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RESEARCH OF PHYSICO-CHEMICAL REGULARITIES OF ENVIRONMENTALLY SAFE TECHNOLOGY FOR EXTRACTION OF METALS FROM DUMP SLAG

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ABSTRACT

Pollution of the environment with metals such as lead, nickel, copper, titanium, and zinc is a worldwide public problem, as evidenced by the elevated levels in the blood of people living in polluted areas. The physicochemical analysis of the initial waste slags determined the phase and mineralogical features, as well as the elemental composition of the waste slags of lead production and refractory clays of the Sairam district of the Turkestan region. Thermodynamic studies of the calculation of the Gibbs energy of possible reactions of joint chlorinating roasting of non-ferrous and refractory metals have established the probability of reactions involving lead oxides, and nickel oxides in the presence of aluminum oxides, iron, and calcium chloride. An analysis of the obtained calculated data of the Gibbs energy showed that only in the high-temperature region is possible the joint chlorination of copper and nickel oxides in the presence of aluminum oxide, and in the presence of iron oxide, thermodynamic reaction 6 is likely. Mathematical planning of the experiment determined the technological parameters of the process, ensuring the extraction of nickel up to 94% when firing a mixture of slag and clay at 87-8%.

Keywords: Heavy Metals, Waste, Environment, Harmful Effects, Complex Processing, Chlorine Roasting, Expanded Clay.

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INTRODUCTION

Slag heaps are man-made deposits of a mixture of metal and oxide components, each of which is a valuable raw material. Extraction of residual metal components from slag containing, in addition to iron, such popular elements as nickel, and chromium mixed with zinc, lead, and copper can significantly increase the economic performance of complex processing. The higher volume of by-products (slags) generated during the production of heavy and non-ferrous, draws attention to the need to process it in a more efficient way over the past decades, with the rapid growth of industrialization.[1] The entry of heavy metals/metalloids into the food chain is a critical public health issue today.[2]

Environmental protection and safety measures for human health, and slag processing has attracted the attention of scientists and environmentalists in recent years from the point of view of the conservation of natural resources.[3] Pollution of the environment with metals such as lead, nickel, copper, titanium, and zinc is a worldwide public problem, as evidenced by the elevated levels in the blood of people living in polluted areas.[4] These metals are among the most common heavy metals, and their toxic effects affect the environment and human health, and due to their stability in a contaminated place and the complexity of the mechanism of biological toxicity.[5] Currently, metallurgical production occupies one of the first places in terms of the amount of pollution released into the environment. In metallurgical production, during the preparation and loading of raw materials, ore, and processing, a huge amount of dust and slag is generated containing various non-ferrous and heavy metals. In most cases, this waste is partially reused or not used at all.[6] The harmful effects of metallurgical production are caused by a number of reasons.[7]

Protection of the environment and safety measures for human health, the processing of waste slag with the extraction and associated use in the production of building materials is a more acceptable way for sustainable development from the point of view of conservation of natural resources.[8]

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The integrated use of non-ferrous metallurgy raw materials is closely related to the involvement in the production of resource-saving technologies, as a means of replenishing resources and obtaining additional production of non-ferrous and heavy metal chlorides, they increase the efficiency of resource use that meets the basic requirements of the economy and ecology.[9] Waste from the lead plant in the South Kazakhstan region has a direct negative impact on all components of the environment, in particular on the Kazygurt residential area, polluting soil and water with compounds of lead, zinc, copper, titanium, chromium, cadmium, and other metals. In this regard, the development of ways to use waste slag is an urgent environmental and social task. The purpose of this work is to evaluate the technological possibilities of the complex processing of technogenic slag wastes with the simultaneous production of metal chlorides and composite material.

EXPERIMENTAL

The following methods of analysis and instruments were used to study the chemical and physicochemical characteristics of waste slags and processed products. To determine the chemical composition of the initial waste metallurgical slag, calcium chloride, and refractory clay, complexometric and atomic adsorption methods of analysis were used. The effect of heat treatment was studied on a Q-1500 D derivatograph. Carrying out differential thermal analysis is a study of mass loss in the temperature range from 20 to 1500°C, the study of interaction mechanisms, and phase transformations, melting temperatures in various systems. In the process of continuous programmable heating of the sample, the changes occurring in it are recorded:

- Weight loss due to the release of volatile components or the occurrence of a chemical reaction with a change in the mass of the sample (for example, decomposition with the formation of volatile products);
- Absorption or release of heat.

