2	$FeS_2=FeS+0.5S_2$	-9	-42	-75	-91	$\Delta G^\circ_T=170.75-0.167T$
3	$4Cu2O+3S_2=4Cu_2S+2SO_2$	-579	-589	-599	-594	$\Delta G^\circ_T=-542.84+0.036T$
4	$Cu_2O+FeS=Cu_2S+FeO$	-96	-107	-116	-119	$\Delta G^\circ_T=-47.88-0.046T$
5	$Cu_2O+ZnS=Cu_2S+ZnO$	-80	-89	-98	-100	$\Delta G^\circ_T=-37.254-0.041T$
6	$Cu_2O+PbS=Cu_2S+PbO$	-46	-56	-66	-67	$\Delta G^\circ_T=3.207-0.046T$
7	$PbO+ZnS=PbS+ZnO$	-34	-33	-32	-33	$\Delta G^\circ_T=-40.461+0.006T$
8	$2FeO+1.5S_2=2FeS+SO_2$	-97	-81	-67	-60	$\Delta G^\circ_T=-175.66+0.074T$
9	$4Fe_3O_4+S_2=12FeO+2SO_2$	259	133	6	-58	$\Delta G^\circ_T=938.95-0.633T$
10	$3Fe_3O_4+FeS+5SiO_2=5(2FeOxSiO_2)+SO_2$	-75	-78	-79	-92	$\Delta G^\circ_T=-50.695-0.021T$
Second group						
11	$2PbO+1.5S_2=2PbS+SO_2$	-198	-182	-167	-162	$\Delta G^\circ_T=-277.84+0.075T$
12	$PbO+FeS=PbS+FeO$	-50	-50	-50	-51	$\Delta G^\circ_T=-51.089+0.001T$
13	$2PbOxSiO_2+2FeS=2PbS+2FeOxSiO_2$	-78	-54	-33	-31	$\Delta G^\circ_T=-182.86+0.1T$
14	$2PbOxSiO_2+2ZnS=2PbS+2ZnOxSiO_2$	-54	-44	-38	-38	$\Delta G^\circ_T=-88.356+0.034T$
15	$PbS+2PbO=3Pb+SO_2$	9	-25	-52	-64	$\Delta G^\circ_T=-88.356+0.034T$
Third group						
16	$2As_2O_5+5.5S_2=2As_2S_3+5SO_2$	-821	-841	-856	-862	$\Delta G^\circ_T=-73.48-0.082T$
17	$2Sb_2O_5+5.5S_2=2Sb_2S_3+5SO_2$	-704	-728	-742	-746	$\Delta G^\circ_T=-62.61-0.084T$
18	$As_2O_5+5FeS=As_2S_3+5FeO+S_2$	-169	-217	-261	-282	$\Delta G^\circ_T=71.90-0.226T$
19	$Sb_2O_5+5FeS=Sb_2S_3+5FeO+S_2$	-110	-161	-204	-224	$\Delta G^\circ_T=130.34-0.227T$

The first group of reactions in table 3.2 includes sulfide ($CuFeS_2$, FeS_2) decomposition reactions, reactions between non-ferrous metal oxides and products of decomposition. These reactions describe the processes that occur during the formation of matte and slag. Gibbs free energy of these reactions under smelting conditions is high (60–150 kJ/mol). Only for reaction (9) is ΔG negative for temperatures above 1473 K. Thermodynamic calculations indicate that the reaction of copper oxide from converter slag with products of the sulfide decomposition and sulfides (ZnS, FeS, PbS) from the Cu- Zn ore with matte phase formation is possible within a wide temperature range, including the range of interest 1473–1573 K. The main effect on the recovery of copper to the matte is achieved by reactions (3)–(6) and of zinc to the slag by reactions (5. 7). Reaction (10) primarily reduces magnetite. The second group of reactions in table 4.4 includes the reaction between lead compounds (PbO, PbS, PbO $9SiO_2$) and products of the sulfide decomposition with formation of the lead bullion bottom phase (reaction 15). The thermodynamic probability of reactions (11)–(15) is ensured over the entire temperature range. The largest value of the Gibbs free energy is ΔG_{1573K} = 162 kJ/mol for reaction (11). In practice, reaction between zinc sulfide and lead silicate (reaction 14) is very important. Reaction (14) provides a high recovery of zinc from the Cu-Zn ore into the slag with simultaneous transfer of lead into the matte. The Gibbs free energy of reaction (14) is reduced from ΔG_{1073K} = 54 kJ/mol to ΔG_{1573K} = 38 kJ/mol (table 4.4). Thus, the highest probability of reaction (14) can be expected immediately after injection of the Cu-Zn ore. As a result of reaction (14), zinc sulfide from Cu-Zn ore is oxidized, and zinc is transferred into the slag in the form of its oxide. Lead from the lead oxide in the silicate slag phase passes to the matte in the form of PbS and is finally transferred to the lead bullion bottom phase. The quantity of Cu-Zn ore in the mixture should provide the optimal ratio PbS:PbO = 1:2 for formation of metallic lead bullion bottom phase. The third group of reactions in table 3.2 includes the reaction between arsenic and antimony compounds (As_2O_5 and Sb_2O_5) and products of sulfide decomposition to form non-toxic sulfides (As_2S_3 and Sb_2S_3). The Gibbs free energy of these reactions under smelting conditions is high (200–800 kJ/mol). Therefore, when loading a fresh portion of Cu-Zn ore, arsenic and antimony oxides are transformed into non-toxic sublimated sulfide. These results are consistent with a previous study of the sulfurizing process of lead smelter slag [35] in which it was shown that more than 96 % of the zinc in the slag could be converted into sulfides.

4.3 Distribution of copper, lead and related impurities between matte and slag

Figure 4.6 shows the balance of the resulting material flows of mine contractile smelting.

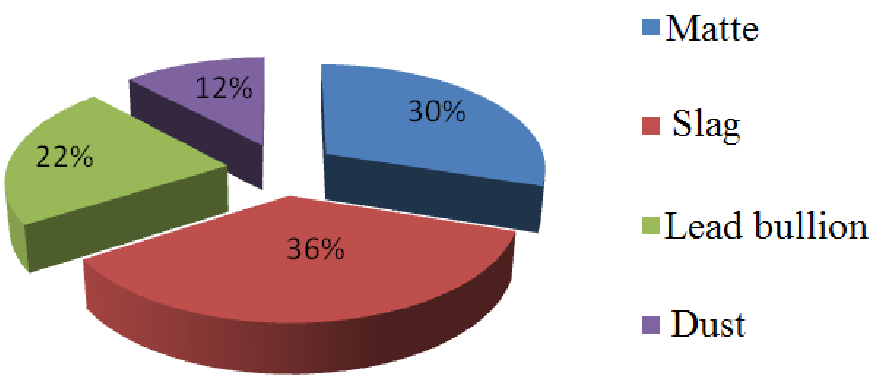


Figure 4.6 - Material balance of the received products

The lead bullion smelting yield is 22 %. Of the total amount of lead in the charge, only 68.8 % of lead passes into the base metal. A significant proportion of it (25.8 %) goes into matte. The lead content in mattes reaches 26 %. The remaining part of lead, 5.4 %, is distributed between slag and dust, 2.1 and 3.3 %, respectively. The data obtained indicate that the decrease in the extraction of lead in the draft metal is mainly due to its losses with matte. A significant part of antimony passes to the lead bullion – 26.9 %. The share of arsenic in the draft metal is insignificant and amounts to 8.8 %.

The copper content in the lead bullion varies from 2 to 5.5 % (according to the material balance, 3.3 %). With this quality of lead, it is impossible to achieve optimal technological indicators of subsequent refining operations, high quality of manufactured products and recycled materials.

The situation with the resulting copper-lead mattes, the yield of which reaches 30 %, is not the best. The copper content in them varies greatly from 25 to 45 %. The main part of copper – 87.5 % of its total amount in the original mixture, goes into matte. 8.4 % of copper goes into dust. The share of copper in the slag is insignificant and amounts to ~ 2 %, 45.4 % of arsenic and 27 % of antimony pass into matte. Of the total amount of zinc in the initial mixture, up to 22 % of zinc is concentrated in the matte. A significant content of impurities - lead, zinc, arsenic and antimony in the resulting mattes - a consequence of their high content in blister copper, and hence in the converter slags.

Slag yield during smelting – 36 %. Slags are characterized by a high concentration of zinc – 7.8 %. 60 % of zinc from its total amount in the initial charge goes to slag. The content of copper and lead in the slags is 0.47 and 1.79 %, respectively. The proportion of arsenic and antimony, rolling in the slag, is minimal, and is 3.0 and 5 %, respectively.

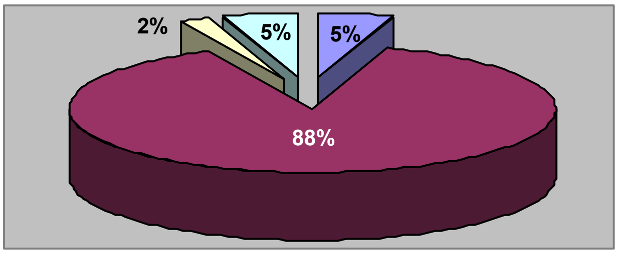
The output of dust in the mine contractile smelting is minimal and is 12 %. In the dust passes 43 % of arsenic and 41 % of antimony, of the total amount in the original mixture. The share of copper and lead, turning into dust, is 4.8 and 3.3 % of their total amount in the initial charge. 17.3 % of the total zinc is transferred to the dust.

Taking into account the data obtained, we carried out metallurgical calculations, including the compilation of the material and heat balance of the mine contractile melting. The results of the calculations are given in Appendix 1.

The distribution of metals between the products of mine contractile smelting is shown in figure 4.7.

The established patterns show that the behavior of metals in the process under consideration cannot be explained solely by the redistribution of metals between the smelting products. The definition and further elimination of the causes and factors affecting the observed negative distribution of metals between the smelting products requires additional studies of the thermodynamics for a number of equilibrium systems characteristic of mine contractile smelting and conversion.

Copper



Lead

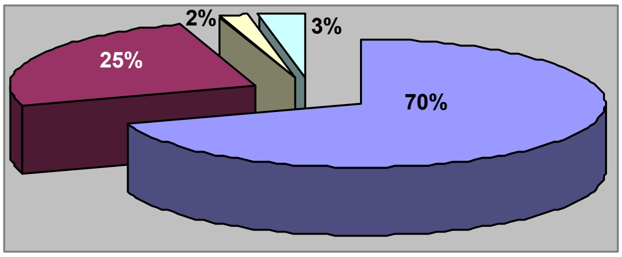


Figure 4.7 - The distribution of metals between the melting products

4.4 Equilibrium studies of copper-lead matte – slag – gas phase system

The study of the distribution of metals between the products of metallurgical production is an important issue of the theory and practice of metallurgical processes, since it, including the extraction of metals into a useful product and their loss with a waste product, determines the economy and technology of the process as a whole. Determination of the thermodynamic limit of solubility of metals in slag, as it was established in the above studies, requires knowledge of the forms of finding metals in the products of melting and the mechanism of their transition from one phase to another. At the same time, if in the technical literature there is a sufficient number of ways to determine the mechanical losses of metals with slags, the definition of dissolved losses of metals with slags requires clarification and additional experimental studies for each case.

Thus, in recent years, the equilibria of copper – slag and copper – matte-slag systems have been studied in detail, the dependences of copper in slag on various factors: temperature, oxidative potential of the gas phase (P_{O_2}), slag composition, copper activity have been determined. Nevertheless, despite the extensive available material, it remained unclear what the differences between the experimental data of different authors: with the difference in the conditions of the experiments or with the errors of the applied methods and experiments. Much worse is the case for the study of the solubility of lead in slag. The determination of solubility of lead in slags is devoted to a limited number of works, where on the basis of the study of the equilibrium of lead – slag, dissolved losses of lead with slag were determined.

There are practically no data on the solubility of copper and lead from copper-lead matte to slag in the technical literature. The limited availability of experimental material strongly inhibits the creation of a predictive thermodynamic model of lead solubility in slag, similar to copper. This requires further research.

4.4.1 Choice justification of research methodology

Research of the form of the presence of metals in solid samples of industrial matte and slag from mine contractile melting were carried out using an x-ray phase analysis method and mineralogical studies.

Elemental analysis of the studied samples was carried out on an Agilent 7700 Series ICP-MS inductively coupled with a plasma mass spectrometer (USA). The study of the forms of finding metals was carried out using an automated x-ray diffractometer DRON-3 with Cu_{K_α}, β-filter. Diffractogram recording conditions: U = 35 kV; I = 20 mA; θ-2θ shooting; 2 degree / min detector x-ray phase analysis on a semi-quantitative basis was carried out on the diffraction patterns of powder samples of slags and mattes using a method of equal weights and artificial mixtures. The quantitative ratios of the crystalline phases were determined. Interpretation of diffractograms was carried out using data from the ICDD card index: PDF2 (Powder Diffraction File) powder diffractometer database and diffractograms of mineral-free impurities. The content was calculated for the main phases. Mineralogical studies of the surface structure of solid samples of mattes and slags were carried out using a Neofot microscope (Carl Zeiss AG, Germany).

4.4.2 Installation diagram and experimental procedure

Experimental studies were carried out using sulfide melts based on sulfides of copper, iron, lead of variable composition. The composition of synthetic iron silicate slag in all experiments was constant. This approach made it possible to clarify the mechanism of copper and lead transition from matte to slags and to evaluate the effect of the composition of the initial sulfide melt on the dissolved losses of copper and lead in slags. The main attention was focused on the quantitative determination of dissolved losses of copper and lead in the slag. Selection of the composition of the initial sulfide alloys was carried out taking into account the compositions of polymetallic sulphide materials obtained in practice. To determine the solubility of non-ferrous metals in iron-silicate slag, a dynamic method is used, which allows to determine the loss of copper and lead with slag at controlled pressures of P_{O_2} and P_{X_2}.The essence of the method is that in equilibrium with a complex gas mixture – CO_2–CO–SO_2 of a given composition, the matte-slag system.The technique of the experiments was as follows. Sample copper-lead matte and silicate slag are placed in the boat, which is placed on a special stand made of foam material.

In [19] it is shown that the contact of the matte with the slag, the resulting matte spreading by wetting them with slag and capillary rise increases mechanical losses of metal with slag. To establish the dissolved metal losses in the slag must be eliminated, or to minimize its mechanical losses. This was achieved by the fact that in the conducted experiments, when the initial sample was heated, the molten slag flowed to the matte. Next, the stand together with the boat is loaded into a quartz reactor, which is equipped with a nozzle for entering and exiting the gas mixture. In the working zone of the quartz reactor at the same time is placed from four to six boats with the initial linkage.The temperature difference along the entire length of the working area is minimal and is no more than ±10 ºC from the set temperature. Temperature control was carried out by thermocouple PP-1.

After loading the boats, the quartz reactor was closed by a branch pipe. A silite furnace was pushed onto the reactor and heated to a predetermined temperature. The supply of a pre-prepared gas mixture of CO-CO_2-SO_2 of a given composition began from the moment of heating the furnace. The flow rate of the gas mixture remained constant throughout the experiment, and was one hours. After the necessary time the furnace was switched off. The gas mixture supply to the reactor was stopped at the moment of complete cooling of the furnace. Further, the furnace was moved away from the quartz reactor and the supports with boats were removed. After separation of matte and slag, they were subjected to chemical analysis.

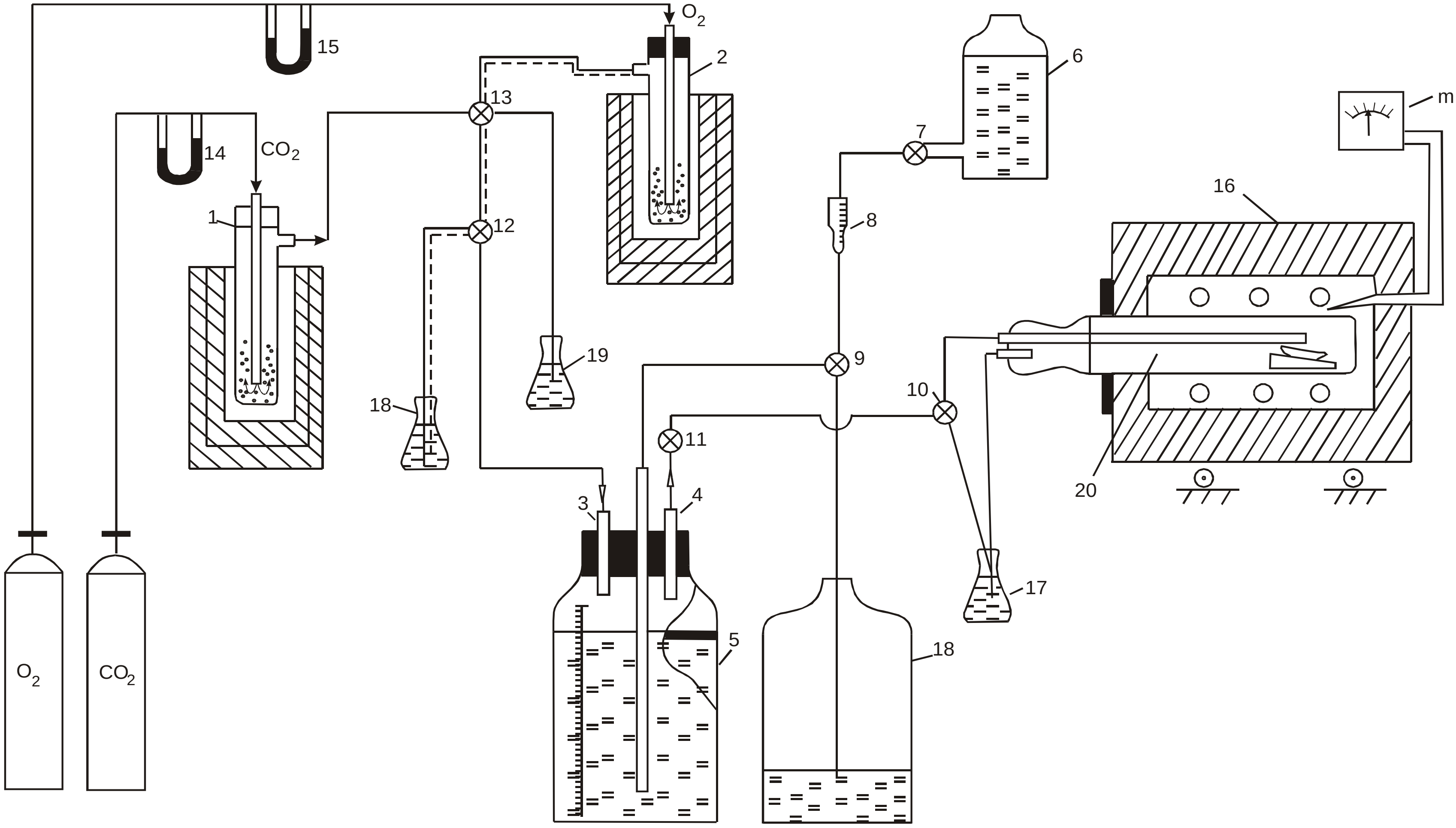


Figure 4.8 – Schematic diagram of the installation for investigation of equilibrium of matte–slag–gas

4.4.3 Preparation of raw materials

The composition of the initial iron silicate slag contained, % mass: 65.46 FeO; 30.8 SiO_2; 3.74 Fe_3O_4.

Synthetic copper-lead mattes of variable composition were prepared by mixing pre-prepared pure sulfides of copper, lead and iron in strictly calculated quantities. Calculations of the required amount of sulfides were based on the assumption that the sum of copper and lead content in the initial matte was equal to 30, 40, 50, 60, 70, 75 and 80 % by weight., and their ratio varied from 0.5 to 3.0. The sample of matte in all experiments was constant and equal to 2 g, and slag - 4 g. all mattes were added to 2 % of arsenic and antimony from the weight of the original matte. The selected compositions of the original matte completely cover the area of matte compositions obtained in practice.

The values of oxygen and sulfur potentials were determined by choosing the necessary composition of the gas mixture CO – CO_2 – SO_2. The SO_2 content in the gas mixture was 17 %, the ratio of $CO/CO_2=3$, which provided the value of P_{S_2} corresponding to the conditions of the reducing atmosphere. The values of P_{O_2} and P_{S_2} in all experiments remained constant and were maintained at the level of: $P_{O_2} = 2.74\cdot10^{-4}$ Pa and $P_{S_2} = 1.45\cdot10^{2}$ Pa.

The experiments were carried out at a temperature of 1523 K.

Samples of matte and slag, after the experiment, were subjected to chemical analysis for the content of copper, lead, arsenic and antimony.

4.4.4 Results and general discussion

The results of experimental studies are given in table 4.5.

General analysis of the experimental results shows that the content of lead in the initial matte on the copper oxide solubility has only a weak effect. In the case of lead, its solubility in the slag is determined by both a change in the Cu/Pb ratio and the iron content in the matte.

Earlier it was found that for an array of industrial data (table 4.1, section 4.1) in the construction of traditional dependences of type (Me) = f [Me], for copper, a sufficiently close correlation between the values under consideration could not be established, while for lead an equation adequately describing the desired dependence was obtained:

$$(Pb) = 0.082\,[Pb] - 1.01,\ r = 0.79 \qquad (4.1)$$

This phenomenon can be explained by the redistribution of forms of metals in matte and slag. Apparently, in the case of copper, when constructing the dependence (Cu) = f [Cu], it is necessary to take into account not the total content of copper in the matte, but only that its share, which is connected in the form of sulfide.

On this basis, in the presented array of industrial data copper content in the matte was calculated for the content is associated in the sulfide. Figure 4.9 shows the dependence of the copper content in the slag on the copper content in the matte bound to the sulfide form.

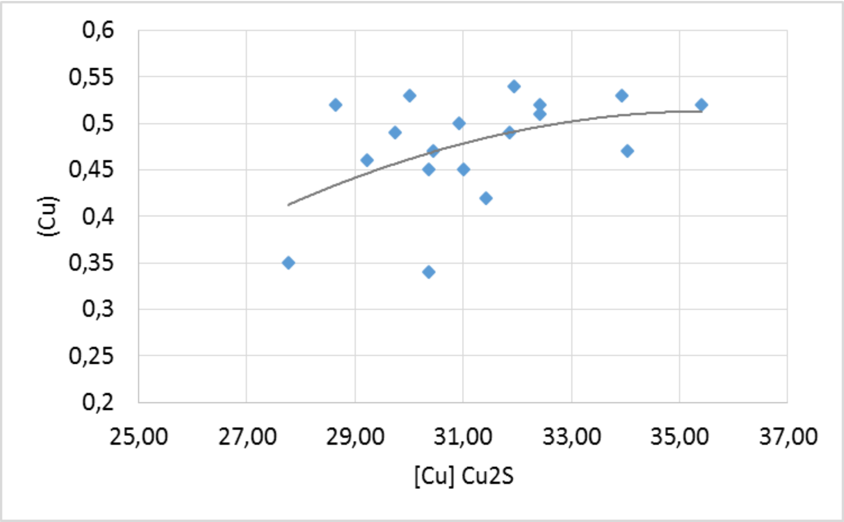


Figure 4.9 - Dependence of copper content in slag on its content in matte

It is easy to see that the copper content in the slag increases with the copper content in the matte. Therefore, despite the complexity of the distribution mechanism between the smelting products, the traditional dependence for copper (Cu) = f [Cu] is preserved in the processing of copper-lead containing raw materials in the conditions of mine contractile melting.

The obtained results of experiments together with industrial data of slag and matte compositions given in table 4.1 (section 4.1) were subjected to mathematical processing. As a result, the equations describing the losses of copper, lead and slag depending on the composition of the original matte are obtained:

$$(Cu) = 0.199 + 3.118*10^{-3}[Cu] - 2.29*10^{-3}[Pb], \qquad r = 0.92; \qquad (4.2)$$

$$(Pb) = 0.431 + 0.011[Pb] - 1.127*10^{-3}[Fe]\ , \qquad r = 0.94. \qquad (4.3)$$

where r is the correlation coefficient.

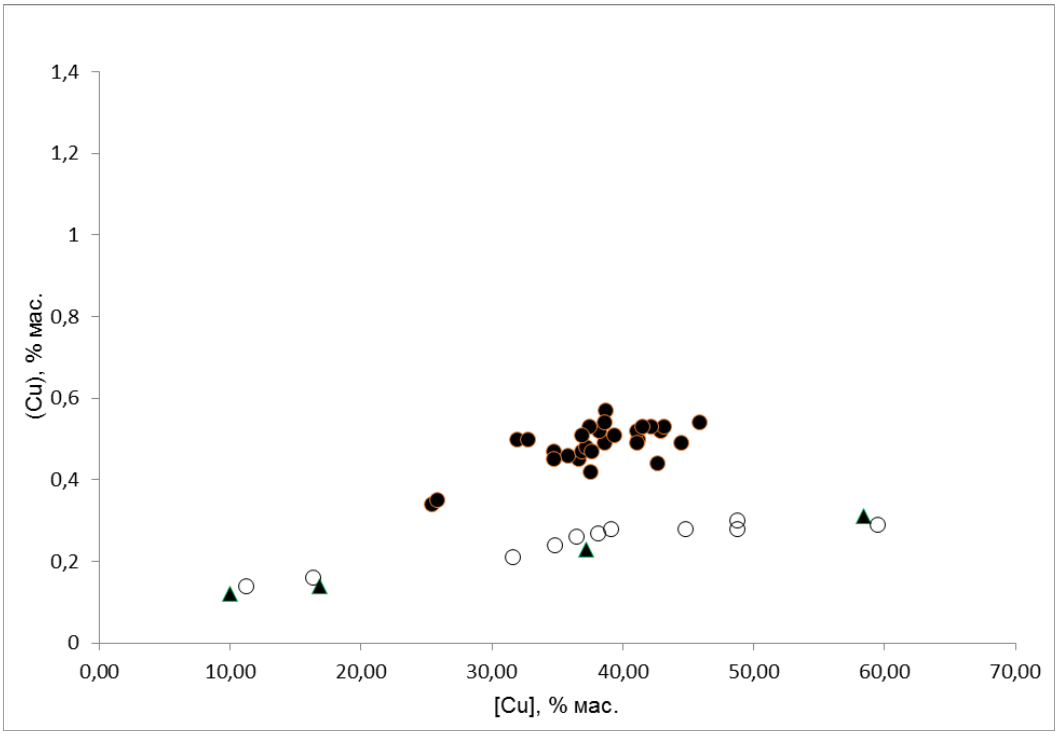
Table 4.5 - Results of chemical analysis and calculated values of the distribution coefficients of metals (L_{Me}) between a matte and a slag

№	Metal content in final matte, % by weight.				Composition of final slag, % wt.						The distribution coefficient of the metal, L_{Me}			
	[Cu]	[Pb]	[As]	[Sb]	(Cu)	(Pb)	(As)	(Sb)	(FeO)	(SiO_2)	L_{Cu}/10	L_{Pb}	L_{As}	L_{Sb}
1	11.2	19.4	0.22	0.89	0.14	0.58	0.13	0.24	64.03	28.31	8.0	33.45	1.7	3.7
2	16.3	13.72	0.36	1.0	0.16	0.12	0.14	0.28	59.23	27.84	10.2	114	2.6	3.6
3	31.62	8.67	0.78	0.83	0.21	0.3	0.19	0.23	59.87	29.1	15.1	28.9	4.1	3.6
4	36.42	23.17	0.86	0.48	0.26	0.89	0.21	0.13	64.02	27.97	14.0	26.03	4.1	3.7
5	39.07	19.42	0.9	0.57	0.28	0.58	0.21	0.16	60.73	29.54	13.95	33.48	4.3	3.56
6	34.8	32.86	0.84	0.25	0.24	1.68	0.2	0.1	57.9	28.78	14.5	19.56	4.2	2.5
7	38.1	28.57	1.15	0.31	0.27	1.33	0.24	0.09	62.87	27.97	14.1	21.48	4.8	3.4
8	44.8	23.18	1.18	0.39	0.28	0.89	0.25	0.11	59.74	29.45	16.0	26.05	4.72	3.5
9	48.74	22.8	1.16	0.35	0.3	0.86	0.19	0.1	61.83	28.64	16.25	26.5	6.1	3.5
10	48.72	27.92	1.23	0.22	0.28	1.28	0.26	0.06	62.49	29.47	17.4	21.81	4.7	3.66
11	59.47	17.09	1.47	0.39	0.29	0.39	0.29	0.19	61.92	28.97	20.5	43.82	5.1	2.1

High values of correlation coefficients r = 0.92 and r = 0.94 indicate a strong relationship between the values under consideration. It is easy to see that the solubility of lead in the slag decreases with increased iron content in the matte. This is confirmed by the oxide mechanism of lead transition to slag.

Equations (4.2), (4.3) allow us to estimate the effect of matte composition on the final content of copper and lead in slag and can be used to quantify their content with slag in practice.

Figure 4.10 shows the dependence of copper oxide solubility in slag on its content in matte. The figure also shows the data of industrial results showing the dependence of the copper content in the slag on the copper content in the matte bound in the sulfide.



○ – experimental data; ● – industrial area; ▲ – data work [23].

Figure 4.10 - Dependence of dissolved copper losses in slags from the copper content in the matte

A comparative analysis of the results shows a good consistency: the nature of the dependence of the copper content in the slag on its content in the matte is identical and confirms the traditional patterns.

It can be seen that the data of this work are below the results of industrial data. This seems quite natural. The overestimated values of the industrial results are explained by the higher temperature of the process, the increase of which leads to an increase in the copper content in the slags. In addition, the content of copper in industrial slags characterizes its total content, while in our studies only the oxide solubility of copper is taken into account.

Similar direct evidence of the retention of the mechanism of transfer of copper from the matte to the slag in the dissolved form ($CuO_{0,5}$) throughout the range of compositions of mattes.

Figure 4.10 - 4.11 shows the dependence of the metal distribution coefficients between matte and slag on their content in the matte at a constant pressure of oxygen and sulfur, as well as temperature.

It is easy to see the General pattern for copper and arsenic – the distribution coefficients increase with their content in matte (figure 4.9-4.11). The results on the distribution coefficient of these metals practically fall on a straight line, with a slight spread.

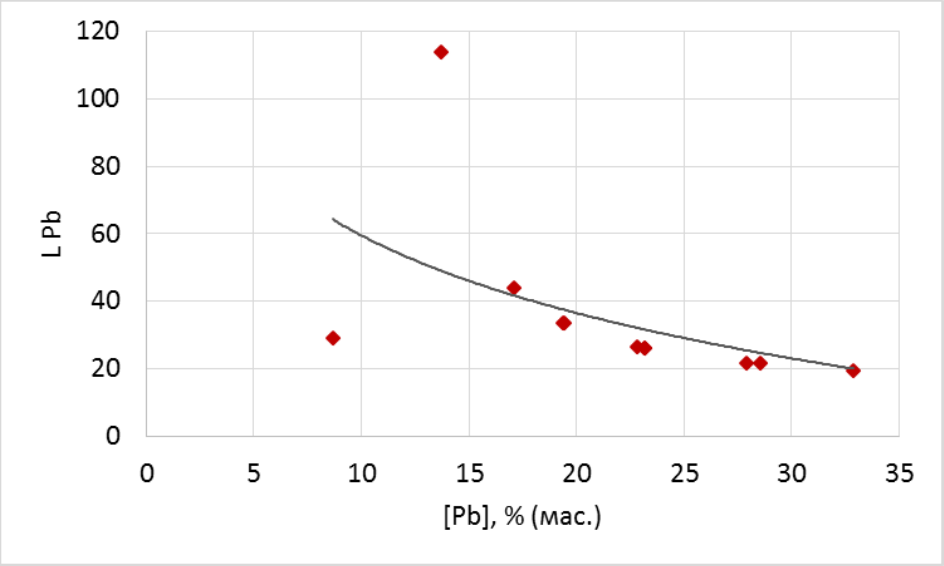


Figure 4.11 - Dependence of the distribution coefficient of lead (Pb) from its content in matte, % (wt.)

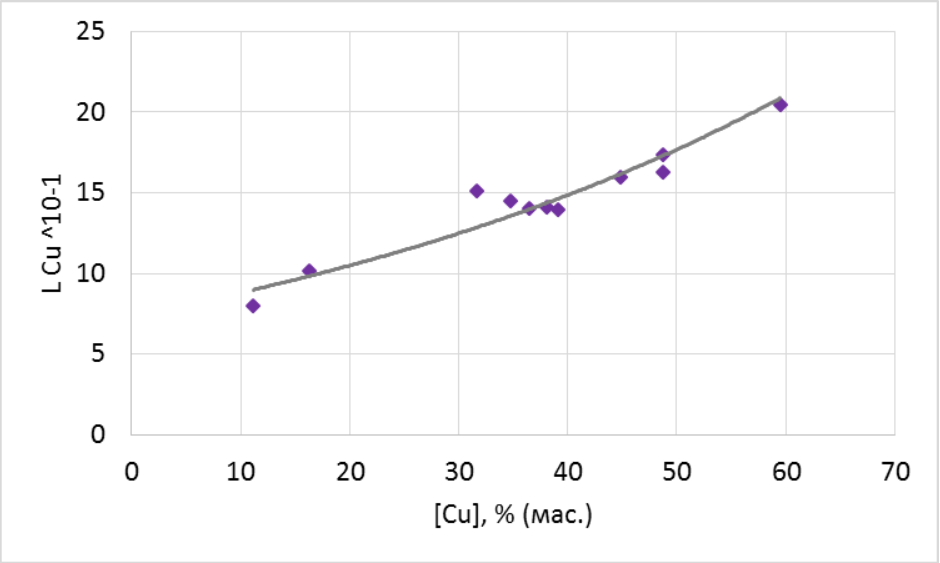


Figure 4.12 - Dependence of the copper distribution coefficient (L_{Cu}*10^{-1}) from its content in matte, % (wt.)

This indicates that in the system under consideration the mechanism of copper and arsenic transition to slag is described by their oxidation reactions. At the same time, their losses with slag are determined by the oxide form of solubility in slags.

It is noteworthy that the distribution coefficient of lead between matte and slag gradually decreases with increasing lead content in the matte. And at low concentrations of lead, there is a noticeable spread of data (figure 4.8).

The dependences observed in figure 4.10 - 4.11 are well described by equations constructed as a result of mathematical processing of experimental data, which have the form:

$$L_{Cu} / 10 = 0.93 + 0.37\,[Cu], \qquad r = 0.91; \qquad (4.4)$$

$$L_{Pb} = 45.23 - 0.69\,[Pb], \qquad r = 0.77; \qquad (4.5)$$

where r - is the pair correlation coefficient.

The relatively high correlation coefficients of equations (4.4) and (4.5) indicate a strong relationship between the values under consideration.

Thus, the results show that in order to reduce the loss of lead with slag, it is necessary, first of all, to minimize the proportion of lead dissolved in the matte in the form of metal, and then to influence the reduction of lead sulfide content in the matte.

4.5 Ways to improve the process performance of mine contractile melting

The work presents a theoretical assessment of copper, lead, arsenic, antimony in mine contractile melting is determined mainly by the composition of the initial charge. It is established that during the melting of semi-products and circulating materials of lead production the consumption of quartz flux is unreasonably high, which increases the slag yield and affects the final distribution of metals between the matte and slag.

Based on the results obtained, the composition of the initial charge was adjusted by determining the optimal flow rate of quartz flux. The essence of the chosen approach is that the optimization of the flux consumption of the furnace and the thermal balance of the furnace show that the excess heat available in practice allows to process up to 14 % of copper-zinc ore from the weight of the charge. This conclusion is of fundamental importance for practice, based on the following possibilities:

a) There is an additional possibility of direct processing of complex composition of copper-zinc ore in one operation with the transfer of copper and zinc in the target products-matte and slag, respectively, with their high extraction;

b) The use of an additional amount of quartz contained in the ore will significantly reduce the consumption of quartz flux, which will affect the reduction of material costs;

c) Processing of copper-zinc ore, together with intermediates and recycling materials of the lead production will allow to use it as sulfuring agent for the transfer of arsenic and antimony in their high-volatile sulfides, which will greatly increase there is license valid is provided based on the content of quartz present in the dust;

d) Loading of high-sulfur copper-zinc ore will also create favorable conditions for the sulfide reactions of lead media, which will significantly reduce their losses with slag.

X-ray phase analysis of a number of ore samples was carried out to determine the phase composition of copper-zinc ore. The results of the research showed that the main sulfide components are Cu_2S, $CuFeS_2$, FeS_2, FeS and ZnS.

When structuring the composition of the initial charge, the quantitative ratios of its main components - copper slurry, converter slag and charge CM – were left unchanged. Quartz and calcium oxide are 3 % and 2 %, respectively.

Selection of the required amount of copper-zinc ore was carried out by calculation, taking into account the content of copper, zinc, iron, silica and sulfur in it, bound in various compounds.

Metallurgical calculations of the initial charge composition were carried out using specially developed mathematical programs. The calculations used the data of factory practice and the results of mineralogical studies on the forms of non-ferrous metals, arsenic and antimony in the components of the initial charge and smelting products (Appendix B).

When choosing the optimal flow rate of copper-zinc ore, we proceeded from the possibility of complex use of its high-sulfur components (pyrite, chalcopyrite) as a sulfuring component and the amount of quartz, since it is contained in the ore.

The calculated composition of the initial charge of the shaft contractile melting, obtained as a result of metallurgical calculations, is shown in figure 3.3 and 3.4 (section 3.3)

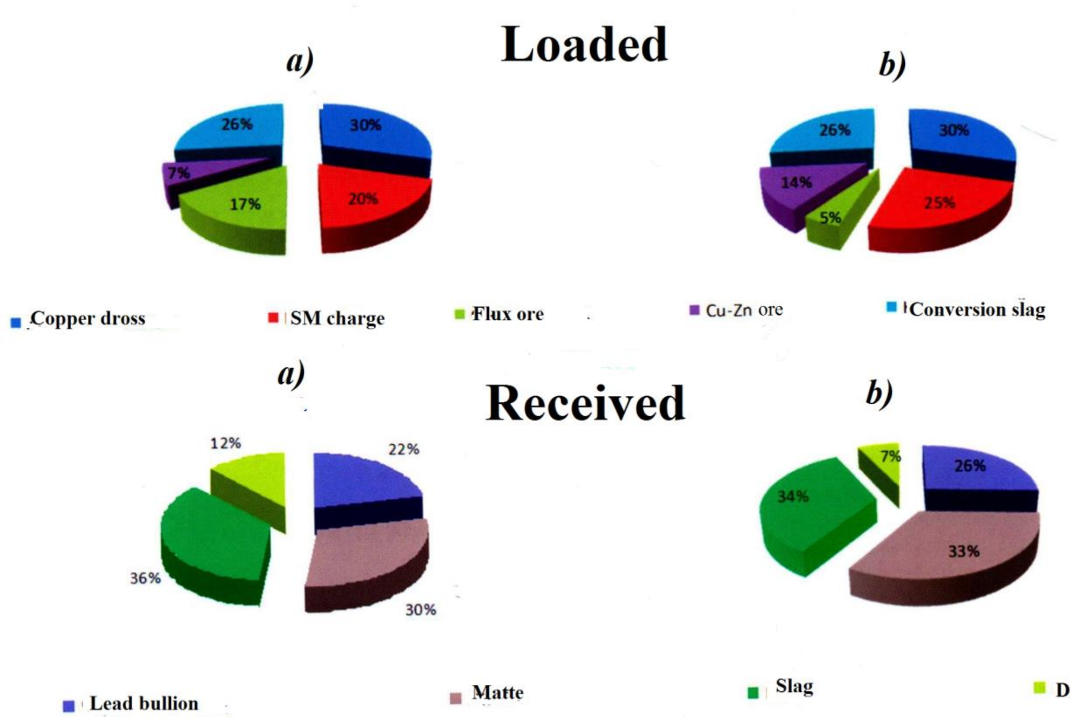
A comparative analysis of the existing initial charge with its corrected structure shows that when melting the charge of a given composition by the mechanism of the process itself, it is possible to achieve favorable conditions for obtaining copper and lead-poor slags.

Thus, in figure 4.13 it can be seen that the yield of products of mine contractile melting is markedly different from the composition of the charge of the existing technology. The content of copper in the slag is reduced from 0.92 % to 0.3 %, lead – from 1.2 % to 0.2 %.

Increases the content of arsenic and antimony in the dust. Check them out in the dust, 85 % and 77 %, respectively.

The distribution of copper and lead between smelting products has been significantly improved. The composition of the slag contains a minimum content of copper (0.3 %), lead (0.2 %) and arsenic (0.2 %), which leads to an increase in its quality. Matte quality is improved: the copper content in it is increased to 92 %.