The structure of the phase composition of waste slag from lead production and processing products was analyzed on an XPert PRO Pan analytical instrument. The diffractometer uses a high-resolution horizontal goniometer. The elemental composition and microstructure of the starting materials and the obtained products were analyzed using a JSM-6490LV (JOEL, Japan) scanning electron microscope.

The use of an electron microscope makes it possible to study the microstructure and dimensions of individual crystals, as well as the elemental and weight composition. Thermodynamic analysis of the possibility of chemical reactions of joint chlorination of non-ferrous and heavy metals in the presence of oxides of iron, aluminum, and silicon was determined by the change in the Gibbs energy in the range of 293–2000 K.[9]

RESULTS AND DISCUSSION

Samples were taken from the storage of dump slags of lead production in order to study the possibility of complex processing, at a height of 1-1.5 m from a depth of 0.20-0.40 m. The eastern part of the Sairam region is shown in Tables-1 and 2.

Table-1: Waste Slag Chemical Composition

Component	Zn	Pb	Cu	SiO_2	Fe_2O_3	CaO	S	H_2O	Others
Content, %	1.86	2.07	0.64	28.78	39.44	24.5	0.43	0.13	2.15

Table-2: Chemical Composition of Cay, (mass, %)

Clay name	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	S	Na_2O	K_2O	Others
Refractory Clay	59.86	20.46	6.15	0.75	1.32	1.41	0.14	0.26	2.8	6.8

As a chlorinating component, technical calcium chloride is used - a waste of the Ust-Kamenogorsk titanium-magnesium plant. The results of X-ray phase analysis showed clear structural lines related to the formation of a phase transition of a number of elements S, K, Ca, Ti, Ba, Mn, Fe, Ni, Cu, and Zn (Fig.-1).

The maximum of the film peak shifts towards short angles with increasing film thickness, which indicates an increase in the concentration of heavy metals with increasing film thickness. The maximum intensity of the peak corresponds to iron, which indicates the predominance of ferrites. Analysis of the results of differential thermal analysis of the initial sample of waste slag showed that the curve of DTA dependence on temperature is characterized by the presence of one non-intensive endo-effect and one intense exo-effect. The end effect in the region of 300-350°C is characterized by a slight weight loss and indicates the process of removal of crystalline moisture. An intense exoeffect in the region of 700-750°C indicates the process of oxidation or burnout of sulfur compounds and phase changes in the iron-containing components of fayalite. Analysis of the microstructure of the sample (Fig.-2) has a slight difference in the content of minerals of the slag component by the presence of fayalite and calcium ferrite crystals.

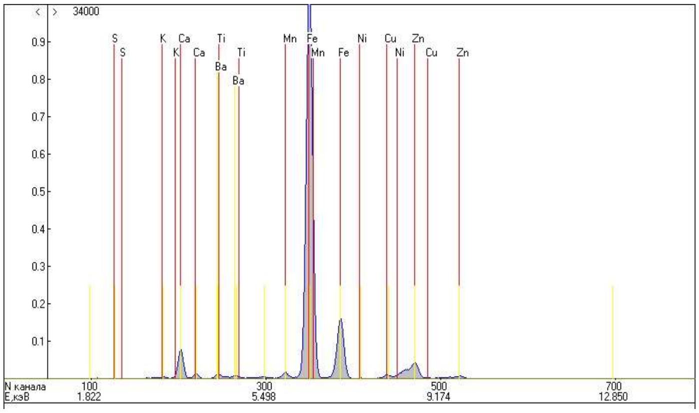

Fig.-1: Results of X-ray Phase Analysis of the Studied Sample of Waste Slag

Element	Wt. %
O	46.74
Na	0.96
Mg	1.77
Al	5.26
Si	17.51
S	0.41
Pb	1.62
Ca	10.15
Ni	0.45
Fe	12.83
Cu	1.07
Zn	1.24
Total	100.00