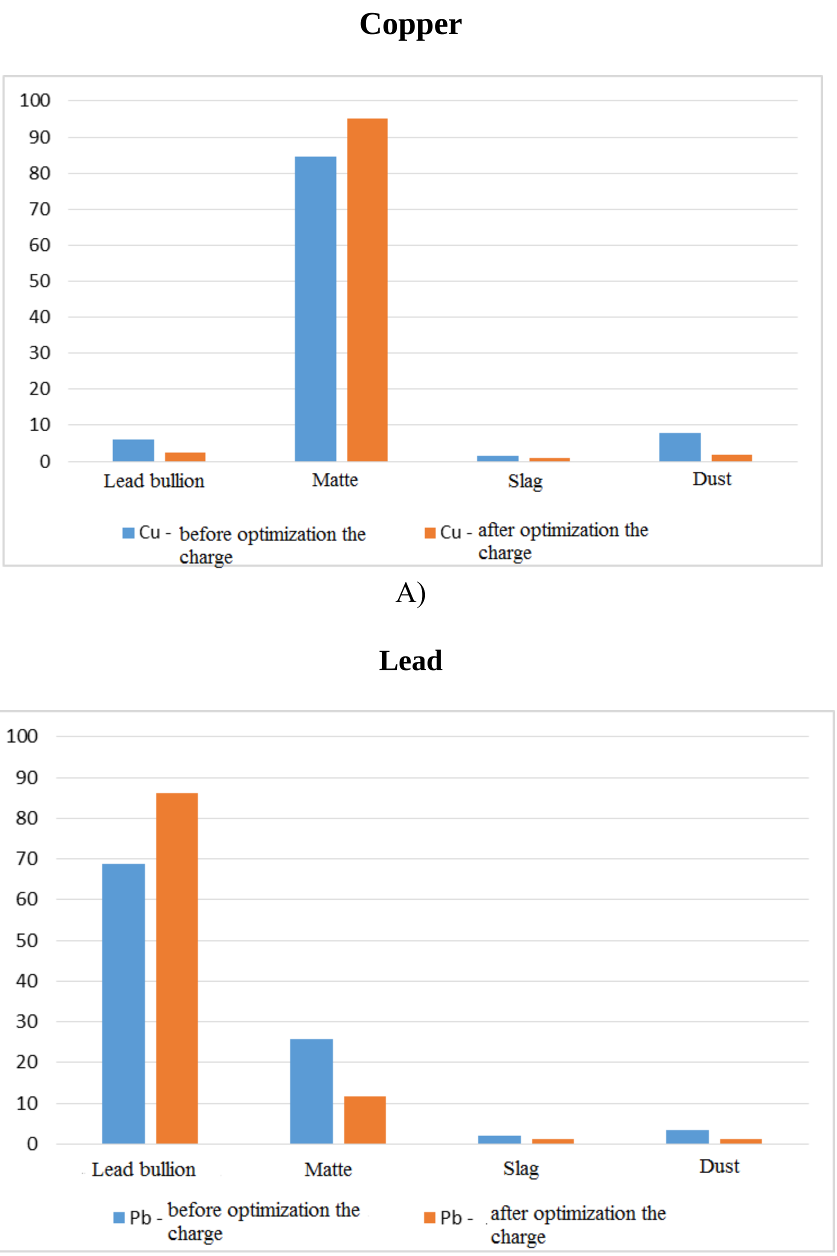
Exceeds its content according to the existing scheme.



a) - initial charge according to the existing technology; b) - adjusted composition of the initial charge

Figure 4.13 - comparative analysis of material flows when processing the original charge of different composition

A comparative analysis of the distribution of metals between the products of mine contractile melting, obtained by the existing and proposed technology is shown in figure 4.13.



A)

B)

Figure 4.14 – A comparative analysis of the distribution of metals

As can be seen with the optimal composition of the initial charge, the content of copper sulfide in the matte increases and favorable conditions for the sublimation of arsenic and antimony are provided.

The amount of slag is reduced by reducing the consumption of quartz flux.

In table B.12 (Appendix B) a comparative analysis of the technological parameters of the process of mine contractile melting in the processing of the existing charge and the adjusted composition of the original charge by adding m-TS ore.Thus, the obtained results show the principal possibility of improving the technological parameters of the process of mine contractile melting by direct processing of copper-zinc ore and optimization of its consumption.

5 Possibility of using the Vanyukov process to process semi-products and recycled materials for lead production

5.1 Research methods

The data on thermodynamic equilibrium of matte – slag system – gas phase and lead bullion – slag are widely used in the work. Evaluation of the possibility of joint processing of semi-products of lead production (copper slurries, the poor copper-lead mattes) sulfide lead concentrate is carried out on the basis of the calculation of material balance of two zone Vanyukov furnace using a specially developed program.

The composition structure of the initial charge is selected based on melting on matte to produce lead-rich slag in the oxidizing zone of the Vanyukov′s furnace. Extraction of lead from slag is provided in the recovery zone of the furnace.

Compositions of components of initial charge are accepted according to factory practice of LLP “Kazzinc” (table 5.1).

Table 5.1 - Chemical composition of the components of the initial charge

Name of products	Chemical composition, % wt.					
	Cu	Pb	Zn	S	Fe	SiO_2
Copper slickers	29.0	36.0	4.0	8.8	-	-
Lead concentrate	1.7	41.5	5.1	28.0	16.3	1.4
Copper gold-containing concentrate	4.9	2.7	6.9	2.0	3.7	66.0
Lead dust	0.1	53.6	9.8	14.2	0.9	0.7

Calculation of the thermal balance of the process was a traditional task and was reduced to establishing a heat deficit in order to determine the optimal fuel consumption (coal) and reducing agent (carbon) required for melting. As fuel and reductant used coal of Shubarkul deposit of the following composition, %: 87.5; 12.5 other.

In was used as a flux silica flux composition, %: Fe – 3.5; 75.0 – SiO_2; CaO – 5.0; 16.5 – other.

The composition of the slag melting, % wt.: 0.19 Cu; Pb 42.97; of 9.26 Fe; 7.20 Zn; of 15.09 SiO_2; CaO 0.16; 7.76 O_2; other of 17.38.

Melting temperature is 1300°C.

The calculations used the blast is enriched with oxygen.

The number of forms in the oxidation zone of magnetite was determined according to the state diagram of the system $FeO-Fe_2O_3-SiO_2$ on the basis of $FeO/Fe_2O_3=4$ and the content of silica in the slag [24].

5.2 Results and discussion

The schematic diagram of the proposed technology for processing semi-products and recycled materials of lead production is presented in Figure 5.1.

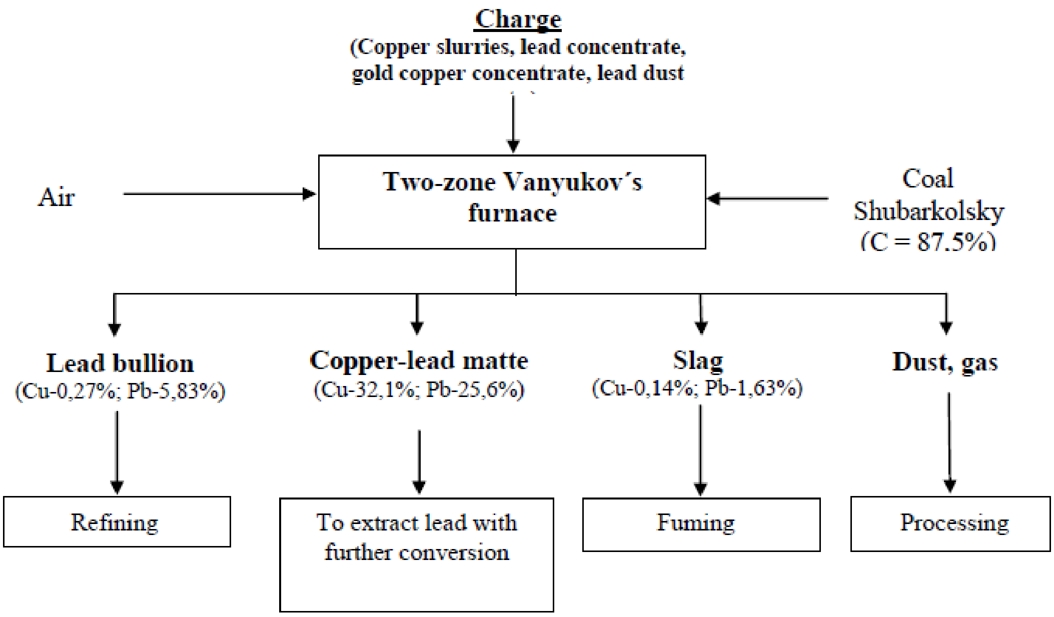


Figure 5.1 - Schematic diagram of the processing of semi-products and recycling materials of the lead production

The structure of the initial charge composition is shown in Figure 5.2.

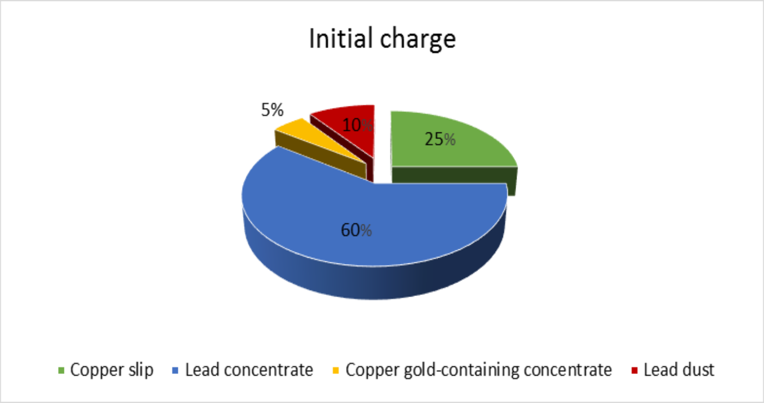


Figure 5.2 - Composition of the initial charge

The choice of composition of the components of the initial charge is chosen so that under conditions of oxidizing atmosphere to prevent the flow of melting reaction between the sulfide and oxide of lead. This is achieved by selecting the optimal ratio between the composition of the initial charge and the flow rate of the blast enriched with oxygen required for the oxidation of a given amount of iron sulfide. Set the degree of enrichment of blast air with oxygen provides the minimum output lead of the sublimates and the necessity of a given level of desulfurization. Consumption of added flux promotes binding produced minor amounts of lead oxide and zinc silicate chemical resistant connection that prevents the leakage of the melting reaction between the sulfide and oxide of lead.

The products of melting of the oxidizing zone are copper-lead matte and slag rich in lead.

Copper-lead matte contains up to 15 % lead and can be processed according to the existing conversion technology to obtain copper bullion. The existing practice of copper-lead matte processing shows that the conversion process is accompanied by a large yield of lead dust, which, as a negotiable material, leads to significant losses of lead between the products of agglomerating firing and mine smelting. The source of losses of base metals is also converter slag with a high content of copper and lead (up to 3 % and 25 %, respectively), which is sent to mine contractile melting for their extraction. Based on this, in our opinion, the most appropriate is the organization of separate, independent processing of copper-lead matte obtained in a separate furnace for the purpose of additional extraction of lead from the matte to lead bullion. This approach will improve lead recovery and significantly improve the quality of copper matte with the exception of all shortcomings inherent in the existing technology. Our preliminary research experiments on the extraction of lead from matte in various ways have shown good results and will be published in the scientific literature in the near future.

The slag obtained in the oxidizing zone of the furnace contains up to 42.97 % of lead and is sent to the reduction zone to extract lead to lead bullion. The content of lead in draft the lead is 95.83 %. The minimum content of impurity metals (Cu, As, Sb) will significantly reduce the load on further refining operations of lead bullion. Obtained after the restoration of slag is suitable for use for its intended purpose – for the production of building materials or iron.

The material balance of the fluxes of the oxidizing zone of the furnace is shown in Figure 5.3.

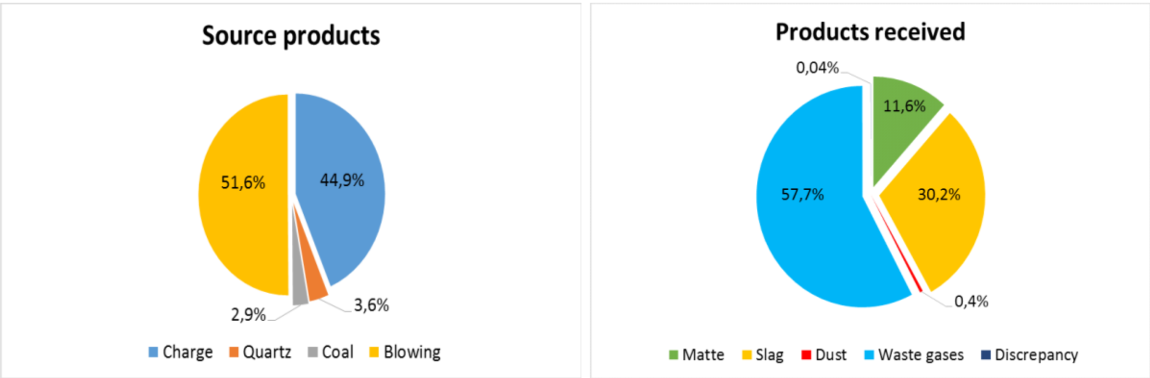


Figure 5.3 - Material balance of the flows of the oxidizing zone of the Vanyukov´s furnace

It is easy to see that the matte output is 11.63 % at the selected process organization. At the optimal level of oxidation of iron sulfide, preventing the formation of lead metal copper content in matte is 32.09 %. The extraction of copper in the matte reaches 97.5 %.

The compositions of the obtained products of the oxidizing and reducing zone are presented in table 5.2, 5.3 respectively.

Table 5.2 - Chemical composition of products obtained in the oxidizing zone

Products	Quantity, t	Chemical composition, % wt.							
		Cu	Pb	Fe	Zn	S	CaO	SiO_2	Other
Matte	25.9	32.1	25.1	15.4	0.6	21.1			5.7
Slag	67.4	0.2	42.6	9.2	7.1		0.2	14.9	18.1
Dust	1.0	8.6	39.4	10.1	5.4	20.6	0.1	4.2	11.7
Waste gas	128.6		2.7		0.2	11.2			
In total:	222.9								

Table 5.3 - Chemical composition of products obtained in the recovery zone

Products	Quantity, t	Chemical composition, % wt.							
		Cu	Pb	Fe	Zn	S	CaO	SiO_2	Other
Lead bullion	28.7	0.1	35.1				1.4	28.7	0.1
Slag	35.5	0.1	0.7	5.9	0.1	12.9	13.7	35.5	0.07
Waste gas	13.1		1.1	0.3				13.1	
In total:	77.3								

Results calculation of the heat balance of the oxidizing and reducing zone of the Vanyukov´s furnace is presented in table 5.4, 5.5 respectively.

Table 5.4 - Thermal balance of the oxidizing zone

The arrival of the heat			Heat consumption		
Articles coming	kJ	%	Item of expenditure	kJ	%
The heat of the charge	1004.2	0.4	Heat matte	24406.3	9.3
Warm air	5201.2	2.0	The heat of slag	96032.1	36.4
The heat of oxidation reaction of metals	117702.0	44.7	Heat gases	143032.3	54.3
The heat of combustion of coal	134308.4	51.0			
The heat of slag formation	5255.0	2.0			
In total:	263470.8	100	In total:	263470.7	100

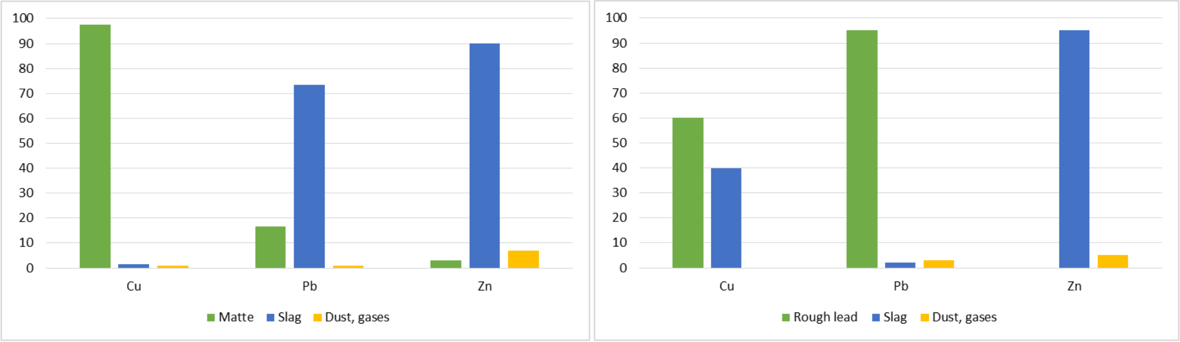
Table 5.5 - Heat balance of the recovery zone

The arrival of the heat			Heat consumption		
Articles coming	kJ	%	Item of expenditure	kJ	%
The heat of slag	79686.21	70.57	Draft lead heat	3466.26	3.07
Warm air	436.97	0.39	The heat of slag	50569.65	44.78
The heat of combustion of coal	27545.95	24.39	Heat gases	29215.54	25.87
The heat of slag formation	5255.01	4.65	The heat absorbed by the caissons	29672.69	26.28
In total:	112924.1	100	In total:	112924.1	100

From the results table 5.5 it follows that the selected process mode and the specified parameters ensure a stable operation of the Vanyukov´s furnace. The main share of heat coming up to 45.0 % of the heat generated from oxidation of iron sulfide. The heat deficit resulting from the incomplete oxidation of sulfide of iron, is covered with downloading the additional quantity of fuel (coal). At the same time, the required coal consumption is estimated to be insignificant and amounts to ~5 %.

To maintain the heat balance of the furnace recovery zone, 27545.9 kJ (~25 %) of the heat deficit must be covered (table 5.5). The established deficit of heat without much effort and costs is blocked by additional burning of coal.

Of great interest from the point of view of practice is the evaluation of the distribution of base non-ferrous metals between smelting products. In figure 5.4 shows the distribution of copper, lead and zinc between the melting products of the oxidation and reduction zone.



A)

B)

A) to the oxidation zone; B) rehabilitation area

Figure 5.4 - The distribution of Cu, Pb, Zn smelting between products:

It is easy to see that the oxidizing zone achieves a high copper distribution to ~98 % in matte, with its slight transition to slag and dust (1.5 % and 1.0 %, respectively).

High extraction of copper in the matte provides a sufficiently high quality of lead bullion: the copper content in the lead bullion is minimal and is – 0.27 %. The content of lead in the lead bullion reaches ~ 96.0 %.

The total balance of material flows of processing of semi-products and circulating materials in conjunction with the matte Vanyukov´s furnace shown in Figure 5.5.

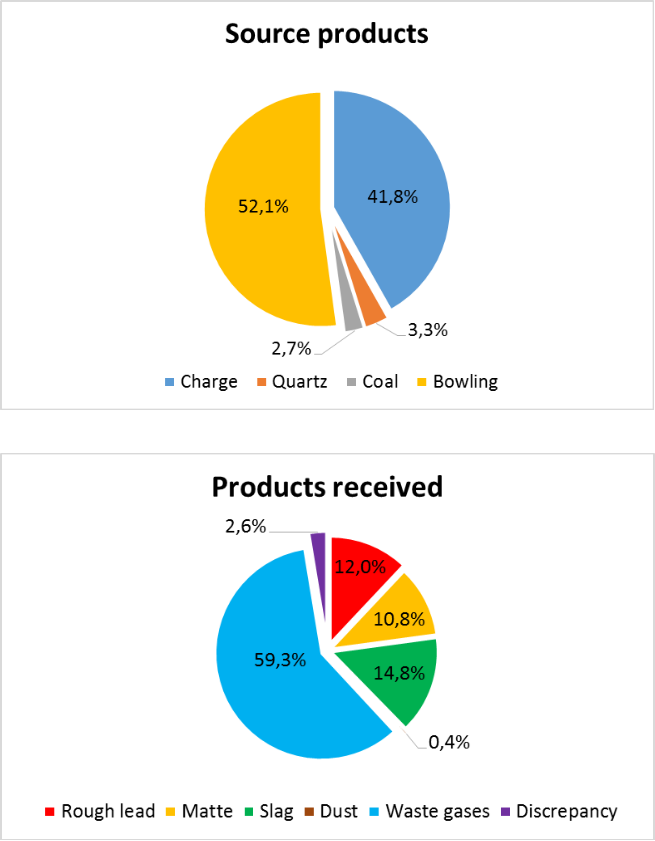


Figure 5.5 - The overall material balance the streams of the Vanyukov´s furnace in the processing of semi-products and recycling materials of the lead production.

The final distribution of non-ferrous metals between the fusion products is shown in Figure 5.6.

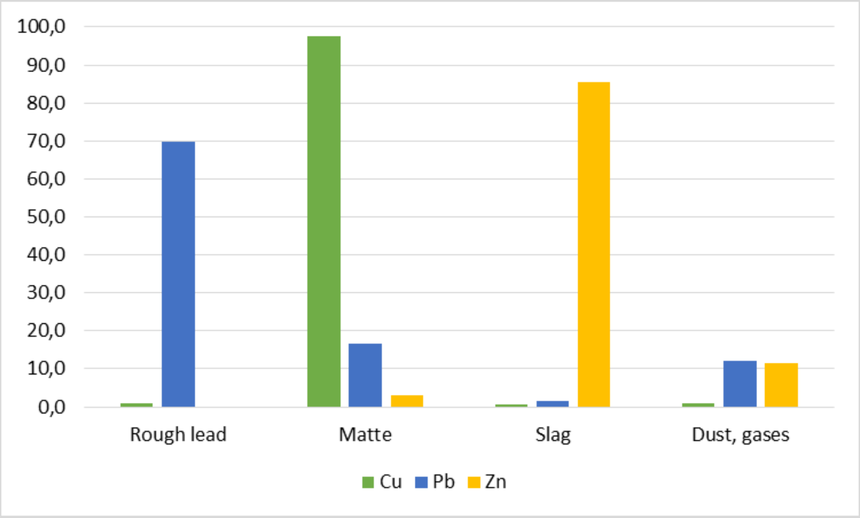


Figure 5.6 - Distribution of non-ferrous metals between smelting products

The results obtained show a high recovery of copper matte and lead lead bullion. In this case, zinc is mainly concentrated in slag and can be extracted without much effort and material costs by known methods, for example, fuming process. Implementation of the proposed technology in practice will ensure high efficiency of physical and chemical interactions between the components of the charge, elimination of the use of expensive coke reducing agent, as well as significantly improve the quality of the products. Separate independent processing of copper-lead matte will allow to achieve deep extraction of lead from matte and get rich (up to 50 %) on the content of copper matte. Further processing of these rods will significantly reduce the material costs of the conversion process and losses of copper and lead, arising from their circulation in the melting-conversion chain.

Summary:

a) On the basis of common positions of technological calculations the principal possibility of using two zone Vanyukov´s furnace for processing of semi-products and circulating materials with sulfide lead concentrate complex in chemical and phase composition is shown. It is shown that the choice of the structure and composition of the initial charge is of great importance in the organization of the process.

b) The use of a two-zone Vanyukov´s furnace allows to achieve selective separation of copper and lead into target products and to ensure their high extraction into matte and lead, respectively.

c) The obtained results will be used to select the optimal composition of the initial charge, determine the optimal process parameters in order to improve the existing technology of mine contractile melting, in relation to the conditions of LLP "Kazzinc".

CONCLUSION

The increase in the volume of semi-products and circulating materials of lead production requires the search for new approaches and solutions for their processing. The relevance of the issue is due to the fact that these products contain high content of copper, lead and related precious metals, have a complex chemical and mineralogical composition. The semi-products and circulating materials obtained at lead plants are characterized by a high content of arsenic and antimony, which have a negative impact on the environment and the final technological indicators during their processing.

As the analysis shows, in the technical literature there is practically no data on the study of thermodynamics of complex sulfide systems describing the compositions of intermediates and recycled materials. In the literature, there is practically no work on the study of the equilibrium of the copper-lead matte-slag-gas phase system. The coverage of such theoretically important issues as the mechanism of copper and lead transition from polymetallic copper-lead matte to slag seems insufficient. There is no data on the study of the forms of finding metals in smelting products in the processing of complex composition of copper, lead containing raw materials. All these gaps and their solution formed the scientific basis and direction of research of this work.

As a result of the complex research, including the study of thermodynamics of complex composition of oxide-sulfide systems, determination of the composition and structure of industrial slag and matte using high-precision technical means and metallurgical calculations in the new data complementary gaps in the technical literature and are of great importance for practice, namely:

a) It is established that during the reduction smelting semi-products and recycling materials of the lead production the mechanism of the transition lead and copper out of matte in the slag is determined by the occurrence of several reactions: the exchange between sulphides and precious metals and iron oxide; joint transition in the slag of lead cations and anions of sulfur and the reaction between sulphide of lead and copper with magnetite.

b) The results of x-ray phase analysis and mineralogical studies of the form of finding metals in solid samples of industrial matte and slag mine contractile melting showed that the copper content in the matte varies from 25 to 42 % (by weight), lead - from 19 to 30 % (by weight). There is a high content of arsenic and antimony in the matte, which vary from 1.5 % to 5 % and from 0.8 % to 2.5 % (mass.), respectively.

c) In the conditions of mine contractile melting, low extraction of copper in the matte is due to an increase in the total loss of copper with slag. It was found that the proportion of copper oxide losses during melting prevails over sulfide losses and is ~78 %. Therefore, to reduce copper losses with slag, first of all, it is necessary to provide measures to reduce copper oxide losses.

d) It was found that the proportion of lead in the slag in the form of its sulfide is high enough (~50 %), indicating incomplete recovery of lead sulfide and separation of matte and slag during melting. The presence of dissolved form of lead in the form of metal in slags requires measures to reduce the solubility of lead in the matte.

e) Significant losses of lead with matte (up to 25 %), the presence of which in the matte has a significant impact on reducing its extraction in the lead and loss of precious metals, both with matte and slag. The study of this issue is of great interest for practice.

Thus, the results obtained show that in order to reduce the loss of lead with slag, it is necessary, first of all, to minimize the proportion of lead dissolved in the matte in the form of metal, and then to influence the reduction of lead sulfide content in the matte.

On the basis of common positions of technological calculations the principal possibility of using two zone Vanyukov´s furnace for processing of semi-products and circulating materials with sulfide lead concentrate complex in chemical and phase composition is shown. It is shown that the choice of the structure and composition of the initial charge is of great importance in the organization of the process.

The use of a two-zone Vanyukov´s furnace allows to achieve selective separation of copper and lead into target products and to ensure their high extraction into matte and lead bullion, respectively.

The obtained results will be used to select the optimal composition of the initial charge, determine the optimal process parameters in order to improve the existing technology of mine contractile melting, in relation to the conditions of LLP "Kazzinc".

REFERENCES

1 Алтушкин И.А., Король Ю. А., Бакин А. В., Красильников Ю. В. Инновации в металлургии меди на примере реализации проекта реконструкции ЗАО «Карабашмедь». Часть 2. Опыт освоения печи Ausmelt // Цветные металлы. 2012.– № 8. – С.35-45.

2 Мечев В.В., Быстров В.П., Тарасов А.В. Автогенные процессы в цветной металлургии. –М.: Металлургия, 1991. – 413 с.

3 Такежанов С.Т., Ерофеев И.Е. Концепция «Комплекс» технико-технологического развития цветной металлургии Казахстана. – Алматы. 2001. – 136 с.

4 Чудаев И., Верещагин Ю. Металлургия меди – с древнейших времен до наших дней (Часть 2). // Сб. трудов I Международной конференции «Уральский рынок лома». Екатеринбург, 2008. – С.60-64.

5 Шмонин Ю.Б. Пирометаллургическое обеднение шлаков цветной металлургии. – М.: Металлургия, 1981. –132 с.

6 Chen L., Bin W., Yang T., Liu W., Bin Sh. Research and industrial application of Oxygen-rich Side-blow bath smelting technology // The Minerals, Metals & Materials Society. 2013. –P.49-55.

7 Chen Ch., Zhang L. and Jahanshahi Sh. Thermodynamic Modeling of Arsenic in Copper Smelting Processes // Metallurgical and Materials Transactions. 2010. Vol.41B. −P.1175−1185.

8 M.E. Schlesinger, M.J. King, K.C. Sole, W.G. Davenport. Extractive Metallurgy of Copper. – 2011. – 411 p.

9 Stoic S. G., Tsemekhman L. S., Seregin P. S., Popov V. A., V. M. Paretsky, Besser A. D. Thermodynamic calculation of the distribution of lead in the products of direct melting of lead raw materials // Non-ferrous metallurgy. – 2011. – No. 2. – P. 32-37.

10 Development and improvement of technologies for the production of non-ferrous metals with the solution of problems of environmental protection: SB. scientific. labours. – Ust-Kamenogorsk: Vniitsvetmet. – 2001.

11 Z. Asaki, T. Taniguchi, and M. Hayashi. Kinetics of the Reactions in the Smelting Furnace of the Mitsubishi Process // JOM. - May 2001. – P. 25-27

12 Sofra George. Hughes R. A. the Application of the technological process Ausmelt smelting plants and on the Lead-Zinc 2005, Kyoto, Japan, October 17-19, 2005.

13 J. W. Matousek. Oxidation Potentials in Lead and Zinc Smelting // – JOM. - December 2011. – P. 63-67.

14 A. Yazawa. Thermodynamic evaluation of extractive metallurgical processes // Met. Trans. –1979, 10B. – P. 307-321.

15 Досмухамедов Н.К., Даулетбаков Т.С., Егизеков М.Г., и др. Медное производство Казахстана. Алматы. 2010. 472 с.

16 Смирнов М. П. Рафинирование свинца и переработка полупродуктов. М.: Металлургия, 1977. С. 39-47.

17 Dosmukhamedov N. K., Fedorov A. N., Zholdasbay E. E. Thermodynamics of Cu – Me – Fe – S – O system: peculiarities of Cu, Pb, Zn, Fe, As and Sb behavior during joint processing of lead semi-products, negotiable materials and copper-zinc concentrate // Non-ferrous metals. – 2016. – No. 8. – P. 45-52

18 Dosmukhamedov N.K. To., Zholdasbay E. E., Kabylbekov J. J., M. B. Kurmanseit. The Composition of the initial charge of the mine contractile melting // The Mining Journal of Kazakhstan. - 2013. - No. 8. - P. 18-21.

19 Ванюков А. В., Зайцев В. Я. Шлаки и штейны цветной металлургии. М.: Металлургия, 1969. 389 с.

20 Ванюков А. В., Зайцев В. Я. Теория пирометаллургических процессов.М.: Металлургия, 1973, 504 с.

21 Есин О. А., Гельд П. В. Физическая химия пирометаллургических процессов. М.: Металлургия. Ч.2, 1965. 703 с.

22 Васкевич А. Д., Сорокин М. Л. Модель оксидной растворимости меди в шлаках // Цветные металлы. 1982. № 7. С. 25-28.

23 Kameda M., Yazawa A. Effect of Partial Pressure of Oxygen and Sulfur on the Oxygen in Copper Matte Studies in Metallurgy / Tohoku Univ, 1969. P.159-166.

24 Володченко С.Н., Васкевич А.Д., Ванюков А.В. Исследование фазовых равновесий в системе Cu – Pb – S при 1473 К. – РЖ. Металлургия, 1982, № 9.

25 H.M. Henao, F. Kongoli and K. Itagaki. High Temperature Phase Relations in FeO_X (X=1 and 1.33) –CaO – SiO_2 Systems under Various Oxygen Partial Pressure // Materials Transaction. –2005. Vol. 46, No.4. – P.812-819.

26. D.C. Lynch, S. Akagi, and W.G. Davenport, Metall. Trans. B 22B, 677 (1991).

27. P.C. Chaubal, H.Y. Sohn, D.B. George, and L.K. Bailey, Metall. Trans. B 20B, 39 (1989).

28. D.R. Swinbourne and T.S. Kho, Metall. Trans. B 43B, 823 (2012).

29. E.T. Turkdogan, Physical Chemistry of High Temperature Technology (New-York: Academic Press, 1980).

30. O. Kubaschewski and C.B. Alcock, Metallurgical Thermochemistry (New-York: Pergamon Press, 1979).

31. A.G. Bulah, Thermodynamic and Mineralogy Methods (Leningrad: Nedra, 1974).

32. N.K. Dosmuhamedov, Theoretical and Technological Characteristics of Industrial Recycled Materials of Nonferrous Metallurgy (Almaty: KazPTU, 2008).

33. I.P. Polyvyannyi and V.A. Lata, Antimony Metallurgy (Alma-Ata: Metallurgia, 1991).

34. V.G. Rchiladze, Arsenic (Moscow: Metallurgia, 1969).

35. H. Junwei, L. Wei, W. Dawei, J. Fen, and Q. Wenqing, Metall. Trans. B

47B, 344 (2016).

36. N.K. Dosmukhamedov, E.E. Zholdasbay, T.S. Dauletbakov, U.A. Balgimbayeva, M.B. Kurmanseitov, G.Zh. Moldabaeva. Ways of improving the technology of processing of semi-products and recycling materials of the lead production // Vestnik KazNRTU – 2018. №5 (129) – P.106-112.

Appendix A

Metallurgical calculations: material and heat balance of mine contractile melting of semi-products and circulating materials of lead production (Existing technology).

The rational composition of semi-products and circulating materials of the process is calculated and the values are given in the tables. Charge copper slurries of 30 %; converter slag 26 %; mixture CM – 44 %.

Table A.1 – Rational composition of copper slurry

Composition	Cu	Pb	Zn	S	As	Sb	Other:	Total:
Cu_2S	29			7.31				36.31
PbS		9.45		1.46				10.91
Pb		26.55						26.55
Zn			4					4
As					3.87			3.87
Sb						1.4		1.4
Other							16.96	16.96
Total	29	36	4	8.77	3.87	1.4	16.96	100

Table A.2 – Rational composition of copper-zinc ore

Composition	Cu	Pb	Zn	Fe	S	SiO_2	Other	Total
$CuFeS_2$	2.72			2.38	2.72			7.82
PbS		0.37			0.06			0.43
ZnS			3.35		1.65			5
FeS				24.44	13.97			38.41
SiO_2						14.7		14.7
Other							33.64	33.64
Total	2.72	0.37	3.35	26.82	18.4	14.7	33.64	100

Continuation of appendix A

Table A.3 – Rational composition of poor matte

Composition	Cu	Pb	Zn	Fe	S	As	Sb	O_2	Other	Total
Cu_2S	6.36				1.59					7.95
Cu	14.49									14.49
Pbs		6.48			1					7.48
Pb		13.02								13.02
ZnS			11.4		5.61					17.01
FeS				5.08	2.9					7.98
Fe_3O_4				10				3.81		13.81
Fe_3As_2				1.23		1.1				2.33
Fe_3Sb_2				0.39			0.56			0.95
Other									14.98	14.98
Total	20.85	19.5	11.4	16.7	11.1	1.1	0.56	3.81	14.98	100

Table A.4– Rational composition of converter slag

Composition	Cu	Pb	Zn	Fe	O_2	As	Sb	SiO_2	Other	Total
Cu_2O	3.83				0.48					4.31
$PbO*SiO_2$		33.5			2.59			9.7		45.79
$ZnO*SiO_2$			4.54		1.12			4.19		9.85
As_2O_5					1.23	2.3				3.53
Sb_2O_5					0.31		0.94			1.25
$2FeO*SiO_2$				12	3.43			6.43		21.86
Fe_3O_4				3	1.14					4.14
SiO_2								1.34		1.34
Other									7.93	7.93
Total	3.83	33.5	4.54	15	10.3	2.3	0.94	21.66	7.93	100

Continuation of appendix A

Table A.5 – Rational composition of alkali alloy

Composition	Cu	Pb	Zn	As	Sb	O_2	Total
Cu_2O	0.08					0.01	0.09
PbO		61.7				4.76	66.46
ZnO			24.48			6.02	30.5
As_2O_5				0.97		0.31	1.28
Sb_2O_5					1.4	0.27	1.67
Total	0.08	61.7	24.48	0.97	1.4	11.37	100

Table A.6 – Rational composition of flux

Composition	Pb	SiO_2	O_2	Other	Total
PbO	0.62		0.05		0.67
SiO_2		74.8			74.8
Other				24.53	24.53
Total	0.62	74.8	0.05	24.53	100

On the basis of the calculated rational compositions of the loaded substances, the average composition of the initial charge of the mine contractile melting, % by weight is established.: Cu – 12.1; Pb – 30.25; Zn – 4.83; Fe – 9.5; As – 2.5; Sb – 0.78; S – 8; SiO_2 – 10.5; CaO – 7.31; others – 14.22.

The calculation of the yield and composition of slag

Take slag of the following composition.

Zinc oxide content in slag:

$$(4.83-0.9)*0.9*81/65=4.9$$

Iron oxide content:

$$5.34*72/56=6.87$$

The content of SiO_2:

$$10.5-0.69=9.81$$

The content of CaO:

$$7.31-0.07=7.22$$

Table A.7 – Calculation of slag yield and composition

Composition	Cu	Pb	Zn	Fe	As	Sb	S	SiO_2	CaO	Other	Total
Slag	0.43	1.63	9.98	13.58	0.15	0.1	1.27	24.96	18.37	29.53	100
Quantity	0.17	0.64	3.93	5.34	0.06	0.04	0.5	9.81	7.22	11.61	39.31

Calculation of the content of products

Table A.8–Dust quantity and content

Name	Cu	Pb	Zn	Fe	As	Sb	S	CaO	SiO_2	Other	Total
Dust	6.75	12.5	5.86	1.37	13.5	4.0	27.63	1.13	1.34	29.88	100
Composition	0.54	1.0	0.47	0.11	1.08	0.32	2.21	0.09	0.09	2.39	8

The sulfur content of the matte:

$$(8-2.21)*0.9=5.22 \text{ kg}$$

Table A.9 –Contents of matte

Name	Cu	Pb	Zn	Fe	As	Sb	S	SiO_2	Other	Total
Matte	33.47	25.9	1.42	13.5	2.81	0.71	17.4	2	2.79	100
Content	10.04	7.77	0.43	4.05	0.84	0.21	5.22	0.6	0.84	30

The content of lead in the leadbullion:

$$30.25-(0.64+1+7.77)=20.84 \text{ kg}$$

The content of copper in the leadbullion :

$$12.1-(10.04+0.54+0.17)=1.35 \text{ kg}$$

Table A.10 – Content of the lead bullion

Name	Cu	Pb	Zn	Fe	As	Sb	S	SiO_2	Other	Total
Lead bullion	5.95	91.85	-	-	0.97	0.93	0.31	-	-	100
Content	1.35	20.84	-	-	0.22	0.21	0.07	-	-	22.69

As a result, we derive the material balance

Continuation of appendix A

The calculation of material balance

Table A.11– Material balance and distribution of metals between the products of mine contractile melting

Name	Quantity, t	Cu			Pb			Zn			As			Sb		
Loaded:		I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
The mixture of CM	44	12.2	5.37	44.4	29.3	12.45	41.2	5.5	2.4	50	1.17	0.75	29.9	0.27	0.12	15.4
Copper slurry	30	19.0	5.7	47.1	30.3	9.09	30.0	4.0	1.2	25	3.87	1.16	46.2	1.4	0.42	53.8
Converter slag	26	3.83	1.0	8.5	33.5	8.71	28.8	4.54	1.23	25	2.3	0.6	23.9	0.94	0.24	30.8
Total:	**100**		**12.1**	**100**		**30.25**	**100**		**4.83**	**100**		**2.51**	**100**		**0.78**	**100**
Received:																
Lead bullion	22	3.3	0.73	6.0	94.6	20.8	68.8	–	–	–	1.0	0.22	8.8	0.97	0.21	26.9
Matte	30	35.3	10.6	87.5	25.9	7.8	25.8	3.4	1.02	22	3.8	1.14	45.4	0.7	0.21	27.0
Slag	36	0.47	0.2	1.7	1.79	0.64	2.1	7.8	2.81	60.7	0.2	0.07	2.8	0.1	0.04	5.1
Dust	12	4.8	0.57	4.8	8.4	1.01	3.3	6.7	0.8	3.3	9.0	1.08	43.0	2.6	0.32	41.0
Total:	**100**		**12.1**	**100**		**30.25**	**100**		**4.63**	**100**		**2.51**	**100**		**0.78**	**100**

I – content, %; **II** – quantity, t; **III** – distribution, %

The calculation of the heat balance of the mine contractile melting

Heat is supplied

The heat from the burning coke:

From burning CO_2 :

$$94052*3.43/12=112478 \text{ kJ}$$

From burning CO:

$$26417*2.28/12=20999 \text{ kJ}$$

From burning H:

$$57798*0.03/2=3628 \text{ kJ}$$

From burning S:

$$70960*0.03/32=280 \text{ kJ}$$

From total fuel combustion:

$$Q_{burn}=137986 \text{ kJ}$$

The physical heat of the charge

$$Q_{mix}=1004 \text{ kJ}$$

Physical heat of fuel

$$Q_{burn}=192 \text{ kJ}$$

Physical air heat

$$Q_{air}=879 \text{ kJ}$$

After exothermic reactions:

$$Q_{exo}=53614 \text{ kJ}$$

The total amount of heat:

$$137986+1004+192+879+53614=193675 \text{ kJ}$$

Continuation of appendix A

Heat consumption

The heat consumption of lead bullion:

$$Q_{\text{lead bullion}}=2820 \text{ kJ}$$

The flow of heat matte:

$$Q_{\text{matte}}=30125 \text{ kJ}$$

The heat consumption of slag:

$$Q_{\text{slag}}=52631 \text{ kJ}$$

The flow of heat dust:

$$Q_{\text{dust}}=1004 \text{ kJ}$$

The heat consumption of gas:

$$Q_g=40539 \text{ kJ}$$

The flow of heat endothermic reactions

$$Q_{\text{end}}=57304 \text{ kJ}$$

Water cooling:

$$Q_w=4393 \text{ kJ}$$

Loss out:

$$Q_l =1079 \text{ kJ}$$

The consumption of the total amount of heat:

$$Q_t=189895 \text{ kJ}$$

A summary heat balance of the process

Table A.12 –Summary heat balance of the process

The arrival of the heat		Heat consumption	
Fuel combustion	137986 kJ	The heat consumption of lead bullion:	2820 kJ
Generated heat of endothermic reactions	53614 kJ	The flow of heat matte:	30125 kJ
The physical heat of the charge	1004 kJ	The heat consumption of slag:	52631 kJ
Physical heat of fuel	192 kJ	The flow of heat dust:	1004 kJ
Physical air heat	879 kJ	The heat consumption of gas:	40539 kJ
		The flow of heat endothermic reactions	57304 kJ
		Heat of cooling caissons	4393 kJ
		Loss out:	1079 kJ
		Discrepancy	3780 kJ
Subtotal	189895 kJ	Subtotal	189895 kJ

Table A.13 – Consolidated material balance

Name		**Cu**		**Pb**		**Zn**		**Fe**		**As**		**Sb**		**S**		**SiO_2**		**CaO**		**Other**	**Total:**
Loaded:																					
	%,t	**%**	**t**	**%**	**t**	**%**	**t**	**%**	t	**%**	**t**	**%**	**t**	**%**	**t**	**%**	**t**	**%**	**t**	**%, t**	**%, t.**
The mixture of the CM	**25**	21.2	5.3	22.8	5.7	8.8	2.2	14.8	3.7	0.8	0.2	0.4	0.1	7.2	1.8	2.7	0.67	3	0.7	4.63	**25**
Copper slurry	**30**	21	6.3	45.3	13.6	5.0	1.5	4.2	1.3	3.9	1.2	1.4	0.4	2	0.6	3.4	1.0			4.1	**30**
Converter slag	**26**	3.8	0.98	33.5	8.7	4.5	1.2	16	4.2	2.3	0.6	0.94	0.24			17.2	4.5	12.7	3.3	2.28	**26**
Copper-zinc ore	**14**	2.4	0.34	0.37	0.1	3.7	0.52	26.6	3.72					31.2	4.4	15.5	2.2	14.0	1.96	0.76	**14**
Quartz flux	**5**							3	0.15							71.8	3.6	3.6	0.18	1.07	**5**
Average composition	**100**	**12.1**		**30.25**		**4.83**		**9.5**		**2.5**		**0.78**		**8**		**10.5**		**7.31**		**14.22**	**100**
Received:																					
Lead bullion	I	0.3		24.2						0.03		**0.07**		0.01						1.41	**26**
	II	1.2		93.1						0.12		0.27		0.05							
	III	2.3		86.1						1.5		9.5		0.2							
Matte	I	12.27		3.25		0.67		**4.1**		0.27		0.11		6.18		1.21				4.94	**33**
	II	37.2		9.85		2.03		12.42		0.82		0.33		18.73		3.66					
	III	95.0		11.6		12.4		31.5		13.5		15.0		91.0		10.1					
Slag	I	**0.11**		**0.3**		**4.33**		**8.82**		**0.03**				**0.48**		**10.5**		**5.9**		**3.53**	**34**
	II	0.31		0.83		12.0		25.9		0.08				1.33		30.8		16.4			
	III	0.8		1.1		80.0		67.8		1.5				7.0		87.7		96.0			
Dust	I	**0.24**		**0.37**		**0.42**		**0.08**		**1.67**		**0.56**		**0.13**		**0.26**		**0.24**		**3.03**	**7**
	II	4.8		4.63		5.25		1.6		20.9		7.0		1.63		3.25		3.0			
	III	1.9		1.2		7.6		0.7		83.5		75.5		1.8		2.2		4.0			
Total:		**12.92**		**28.1**		**5.42**		**13.0**		**2.0**		**0.74**		**6.8**		**11.97**		**6.14**		**12.91**	**100**

Appendix B

Metallurgical calculations: material and heat balance of mine contractile melting of semi-products and circulating materials of lead production (Corrected composition of the initial charge).

The rational composition of semi-products and circulating materials of the process is calculated and the values are given in the tables. Charge copper slurries of 30 %; converter slag 26 %; mixture CM – 44 %.

Table B.1 – Rational composition of copper slurry

Composition	Cu	Pb	Zn	S	As	Sb	Other:	Total
Cu_2S	29			7.31				36.31
PbS		9.45		1.46				10.91
Pb		26.55						26.55
Zn			4					4
As					3.87			3.87
Sb						1.4		1.4
Other							16.96	16.96
Total	29	36	4	8.77	3.87	1.4	16.96	100

Table B.2 – Rational composition of copper-zinc ore

Composition	Cu	Pb	Zn	Fe	S	SiO_2	Other	Total
$CuFeS_2$	2.72			2.38	2.72			7.82
PbS		0.37			0.06			0.43
ZnS			3.35		1.65			5
FeS				24.44	13.97			38.41
SiO_2						14.7		14.7
Other							33.64	33.64
Total	2.72	0.37	3.35	26.82	18.4	14.7	33.64	100

Continuation of appendix B

Table B.3 – Rational composition of poor matte

Composition	Cu	Pb	Zn	Fe	S	As	Sb	O_2	Other	Total
Cu_2S	6.36				1.59					7.95
Cu	14.49									14.49
Pbs		6.48			1					7.48
Pb		13.02								13.02
ZnS			11.4		5.61					17.01
FeS				5.08	2.9					7.98
Fe_3O_4				10				3.81		13.81
Fe_3As_2				1.23		1.1				2.33
Fe_3Sb_2				0.39			0.56			0.95
Other									14.98	14.98
Total	20.85	19.5	11.4	16.7	11.1	1.1	0.56	3.81	14.98	100

Table B.4 – Rational composition of converter slag

Composition	Cu	Pb	Zn	Fe	O_2	As	Sb	SiO_2	Other	Total
Cu_2O	3.83				0.48					4.31
$PbO*SiO_2$		33.5			2.59			9.7		45.79
$ZnO*SiO_2$			4.54		1.12			4.19		9.85
As_2O_5					1.23	2.3				3.53
Sb_2O_5					0.31		0.94			1.25
$2FeO*SiO_2$				12	3.43			6.43		21.86
Fe_3O_4				3	1.14					4.14
SiO_2								1.34		1.34
Other									7.93	7.93
Total	3.83	33.5	4.54	15	10.3	2.3	0.94	21.66	7.93	100

Continuation of appendix B

Table B.5– Rational composition of alkali alloy

Composition	Cu	Pb	Zn	As	Sb	O_2	Total
Cu_2O	0.08					0.01	0.09
PbO		61.7				4.76	66.46
ZnO			24.48			6.02	30.5
As_2O_5				0.97		0.31	1.28
Sb_2O_5					1.4	0.27	1.67
Total	0.08	61.7	24.48	0.97	1.4	11.37	100

Table B.6 – Rational composition of flux

Composition	Pb	SiO_2	O_2	Other	Total
PbO	0.62		0.05		0.67
SiO_2		74.8			74.8
Other				24.53	24.53
Total	0.62	74.8	0.05	24.53	100

On the basis of the calculated rational compositions of the loaded substances, the average composition of the initial charge of the mine contractile melting, % by weight is established.: Cu – 12.1; Pb – 30.25; Zn – 4.83; Fe – 9.5; As – 2.5; Sb – 0.78; S – 8; SiO_2 – 10.5; CaO – 7.31; others – 14.22.

Calculation of slag yield and composition

Table B.7 – Calculation of slag yield and composition

Composition	Cu	Pb	Zn	Fe	As	Sb	S	SiO_2	CaO	Other	Total
Slag	0.31	0.83	12.0	25.9	0.08	-	1.33	30.8	16.4	12.35	100
Quantity	0.11	0.3	4.33	8.82	0.03	-	0.48	10.5	5.9	3.53	34

Calculation of the content of products

Table B.8–Dust quantity and content

Name	Cu	Pb	Zn	Fe	As	Sb	S	CaO	SiO_2	CaO	Other	Total
Dust	0.24	0.37	0.42	0.08	1.67	0.56	0.13	0.26	0.24	-	3.03	**7**
Composition	0.54	1.0	0.47	0.11	1.08	0.32	2.21	0.09	0.09	-	2.39	8

Table B.9 –Contents of matte

Name	Cu	Pb	Zn	Fe	As	Sb	S	SiO_2	CaO	Other	Total
Matte	12.27	3.25	0.67	4.1	0.27	0.11	6.18	1.21	-	4.94	33
Content	37.2	9.85	2.03	12.42	0.82	0.33	18.73	3.66	-	14.96	100

Table B.10 – Content of the lead bullion

Name	Cu	Pb	Zn	Fe	As	Sb	S	SiO_2	CaO	Other	Total
Lead bullion	0.3	24.2	-	-	0.03	0.07	0.01	-	-	1.41	26
Content	1.15	93.08	-	-	0.12	0.27	0.04	-	-	5.42	100

As a result, we derive the material balance

Continuation of appendix B

The calculation of material balance

Table B.11– Material balance and distribution of metals between the products of mine contractile melting

Name	Quantity, t	Cu			Pb			Zn			As			Sb		
Loaded:		I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
The mixture of CM	25	21.2	5.3	43.8	22.8	5.7	18.84	8.8	2.2	45.54	0.8	0.2	7.96	0.4	0.1	12.82
Copper slurry	30	21	6.3	52.06	45.3	13.6	44.95	5.0	1.5	31.05	3.9	1.2	47.8	1.4	0.4	51.28
Converter slag	26	3.8	0.98	8.09	33.5	8.7	28.76	4.5	1.2	24.84	2.3	0.6	23.9	0.94	0.24	30.76
Total:	**100**		**12.1**	**100**		**30.25**	**100**		**4.83**	**100**		**2.51**	**100**		**0.78**	**100**
Received:																
Lead bullion	22	0.3	1.2	2.3	24.2	93.1	86.1	–	–	–	0.03	0.12	1.5	0.07	0.27	9.5
Matte	30	12.27	37.2	95.0	3.25	9.85	11.6	0.67	2.03	12.4	0.27	0.82	13.5	0.11	0.33	15.0
Slag	36	0.11	0.31	0.8	0.3	0.83	1.1	4.33	12.0	80.0	0.03	0.08	1.5	-	-	-
Dust	12	0.24	4.8	1.9	0.37	4.63	1.2	0.42	5.25	7.6	1.67	20.9	83.5	0.56	7.0	75.5
Total:	**100**		**12.1**	**100**		**30.25**	**100**		**4.63**	**100**		**2.51**	**100**		**0.78**	**100**

I - content ,%; **II -** quantity, t; **III -** distribution, %

The calculation of the heat balance of the mine contractile melting

Heat is supplied

The heat from the burning coke:

From burning CO_2 :

$$94052 * 12.43/12 = 97412 kJ$$

From burning CO:

$$26417 * 6.2/12 = 13648 kJ$$

From burning H::

$$57798 * 0.03/2 = 866.97 kJ$$

From burning S:

$$70960 * 10.3/32 = 22840.25 kJ$$

From total fuel combustion:

$$Q_{fuel} = 134767.22 kJ$$

The physical heat of the charge

$$Q_{mix} = 1004 \text{ kJ}$$

Physical heat of fuel

$$Q_{fuel} = 192 \text{ kJ}$$

Physical air heat

$$Q_{air} = 879 \text{ kJ}$$

After exothermic reactions:

$$Q_{exo} = 68614 \text{ kJ}$$

The total amount of heat:

$$134767.22 + 1004 + 192 + 879 + 68614 = 205456.22 kJ$$

Continuation of appendix B

Heat consumption

The heat consumption of lead bullion:

$$Q_{\text{lead bullion}} = 8820 \text{ kJ}$$

The flow of heat matte:

$$Q_{\text{matte}} = 37221 \text{kJ}$$

The heat consumption of slag:

$$Q_{\text{slag}} = 50638 \text{kJ}$$

The flow of heat dust:

$$Q_{\text{dust}} = 2698 \text{ kJ}$$

The heat consumption of gas:

$$Q_g = 52351 \text{kJ}$$

The flow of heat endothermic reactions

$$Q_{\text{end}} = 52314 \text{ kJ}$$

Water cooling:

$$Q_w = 5633 \text{ kJ}$$

Loss out:

$$Q_l = 2035 \text{kJ}$$

The consumption of the total amount of heat:

$$Q_t = 205456.22 \text{kJ}$$

A summary heat balance of the process

Table B.12–Summary heat balance of the process

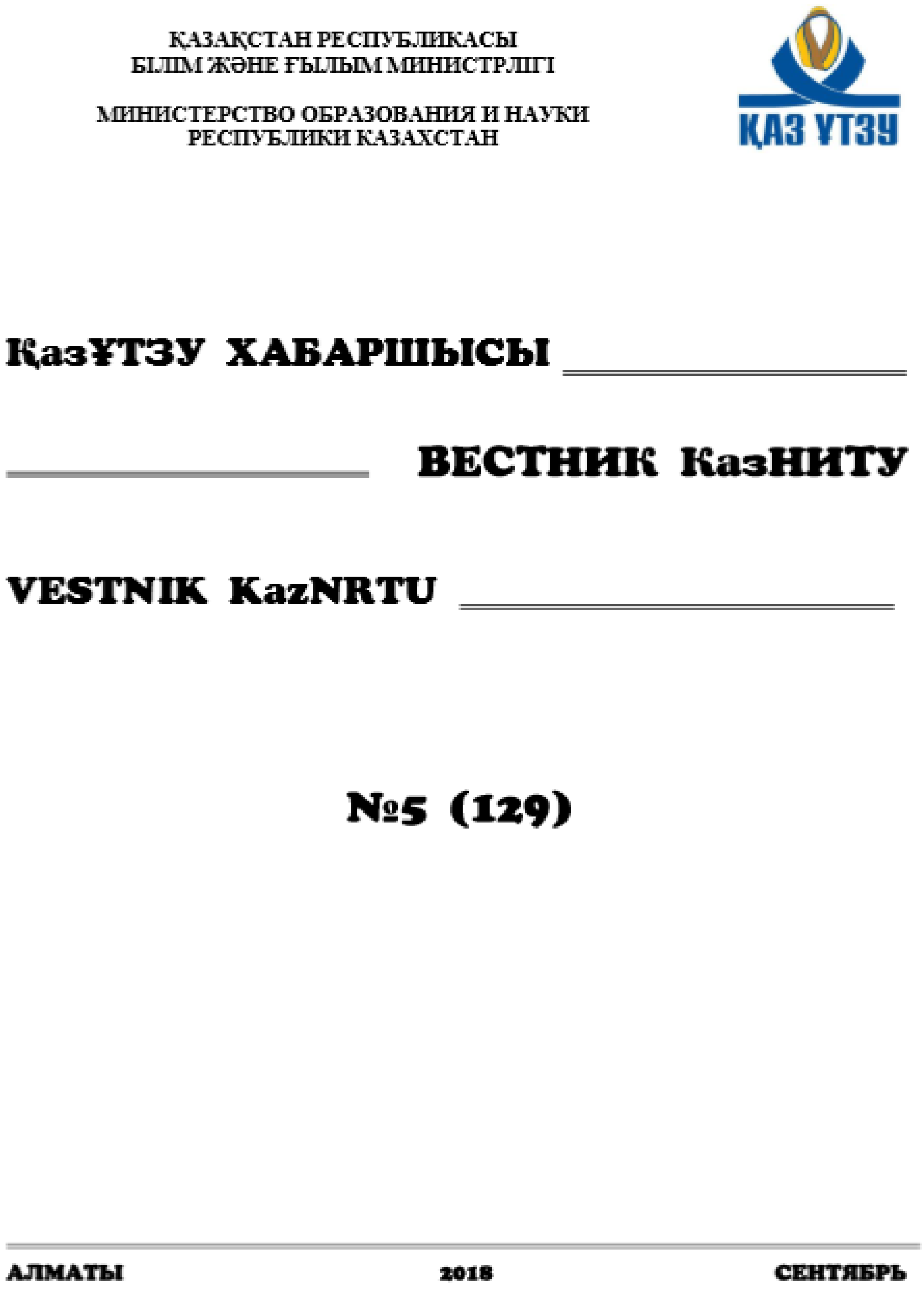
The arrival of the heat		Heat consumption	
Fuel combustion	134767,22 kJ	The heat consumption of lead bullion:	8820 kJ
		The flow of heat matte:	37221 kJ
Generated heat of endothermic reactions	68614kJ	The heat consumption of slag:	50638 kJ
The physical heat of the charge	1004 kJ	The flow of heat dust:	2698 kJ
Physical heat of fuel	192 kJ	The heat consumption of gas:	52351 kJ
Physical air heat	879 kJ	The flow of heat endothermic reactions	52314 kJ
		Heat of cooling caissons	5633 kJ
		Loss out:	2035 kJ
		Discrepancy	6253,78 kJ
Subtotal	205456,22 kJ	Subtotal	205456,22 kJ

Table B.13 –Consolidated material balance

Name		**Cu**		**Pb**		**Zn**		**Fe**		**As**		**Sb**		**S**		**SiO_2**		**CaO**		**Other**	**Total:**
Loaded:																					
	%,t	**%**	**t**	**%**	**t**	**%**	**t**	**%**	t	**%**	**t**	**%**	**t**	**%**	**t**	**%**	**t**	**%**	**t**	**% , t**	**%, t.**
The mixture of the CM	**25**	21.2	5.3	22.8	5.7	8.8	2.2	14.8	3.7	0.8	0.2	0.4	0.1	7.2	1.8	2.7	0.67	3	0.7	4.63	**25**
Copper slurry	**30**	21	6.3	45.3	13.6	5.0	1.5	4.2	1.3	3.9	1.2	1.4	0.4	2	0.6	3.4	1.0			4.1	**30**
Converter slag	**26**	3.8	0.98	33.5	8.7	4.5	1.2	16	4.2	2.3	0.6	0.94	0.24			17.2	4.5	12.7	3.3	2.28	**26**
Copper-zinc ore	**14**	2.4	0.34	0.37	0.1	3.7	0.52	26.6	3.72					31.2	4.4	15.5	2.2	14.0	1.96	0.76	**14**
Quartz flux	**5**							3	0.15							71.8	3.6	3.6	0.18	1.07	**5**
Average composition	**100**	**12,1**		**30,25**		**4,83**		**9,5**		**2,5**		**0,78**		**8**		**10,5**		**7,31**		**14,22**	**100**
Received:																					
Lead bullion	I	0.3		24.2						0.03		0.07		0.01						1.41	**26**
	II	1.2		93.1						0.12		0.27		0.05							
	III	2.3		86.1						1.5		9.5		0.2							
Matte	I	12.27		3.25		0.67		4.1		0.27		0.11		6.18		1.21				4.94	**33**
	II	37.2		9.85		2.03		12.42		0.82		0.33		18.73		3.66					
	III	95.0		11.6		12.4		31.5		13.5		15.0		91.0		10.1					
Slag	I	0.11		0.3		4.33		8.82		0.03				0.48		10.5		5.9		3.53	**34**
	II	0.31		0.83		12.0		25.9		0.08				1.33		30.8		16.4			
	III	0.8		1.1		80.0		67.8		1.5				7.0		87.7		96.0			
Dust	I	0.24		0.37		0.42		0.08		1.67		0.56		0.13		0.26		0.24		3.03	**7**
	II	4.8		4.63		5.25		1.6		20.9		7.0		1.63		3.25		3.0			
	III	1.9		1.2		7.6		0.7		83.5		75.5		1.8		2.2		4.0			
Total:		**12,92**		**28,1**		**5,42**		**13,0**		**2,0**		**0,74**		**6,8**		**11,97**		**6,14**		**12,91**	**100**

Appendix C

Impressions of the publication on the topic of master's thesis



ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
БІЛІМ ЖӘНЕ ҒЫЛЫМ МИНИСТРЛІГІ

МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ
РЕСПУБЛИКИ КАЗАХСТАН

ҚАЗ ҰТЗУ

ҚазҰТЗУ ХАБАРШЫСЫ

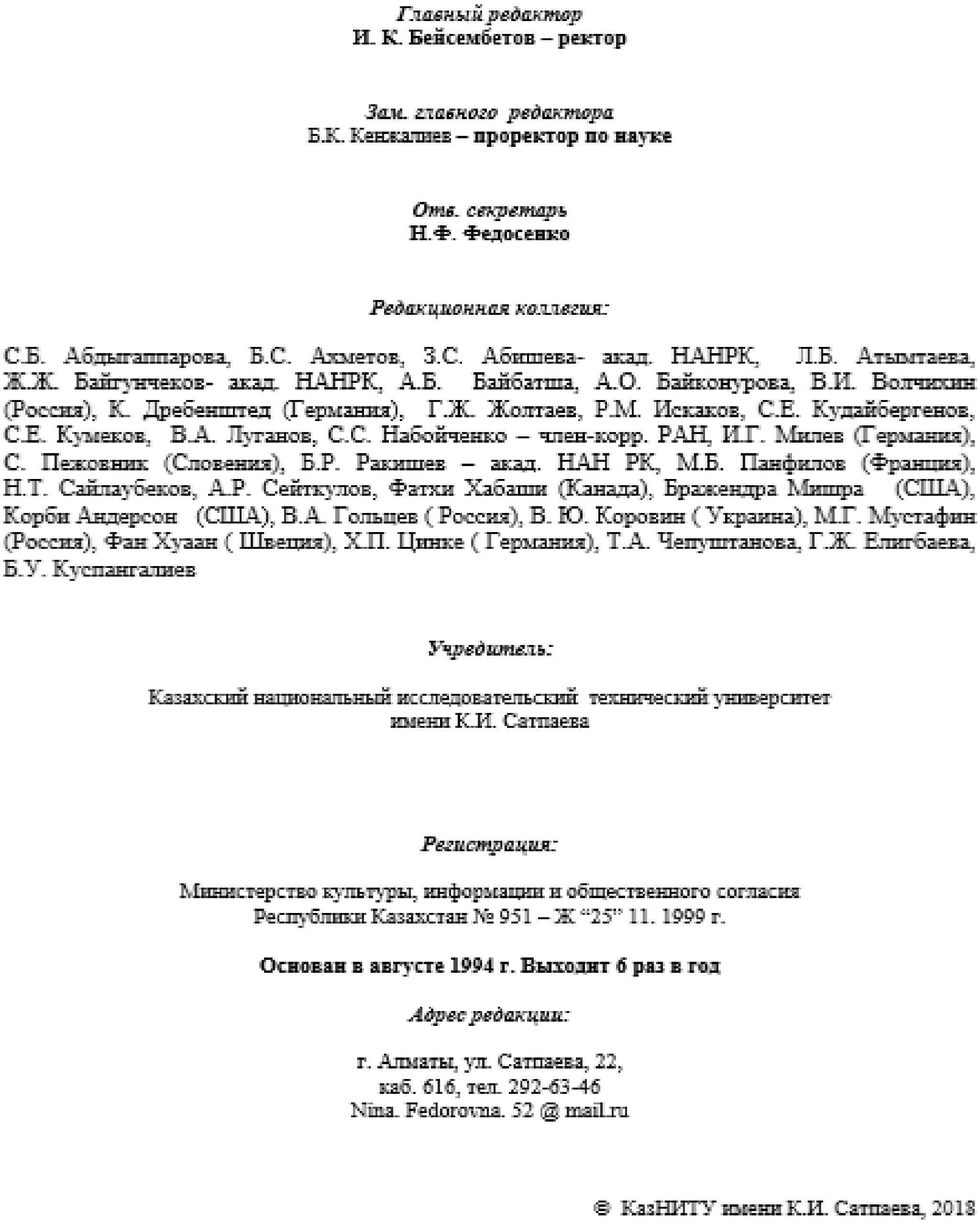
ВЕСТНИК КазНИТУ

VESTNIK KazNRTU

№5 (129)

АЛМАТЫ 2018 СЕНТЯБРЬ

Continuation of appendix C



Главный редактор
И. К. Бейсембетов – ректор

Зам. главного редактора
Б.К. Кенжалиев – **проректор по науке**

Отв. секретарь
Н.Ф. Федосенко

Учредитель:

Казахский национальный исследовательский технический университет
имени К.И. Сатпаева

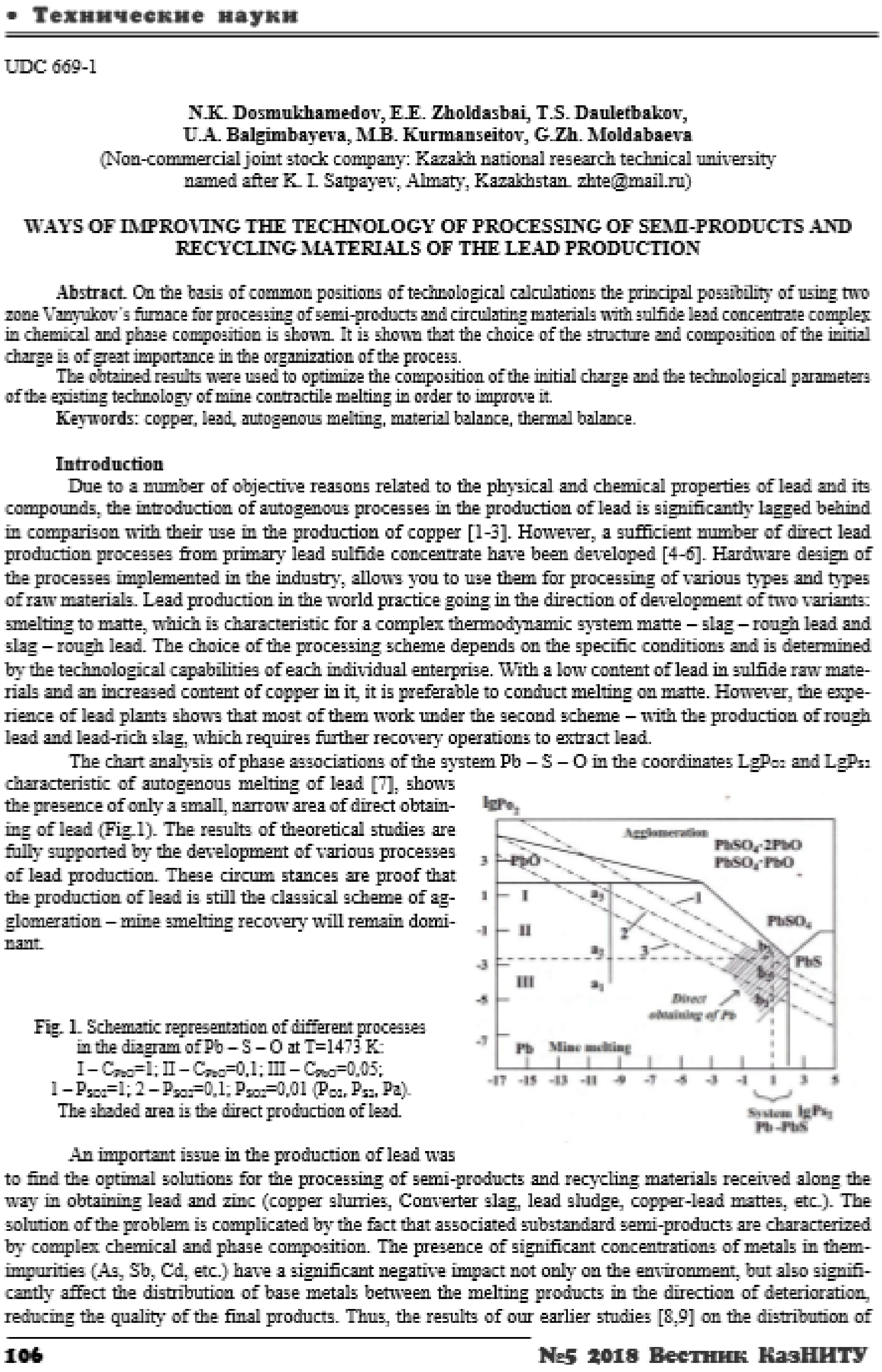
Регистрация:

Министерство культуры, информации и общественного согласия
Республики Казахстан № 951 – Ж "25" 11. 1999 г.

Основан в августе 1994 г. Выходит 6 раз в год

Адрес редакции:

г. Алматы, ул. Сатпаева, 22,
каб. 616, тел. 292-63-46
Nina. Fedorovna. 52 @ mail.ru



UDC 669-1

N.K. Dosmukhamedov, E.E. Zholdasbai, T.S. Dauletbakov,
U.A. Balgimbayeva, M.B. Kurmanseitov, G.Zh. Moldabaeva
(Non-commercial joint stock company: Kazakh national research technical university
named after K. I. Satpayev, Almaty, Kazakhstan. zhte@mail.ru)

WAYS OF IMPROVING THE TECHNOLOGY OF PROCESSING OF SEMI-PRODUCTS AND RECYCLING MATERIALS OF THE LEAD PRODUCTION

Abstract. On the basis of common positions of technological calculations the principal possibility of using two zone Vanyukov´s furnace for processing of semi-products and circulating materials with sulfide lead concentrate complex in chemical and phase composition is shown. It is shown that the choice of the structure and composition of the initial charge is of great importance in the organization of the process.

The obtained results were used to optimize the composition of the initial charge and the technological parameters of the existing technology of mine contractile melting in order to improve it.

Keywords: copper, lead, autogenous melting, material balance, thermal balance.

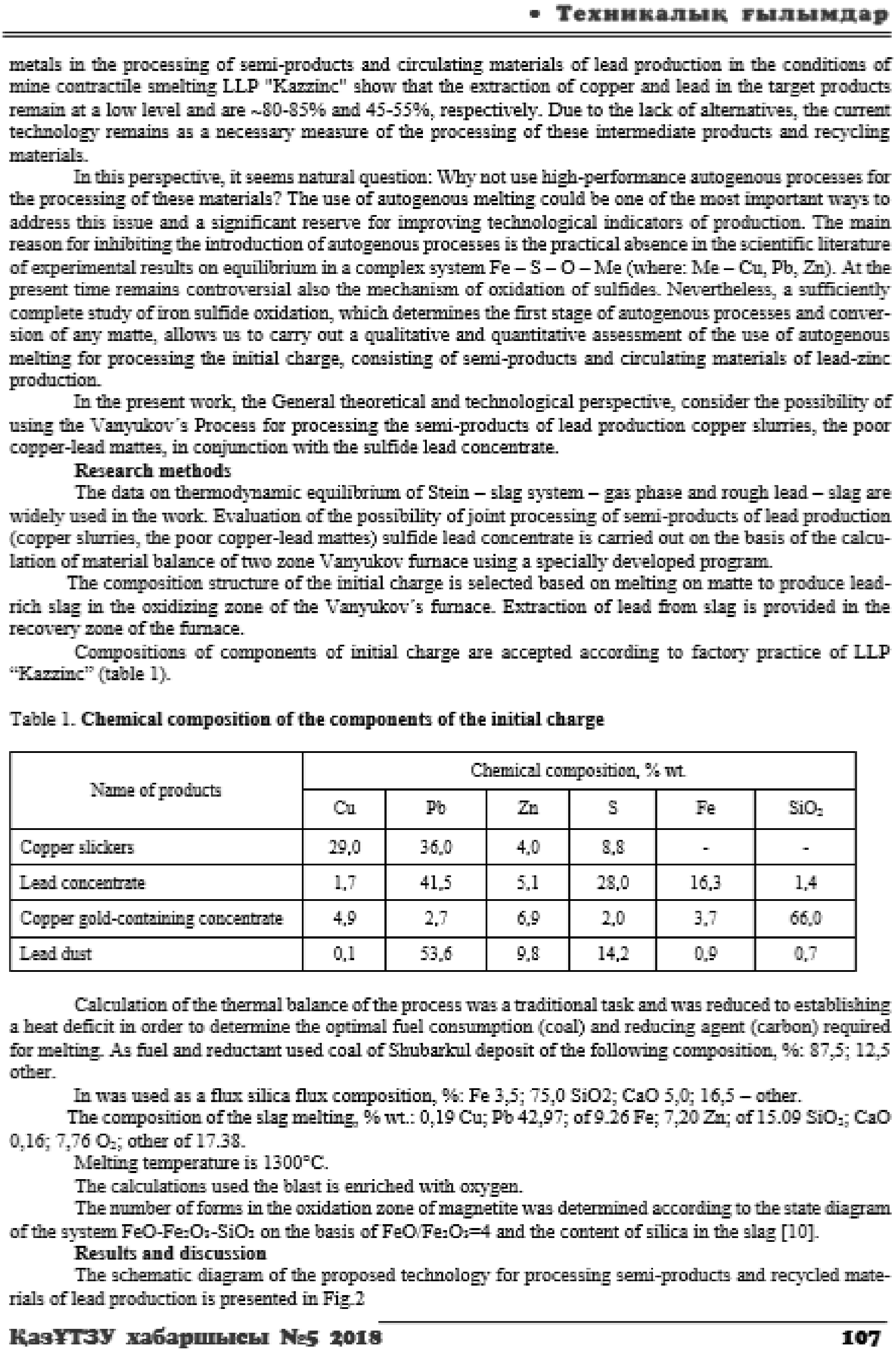
Introduction

Due to a number of objective reasons related to the physical and chemical properties of lead and its compounds, the introduction of autogenous processes in the production of lead is significantly lagged behind in comparison with their use in the production of copper [1-3]. However, a sufficient number of direct lead production processes from primary lead sulfide concentrate have been developed [4-6]. Hardware design of the processes implemented in the industry, allows you to use them for processing of various types and types of raw materials. Lead production in the world practice going in the direction of development of two variants: smelting to matte, which is characteristic for a complex thermodynamic system matte – slag – rough lead and slag – rough lead. The choice of the processing scheme depends on the specific conditions and is determined by the technological capabilities of each individual enterprise. With a low content of lead in sulfide raw materials and an increased content of copper in it, it is preferable to conduct melting on matte. However, the experience of lead plants shows that most of them work under the second scheme – with the production of rough lead and lead-rich slag, which requires further recovery operations to extract lead.

The chart analysis of phase associations of the system Pb – S – O in the coordinates LgP_{O2} and LgP_{S2} characteristic of autogenous melting of lead [7], shows the presence of only a small, narrow area of direct obtaining of lead (Fig.1). The results of theoretical studies are fully supported by the development of various processes of lead production. These circum stances are proof that the production of lead is still the classical scheme of agglomeration – mine smelting recovery will remain dominant.

Fig. 1. Schematic representation of different processes in the diagram of Pb – S – O at T=1473 K:
I – C_{PbO}=1; II – C_{PbO}=0,1; III – C_{PbO}=0,05;
1 – P_{SO2}=1; 2 – P_{SO2}=0,1; P_{SO2}=0,01 (P_{O2}, P_{S2}, Pa).
The shaded area is the direct production of lead.

An important issue in the production of lead was to find the optimal solutions for the processing of semi-products and recycling materials received along the way in obtaining lead and zinc (copper slurries, Converter slag, lead sludge, copper-lead mattes, etc.). The solution of the problem is complicated by the fact that associated substandard semi-products are characterized by complex chemical and phase composition. The presence of significant concentrations of metals in them-impurities (As, Sb, Cd, etc.) have a significant negative impact not only on the environment, but also significantly affect the distribution of base metals between the melting products in the direction of deterioration, reducing the quality of the final products. Thus, the results of our earlier studies [8,9] on the distribution of



metals in the processing of semi-products and circulating materials of lead production in the conditions of mine contractile smelting LLP "Kazzinc" show that the extraction of copper and lead in the target products remain at a low level and are ~80-85% and 45-55%, respectively. Due to the lack of alternatives, the current technology remains as a necessary measure of the processing of these intermediate products and recycling materials.

In this perspective, it seems natural question: Why not use high-performance autogenous processes for the processing of these materials? The use of autogenous melting could be one of the most important ways to address this issue and a significant reserve for improving technological indicators of production. The main reason for inhibiting the introduction of autogenous processes is the practical absence in the scientific literature of experimental results on equilibrium in a complex system Fe – S – O – Me (where: Me – Cu, Pb, Zn). At the present time remains controversial also the mechanism of oxidation of sulfides. Nevertheless, a sufficiently complete study of iron sulfide oxidation, which determines the first stage of autogenous processes and conversion of any matte, allows us to carry out a qualitative and quantitative assessment of the use of autogenous melting for processing the initial charge, consisting of semi-products and circulating materials of lead-zinc production.

In the present work, the General theoretical and technological perspective, consider the possibility of using the Vanyukov's Process for processing the semi-products of lead production copper slurries, the poor copper-lead mattes, in conjunction with the sulfide lead concentrate.

Research methods

The data on thermodynamic equilibrium of Stein – slag system – gas phase and rough lead – slag are widely used in the work. Evaluation of the possibility of joint processing of semi-products of lead production (copper slurries, the poor copper-lead mattes) sulfide lead concentrate is carried out on the basis of the calculation of material balance of two zone Vanyukov furnace using a specially developed program.

The composition structure of the initial charge is selected based on melting on matte to produce lead-rich slag in the oxidizing zone of the Vanyukov's furnace. Extraction of lead from slag is provided in the recovery zone of the furnace.

Compositions of components of initial charge are accepted according to factory practice of LLP "Kazzinc" (table 1).

Table 1. **Chemical composition of the components of the initial charge**

Name of products	Chemical composition, % wt.					
	Cu	Pb	Zn	S	Fe	SiO_2
Copper slickers	29,0	36,0	4,0	8,8	-	-
Lead concentrate	1,7	41,5	5,1	28,0	16,3	1,4
Copper gold-containing concentrate	4,9	2,7	6,9	2,0	3,7	66,0
Lead dust	0,1	53,6	9,8	14,2	0,9	0,7

Calculation of the thermal balance of the process was a traditional task and was reduced to establishing a heat deficit in order to determine the optimal fuel consumption (coal) and reducing agent (carbon) required for melting. As fuel and reductant used coal of Shubarkul deposit of the following composition, %: 87,5; 12,5 other.

In was used as a flux silica flux composition, %: Fe 3,5; 75,0 SiO2; CaO 5,0; 16,5 – other.

The composition of the slag melting, % wt.: 0,19 Cu; Pb 42,97; of 9.26 Fe; 7,20 Zn; of 15.09 SiO_2; CaO 0,16; 7,76 O_2; other of 17.38.

Melting temperature is 1300°C.

The calculations used the blast is enriched with oxygen.

The number of forms in the oxidation zone of magnetite was determined according to the state diagram of the system FeO-Fe_2O_3-SiO_2 on the basis of $FeO/Fe_2O_3=4$ and the content of silica in the slag [10].

Results and discussion

The schematic diagram of the proposed technology for processing semi-products and recycled materials of lead production is presented in Fig.2

Continuation of appendix C

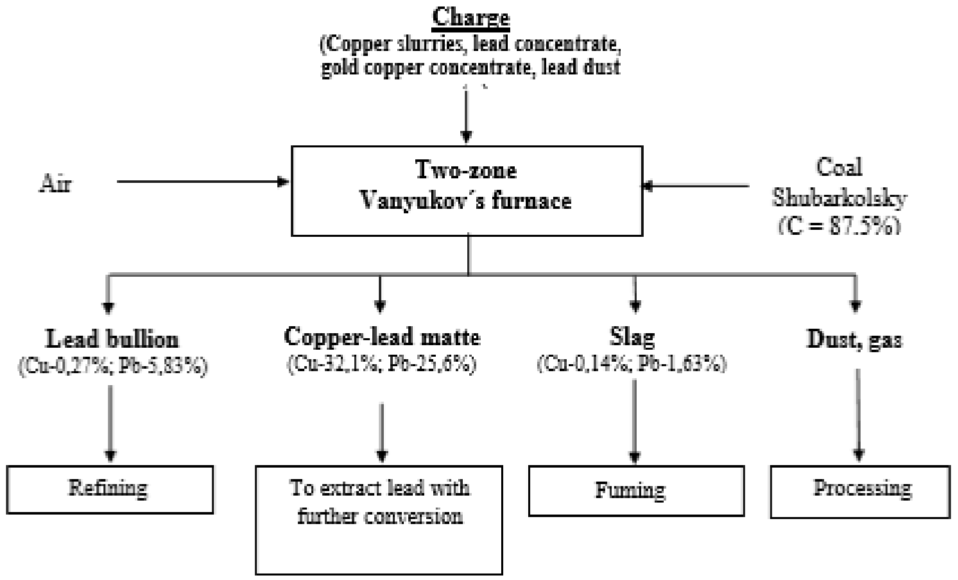


Fig.2. Schematic diagram of the processing of semi-products and recycling materials of the lead production

The structure of the initial charge composition is shown in Fig.3.

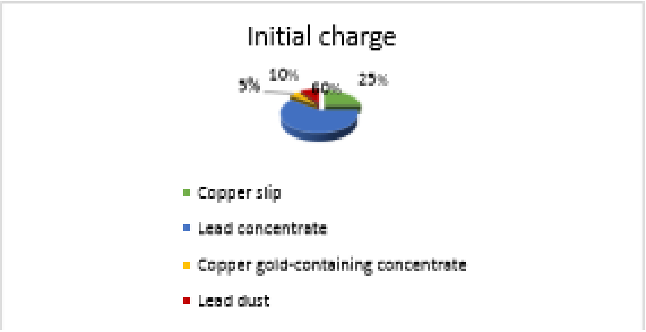


Fig.3. Composition of the initial charge

The choice of composition of the components of the initial charge is chosen so that under conditions of oxidizing atmosphere to prevent the flow of melting reaction between the sulfide and oxide of lead. This is achieved by selecting the optimal ratio between the composition of the initial charge and the flow rate of the blast enriched with oxygen required for the oxidation of a given amount of iron sulfide. Set the degree of enrichment of blast air with oxygen provides the minimum output lead of the sublimates and the necessity of a given level of desulfurization. Consumption of added flux promotes binding produced minor amounts of lead oxide and zinc silicate chemical resistant connection that prevents the leakage of the melting reaction between the sulfide and oxide of lead.

The products of melting of the oxidizing zone are copper-lead matte and slag rich in lead.

Copper-lead matte contains up to 15% lead and can be processed according to the existing conversion technology to obtain rough copper. The existing practice of copper-lead matte processing shows that the conversion process is accompanied by a large yield of lead dust, which, as a negotiable material, leads to significant losses of lead between the products of agglomerating firing and mine smelting. The source of losses of base metals is also converter slag with a high content of copper and lead (up to 3% and 25%, respectively), which is sent to mine contractile melting for their extraction. Based on this, in our opinion, the most appropriate is the organization of separate, independent processing of copper-lead matte obtained in a separate furnace for the purpose of additional extraction of lead from the matte to lead roughing. This approach will improve lead recovery and significantly improve the quality of copper matte with the exception of all shortcomings inherent in the existing technology. Our preliminary research experiments on the extraction of lead from matte in various ways have shown good results and will be published in the scientific literature in the near future.

The slag obtained in the oxidizing zone of the furnace contains up to 42,97% of lead and is sent to the reduction zone to extract lead to rough lead. The content of lead in draft the lead is 95,83%. The minimum content of impurity metals (Cu, As, Sb) will significantly reduce the load on further refining operations of rough lead. Obtained after the restoration of slag is suitable for use for its intended purpose – for the production of building materials or iron.

The material balance of the fluxes of the oxidizing zone of the furnace is shown in Fig.4.

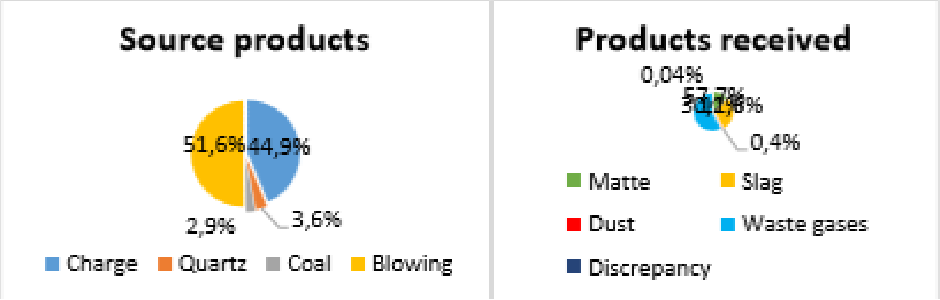


Fig. 4. Material balance of the flows of the oxidizing zone of the Vanyukov´s furnace

It is easy to see that the Stein output is 11,63% at the selected process organization. At the optimal level of oxidation of iron sulfide, preventing the formation of lead metal copper content in matte is 32,09%. The extraction of copper in the matte reaches 97,5%.

The compositions of the obtained products of the oxidizing and reducing zone are presented in table 2, 3, respectively.

Table 2. **Chemical composition of products obtained in the oxidizing zone**

Products	Quantity, t	Chemical composition, % wt.							
		Cu	Pb	Fe	Zn	S	CaO	SiO_2	Other
Matte	25,9	32,1	25,1	15,4	0,6	21,1			5,7
Slag	67,4	0,2	42,6	9,2	7,1		0,2	14,9	18,1
Dust	1,0	8,6	39,4	10,1	5,4	20,6	0,1	4,2	11,7
Waste gas	128,6		2,7		0,2	11,2			
In total:	222,9								

Table 3. **Chemical composition of products obtained in the recovery zone**

Products	Quantity, t	Chemical composition, % wt.							
		Cu	Pb	Fe	Zn	S	CaO	SiO_2	Other
Lead bullion	28,7	0,1	35,1				1,4	28,7	0,1
Slag	35,5	0,1	0,7	5,9	0,1	12,9	13,7	35,5	0,07
Waste gas	13,1		1,1	0,3				13,1	
In total:	**77,3**								

Continuation of appendix C

Results calculation of the heat balance of the oxidizing and reducing zone of the Vanyukov's furnace is presented in Table 4, 5, respectively.

Table 4. **Thermal balance of the oxidizing zone**

The arrival of the heat			Heat consumption		
Articles coming	**kJ**	**%**	**Item of expenditure**	**kJ**	**%**
The heat of the charge	1004,2	0,4	Heat Stein	24406,3	9,3
Warm air	5201,2	2,0	The heat of slag	96032,1	36,4
The heat of oxidation reaction of metals	117702,0	44,7	Heat gases	143032,3	54,3
The heat of combustion of coal	134308,4	51,0			
The heat of slag formation	5255,0	2,0			
In total:	**263470,8**	**100**	**In total:**	**263470,7**	**100**

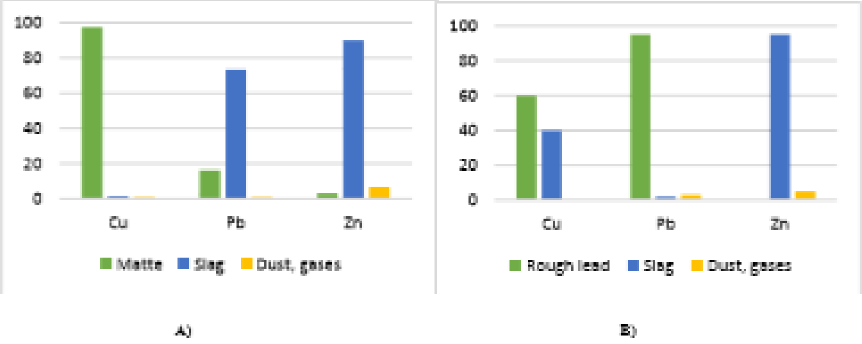
Table 5. **Heat balance of the recovery zone**

The arrival of the heat			Heat consumption		
Articles coming	**kJ**	**%**	**Item of expenditure**	**kJ**	**%**
The heat of slag	79686,21	70,57	Draft lead heat	3466,26	3,07
Warm air	436,9711	0,39	The heat of slag	50569,65	44,78
The heat of combustion of coal	27545,95	24,39	Heat gases	29215,54	25,87
The heat of slag formation	5255,007	4,65	The heat absorbed by the caissons	29672,69	26,28
In total:	**112924,1**	**100**	**In total:**	**112924,1**	**100**

From the results table.4 it follows that the selected process mode and the specified parameters ensure a stable operation of the Vanyukov's furnace. The main share of heat coming up to 45,0% of the heat generated from oxidation of iron sulfide. The heat deficit resulting from the incomplete oxidation of sulfide of iron, is covered with downloading the additional quantity of fuel (coal). At the same time, the required coal consumption is estimated to be insignificant and amounts to ~5%.

To maintain the heat balance of the furnace recovery zone, 27545,9 kJ (~25%) of the heat deficit must be covered (table.5). The established deficit of heat without much effort and costs is blocked by additional burning of coal.

Of great interest from the point of view of practice is the evaluation of the distribution of base non-ferrous metals between smelting products. In Fig.5 shows the distribution of copper, lead and zinc between the melting products of the oxidation and reduction zone.



A)　　B)

Fig.5. The distribution of Cu, Pb, Zn smelting between products:
A) to the oxidation zone; B) rehabilitation area

It is easy to see that the oxidizing zone achieves a high copper distribution to ~98% in Stein, with its slight transition to slag and dust (1,5% and 1,0%, respectively).

High extraction of copper in the matte provides a sufficiently high quality of rough lead: the copper content in the rough lead is minimal and is – 0,27 %. The content of lead in the rough lead reaches ~ 96,0%.

The total balance of material flows of processing of semi-products and circulating materials in conjunction with the matte Vanyukov´s furnace shown in Fig.6.

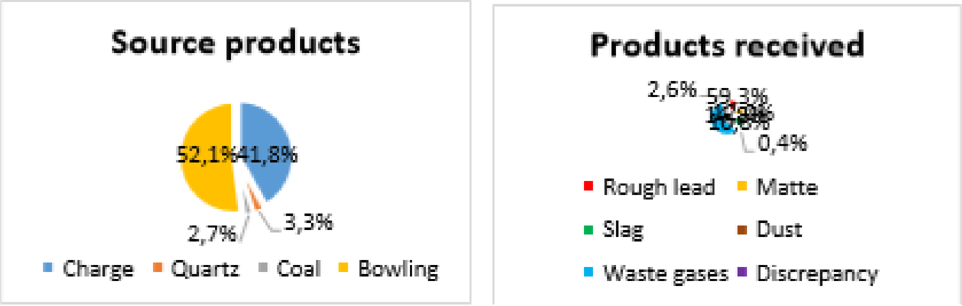


Fig.6. The overall material balance the streams of the Vanyukov´s furnace in the processing of semi-products and recycling materials of the lead production together with the sulfide lead concentrate

The final distribution of non-ferrous metals between the fusion products is shown in Fig.7.

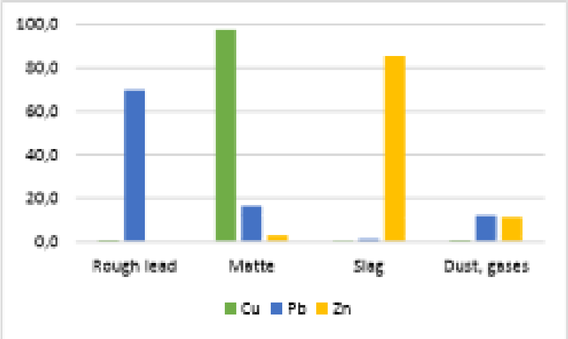
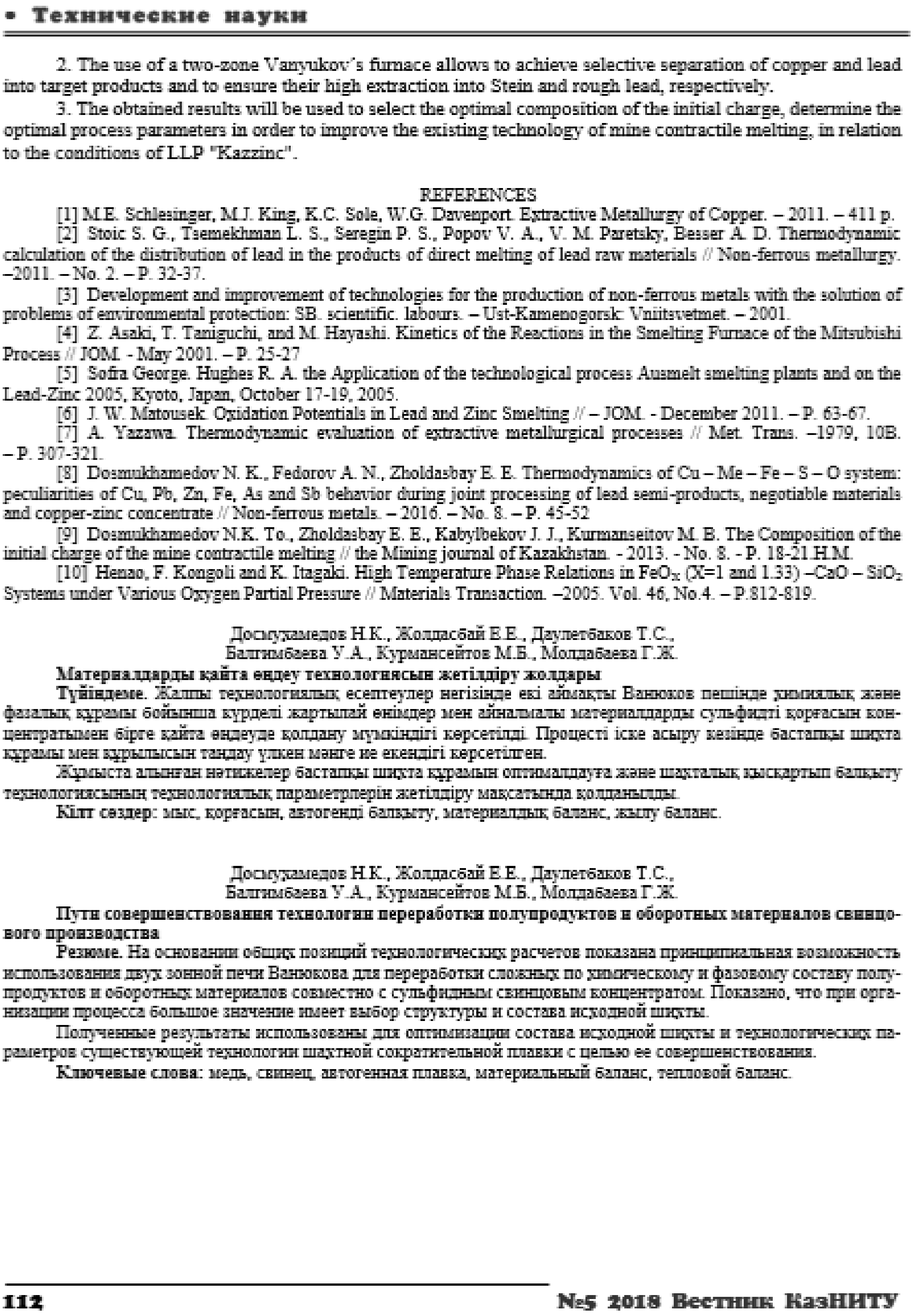


Fig.7. Distribution of non-ferrous metals between smelting products

The results obtained show a high recovery of copper matte and lead roughing lead. In this case, zinc is mainly concentrated in slag and can be extracted without much effort and material costs by known methods, for example, fuming process. Implementation of the proposed technology in practice will ensure high efficiency of physical and chemical interactions between the components of the charge, elimination of the use of expensive coke reducing agent, as well as significantly improve the quality of the products. Separate independent processing of copper-lead matte will allow to achieve deep extraction of lead from matte and get rich (up to 50%) on the content of copper matte. Further processing of these rods will significantly reduce the material costs of the conversion process and losses of copper and lead, arising from their circulation in the melting-conversion chain.

Summary:

1. On the basis of common positions of technological calculations the principal possibility of using two zone Vanyukov´s furnace for processing of semi-products and circulating materials with sulfide lead concentrate complex in chemical and phase composition is shown. It is shown that the choice of the structure and composition of the initial charge is of great importance in the organization of the process.



2. The use of a two-zone Vanyukov´s furnace allows to achieve selective separation of copper and lead into target products and to ensure their high extraction into Stein and rough lead, respectively.

3. The obtained results will be used to select the optimal composition of the initial charge, determine the optimal process parameters in order to improve the existing technology of mine contractile melting, in relation to the conditions of LLP "Kazzinc".

REFERENCES

[1] M.E. Schlesinger, M.J. King, K.C. Sole, W.G. Davenport. Extractive Metallurgy of Copper. – 2011. – 411 p.

[2] Stoic S. G., Tsemekhman L. S., Seregin P. S., Popov V. A., V. M. Paretsky, Besser A. D. Thermodynamic calculation of the distribution of lead in the products of direct melting of lead raw materials // Non-ferrous metallurgy. –2011. – No. 2. – P. 32-37.

[3] Development and improvement of technologies for the production of non-ferrous metals with the solution of problems of environmental protection: SB. scientific. labours. – Ust-Kamenogorsk: Vniitsvetmet. – 2001.

[4] Z. Asaki, T. Taniguchi, and M. Hayashi. Kinetics of the Reactions in the Smelting Furnace of the Mitsubishi Process // JOM. - May 2001. – P. 25-27

[5] Sofra George. Hughes R. A. the Application of the technological process Ausmelt smelting plants and on the Lead-Zinc 2005, Kyoto, Japan, October 17-19, 2005.

[6] J. W. Matousek. Oxidation Potentials in Lead and Zinc Smelting // – JOM. - December 2011. – P. 63-67.

[7] A. Yazawa. Thermodynamic evaluation of extractive metallurgical processes // Met. Trans. –1979, 10B. – P. 307-321.

[8] Dosmukhamedov N. K., Fedorov A. N., Zholdasbay E. E. Thermodynamics of Cu – Me – Fe – S – O system: peculiarities of Cu, Pb, Zn, Fe, As and Sb behavior during joint processing of lead semi-products, negotiable materials and copper-zinc concentrate // Non-ferrous metals. – 2016. – No. 8. – P. 45-52

[9] Dosmukhamedov N.K. To., Zholdasbay E. E., Kabylbekov J. J., Kurmanseitov M. B. The Composition of the initial charge of the mine contractile melting // the Mining journal of Kazakhstan. - 2013. - No. 8. - P. 18-21.H.M.

[10] Henao, F. Kongoli and K. Itagaki. High Temperature Phase Relations in FeO_X (X=1 and 1.33) –CaO – SiO_2 Systems under Various Oxygen Partial Pressure // Materials Transaction. –2005. Vol. 46, No.4. – P.812-819.

Досмұхамедов Н.К., Жолдасбай Е.Е., Даулетбаков Т.С.,
Балгимбаева У.А., Курмансейтов М.Б., Молдабаева Г.Ж.

Материалдарды қайта өңдеу технологиясын жетілдіру жолдары

Түйіндеме. Жалпы технологиялық есептеулер негізінде екі аймақты Ванюков пешінде химиялық және фазалық құрамы бойынша күрделі жартылай өнімдер мен айналмалы материалдарды сульфидті қорғасын концентратымен бірге қайта өңдеуде қолдану мүмкіндігі көрсетілді. Процесті іске асыру кезінде бастапқы шихта құрамы мен құрылысын таңдау үлкен мәнге ие екендігі көрсетілген.

Жұмыста алынған нәтижелер бастапқы шихта құрамын оптималдауға және шахталық қысқартып балқыту технологиясының технологиялық параметрлерін жетілдіру мақсатында қолданылды.

Кілт сөздер: мыс, қорғасын, автогенді балқыту, материалдық баланс, жылу баланс.

Досмухамедов Н.К., Жолдасбай Е.Е., Даулетбаков Т.С.,
Балгимбаева У.А., Курмансейтов М.Б., Молдабаева Г.Ж.

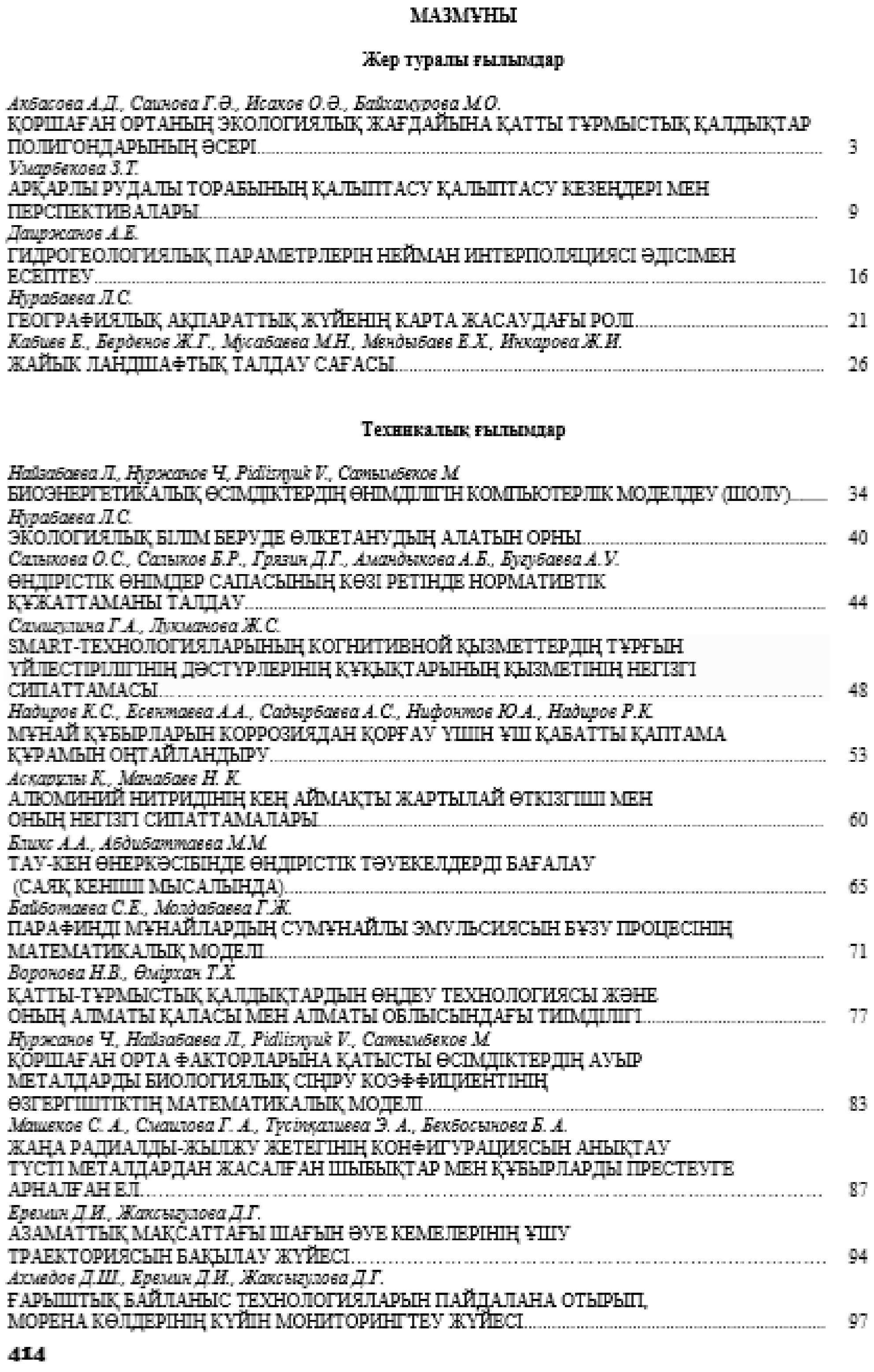
Пути совершенствования технологии переработки полупродуктов и оборотных материалов свинцового производства

Резюме. На основании общих позиций технологических расчетов показана принципиальная возможность использования двух зонной печи Ванюкова для переработки сложных по химическому и фазовому составу полупродуктов и оборотных материалов совместно с сульфидным свинцовым концентратом. Показано, что при организации процесса большое значение имеет выбор структуры и состава исходной шихты.

Полученные результаты использованы для оптимизации состава исходной шихты и технологических параметров существующей технологии шахтной сократительной плавки с целью ее совершенствования.

Ключевые слова: медь, свинец, автогенная плавка, материальный баланс, тепловой баланс.

Continuation of appendix C

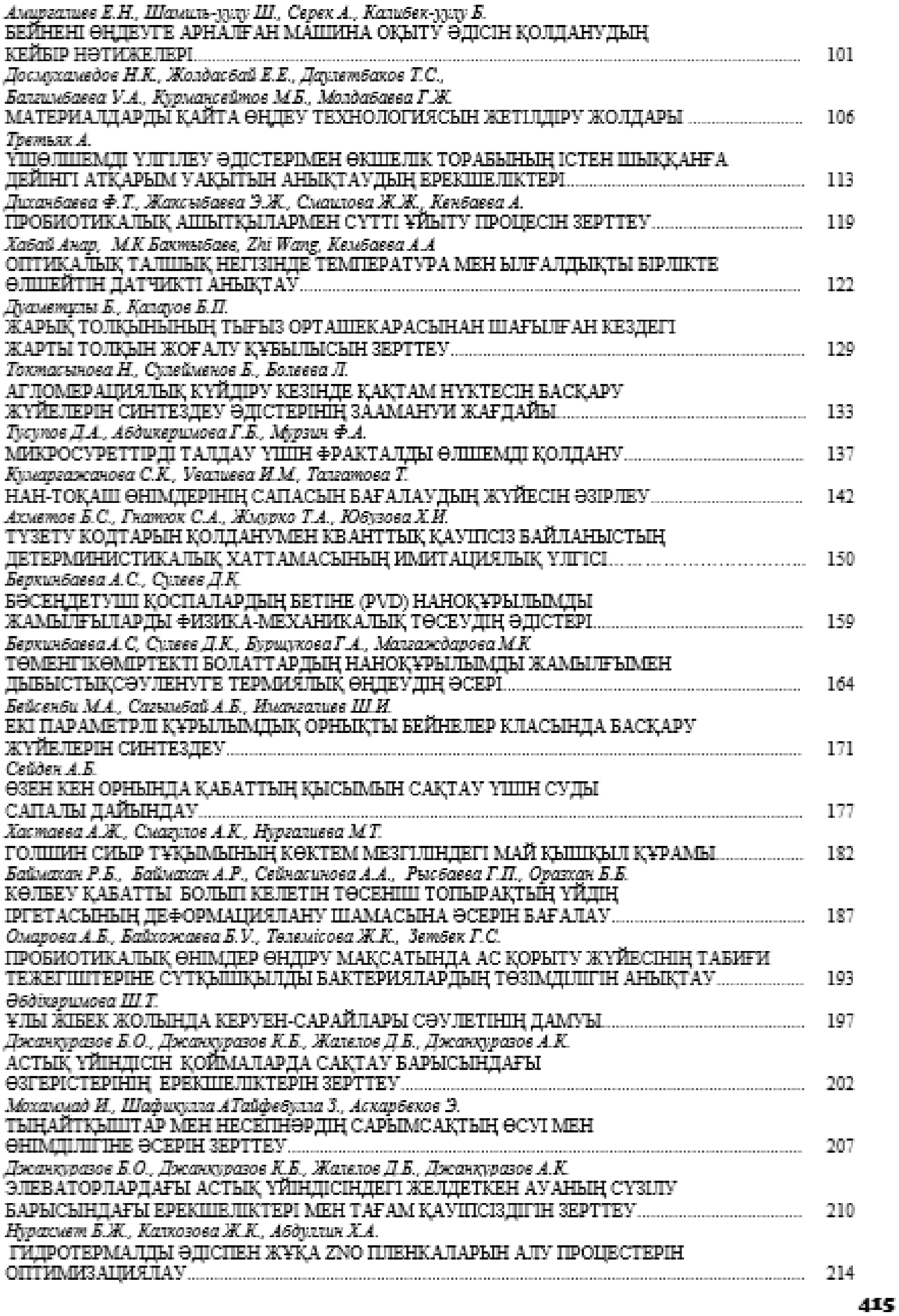


МАЗМҰНЫ

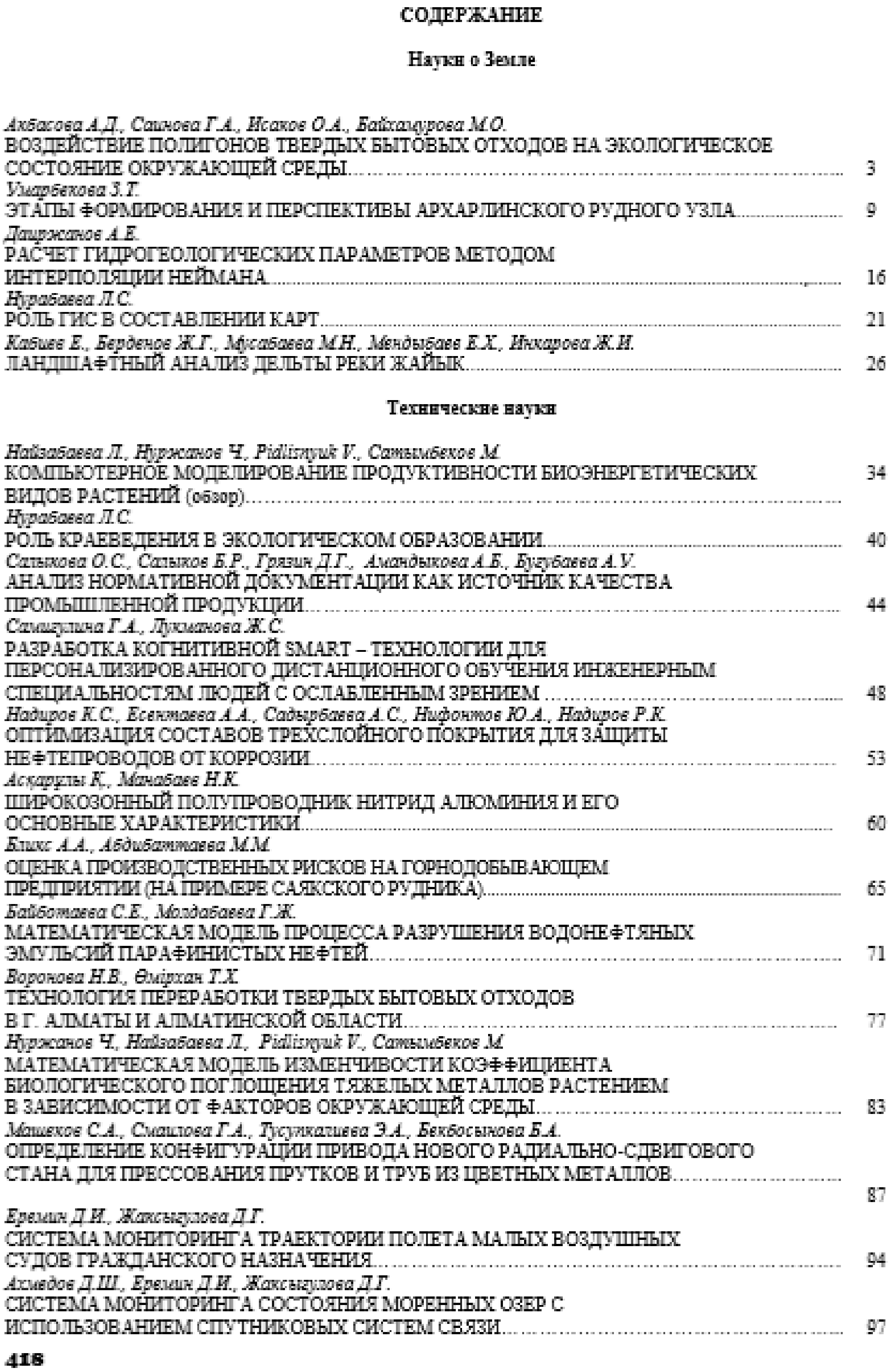
Жер туралы ғылымдар

Техникалық ғылымдар

Continuation of appendix C



Continuation of appendix C



СОДЕРЖАНИЕ

Науки о Земле

Технические науки

Continuation of appendix C

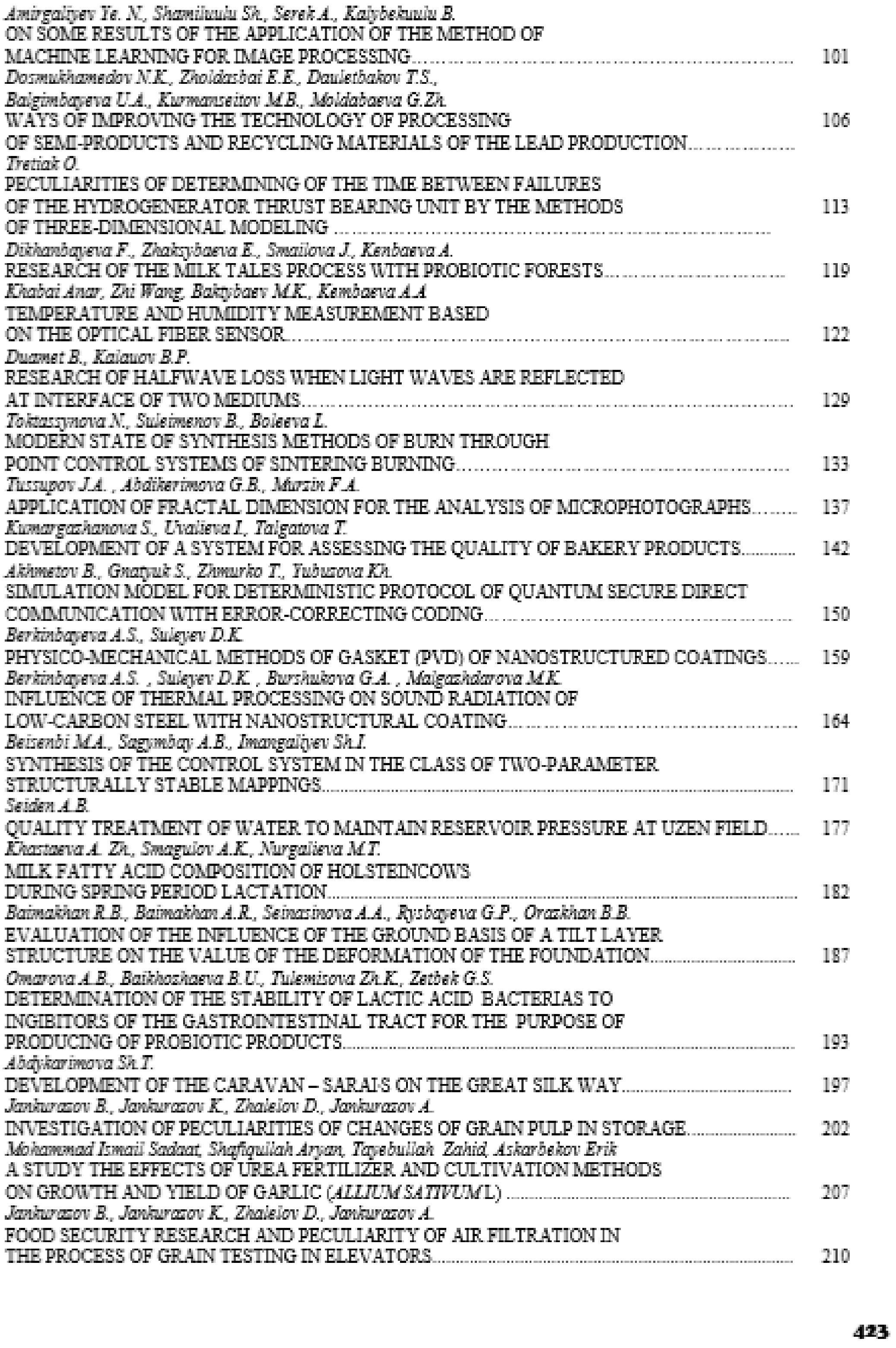
Continuation of appendix C

CONTENTS

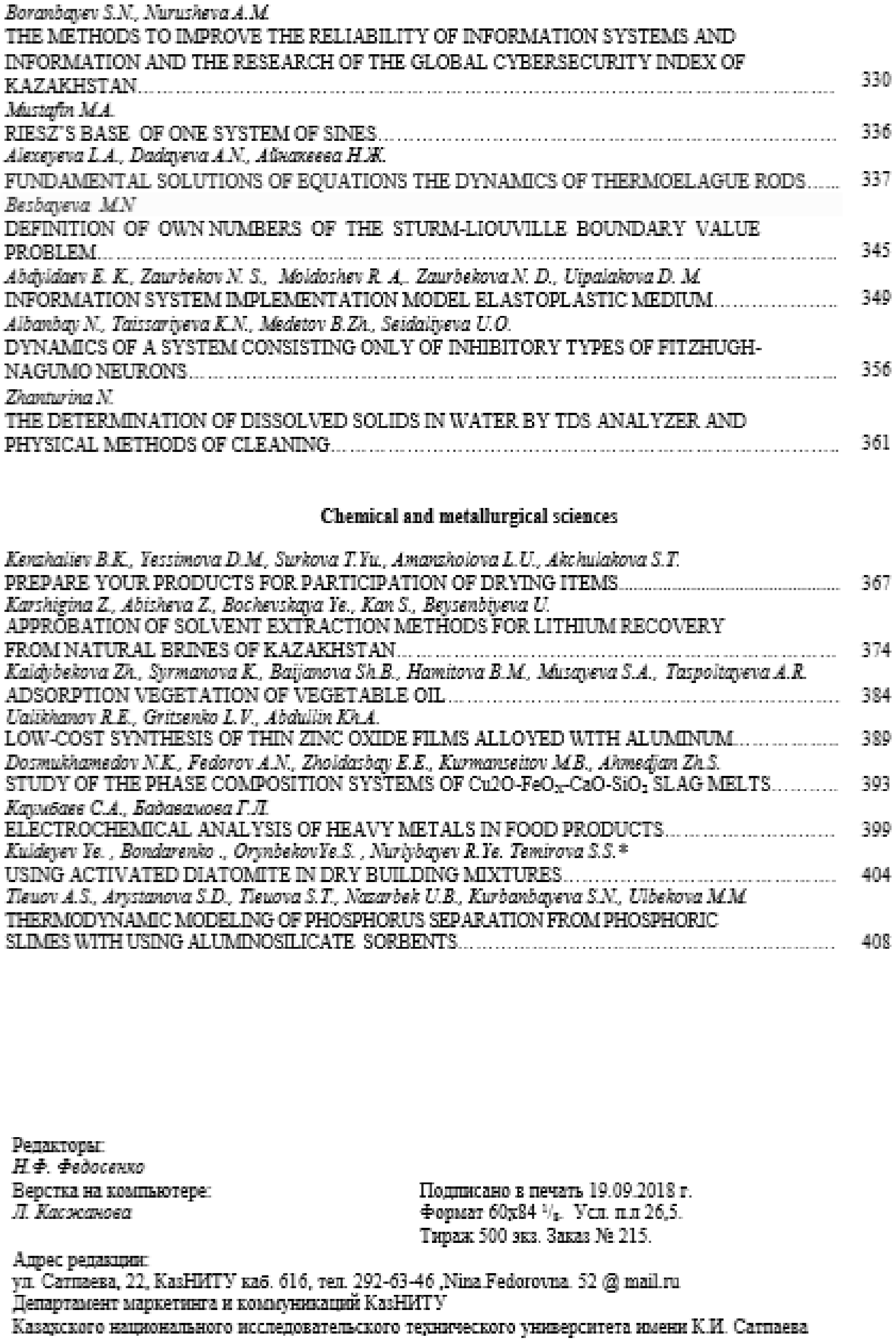
Earth sciences

Technical sciences

Continuation of appendix C



Continuation of appendix C



Chemical and metallurgical sciences

Редакторы:
Н.Ф. Федосенко
Верстка на компьютере:
Л. Касжанова
Подписано в печать 19.09.2018 г.
Формат 60х84 $^{1}/_{8}$. Усл. п.л 26,5.
Тираж 500 экз. Заказ № 215.

Адрес редакции:
ул. Сатпаева, 22, КазНИТУ каб. 616, тел. 292-63-46 ,Nina.Fedorovna. 52 @ mail.ru
Департамент маркетинга и коммуникаций КазНИТУ
Казахского национального исследовательского технического университета имени К.И. Сатпаева

ОТЗЫВ

научного руководителя на диссертационную работу магистранта
группы 6М070900-Металлургия **Балгимбаевой У.А.**
на тему: **«Исследование поведения меди и свинца при шахтной сократительной плавке полупродуктов и оборотных материалов свинцового производства»**

Выпускная магистерская работа Балгимбаевой У.А. посвящена исследованию распределения меди,свинца и сопутствующих металлов между продуктами шахтной сократительной плавки полупродуктов и оборотных материалов свинцового производства и определению путей совершенствования технологического процесса.

В период выполнения магистерской работы Балгимбаевой У.А. был проанализирован обширный материал по рассматриваемому направлению исследований, который охватывает технологию действующего производства, последние достижения в теоретических и экспериментальных исследованиях применительно к переработке бедных штейнов и полупродуктов свинцового производства с применением шахтной сократительной плавки.

Балгимбаева У.А. проявила себя достаточно грамотно, вполне сформировавшимся исследователем, способной творчески подходить к решению поставленных научных задач. Ею правильно и полно проведен анализ литературных данных по распределению меди, свинца, мышьяка и сурьмы в системе металл – штейн–шлак–газ, экспериментально изучены формы нахождения металлов в образцах штейна и шлака, исследовано распределение меди, свинца, мышьяка и сурьмы между штейном и шлаком шахтной сократительной плавки, разработаны практические рекомендации по осуществлению процесса шахтной сократительной плавки. Результаты исследований обработаны и представлены в виде таблиц, регрессионных уравнений и графических зависимостей.

Выпускная магистерская работа заслуживает оценку **отлично (98%)**, а **Балгимбаева Улпан Аманкоскызы** присвоения степени «**Магистр»** по направлению подготовки **«Металлургия»**.

Научный руководитель
ассоц. профессор, к.т.н.
(должность, уч. степень, звание)
______________ **Досмухамедов Н.К.**
(подпись)
«14» мая 2019 г.

Горно-металлургический институт имени О.А. Байконурова

МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ РЕСПУБЛИКИ КАЗАХСТАН
СӘТБАЕВ УНИВЕРСИТЕТІ

РЕЦЕНЗИЯ

на магистерскую диссертацию
(наименование вида работы)

Балгимбаевой Улпан Аманкоскызы
(Ф.И.О. обучающегося)

6М070900 – «Металлургия»
(шифр и наименование специальности)

На тему: «Исследование поведения меди и свинца при шахтной сократительной плавке полупродуктов и оборотных материалов свинцового производства»

Выполнено:
а) графическая часть на ________________ листах
б) пояснительная записка на 110 страницах

ЗАМЕЧАНИЯ К РАБОТЕ

Диссертационная работа **Балгимбаевой У.А.** посвящена исследованию распределения меди, свинца и сопутствующих металлов между продуктами шахтной сократительной плавки полупродуктов и оборотных материалов свинцового производства и определению путей совершенствования данного процесса.

В работе получены новые данные по формам нахождения меди, свинца в промышленных шлаках и штейнах. Установлено, что в окислительно-восстановительных процессах рост потерь меди и свинца со шлаком связаны с перераспределением форм их нахождения между продуктами плавки в зависимости от изменения состава шлака и штейна.

В работе проведены исследования по определению равновесного распределения меди, свинца и сопутствующих металлов в системе штейн – шлак – газовая фаза при контролируемых значениях парциального давления кислорода и серы. Полученные экспериментальные результаты могут быть использованы при переработке сложного по типу и составу исходного медь-, свинец содержащего сырья в условиях шахтной сократительной плавки.

Вопрос по работе: Поведения цинка при переработке сложного по составу шихты?

Оценка работы

Выпускная магистерская работа заслуживает оценку **отлично (98%)**, а **Балгимбаева Улпан Аманкоскызы** присвоения степени «**Магистр**» по специальности 6М070900 – «Металлургия».

Рецензент
Технический директор «Arna Solution», к.т.н.
(должность, уч. степень, звание)
______________________ Рахимбаев Б.С.
(подпись)
«16» мая 2019 г.

Отчет подобия

Университет:	Satbayev University
Название:	The study of the behavior of copper and lead in the mine contractile smelting semi-products and recycling materials of the lead production
Автор:	Balgimbayeva Ulpan Amankoskyzy
Координатор:	Нурлан Досмухамедов
Дата отчета:	2019-05-14 12:03:29
Коэффициент подобия № 1: ?	**1,9%**
Коэффициент подобия № 2: ?	**0,0%**
Длина фразы для коэффициента подобия № 2: ?	**25**
Количество слов:	7 505
Число знаков:	43 214
Адреса пропущенные при проверке:	
Количество завершенных проверок: ?	36

! **К вашему сведению, некоторые слова в этом документе содержат буквы из других алфавитов. Возможно - это попытка скрыть позаимствованный текст. Документ был проверен путем замещения этих букв латинским эквивалентом. Пожалуйста, уделите особое внимание этим частям отчета. Они выделены соответственно.**
Количество выделенных слов 12

>> **Самые длинные фрагменты, определеные, как подобные**

>> **Документы, в которых найдено подобные фрагменты: из RefBooks**

>> **Документы,содержащие подобные фрагменты: Из домашней базы данных**

>> **Документы,содержащие подобные фрагменты: Из внешних баз данных**

>> **Документы,содержащие подобные фрагменты: Из интернета**