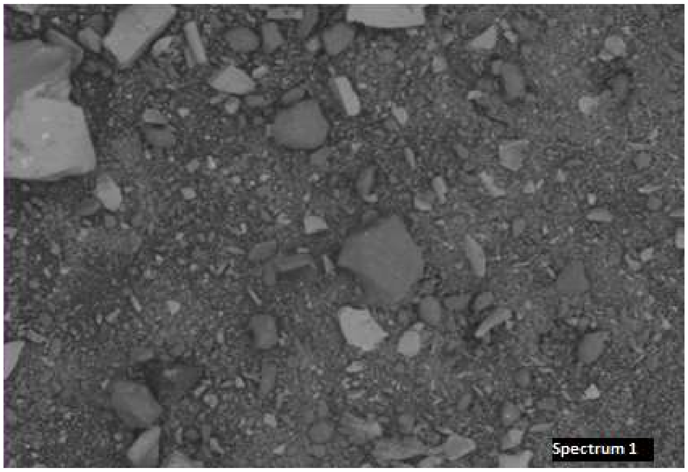

Fig.-2: Analysis of the Microstructure of the Studied Sample of Waste Slag

The surface is characterized by the presence of aluminosilicate components in the form of irregular shapes of light gray lamellar crystals in the general structure of the test sample. Small rounded crystals of monociliate and calcium ferrites are observed around the aluminosilicate crystals. X-ray phase analysis of Sairam refractory clay showed that the main characteristic phases of clays are calcium feldspars with d = 4.21, 4.17Å and potassium feldspars with d = 4.31; 3.31; 3.08; 2.99; 2.97Å. The $Al_2O_3{\cdot}3H_2O$ compound is characterized by diffraction lines with d= 4.37; 4.31; 2.45; 2.38Å. The mineralogical composition of Sairam clay is characterized by calcium and potassium feldspars, as well as hydro aluminate compounds. An analysis of the calculation of the Gibbs energy of the reactions of joint chlorination of lead, zinc and copper oxides with calcium chloride in the presence of nickel and aluminum oxide (1-3) in the range of 293-2000K is thermodynamically impossible (Fig.-3). This is evidenced by the positive values of ΔG in the region of 298-1800K. Only at a temperature of T = 2000K, the joint chlorination of zinc and nickel oxides in the presence of aluminum oxide is thermodynamic, probably, the Gibbs energy is equal to 8660.73 J/mol.

Graphical dependences of the change in the Gibbs energy on the temperature of the reactions of joint chlorination of oxides of nickel, lead, zinc and copper with calcium chloride, in the presence of iron oxide (4-6) are shown in Fig.-4.

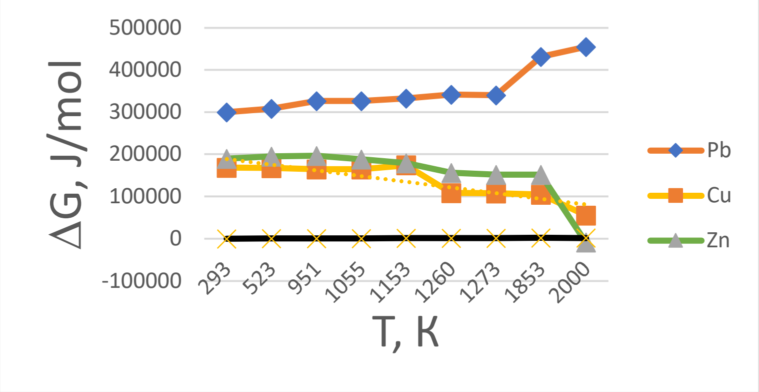

Fig.-3: The Effect of Temperature (T) on the Change in the Gibbs Energy (ΔG) of Reactions 1-3

$PbO+NiO+Al_2O_3+2CaCl_2=PbCl_2+NiCl_2+2CaO\cdot Al_2O_3$ (1)

$CuO+NiO+Al_2O_3+2CaCl_2=CuCl_2+NiCl_2+2CaO\cdot Al_2O_3$ (2)

$ZnO+NiO+Al_2O_3+2CaCl_2=ZnCl_2+NiCl_2+2CaO\cdot Al_2O_3$ (3)

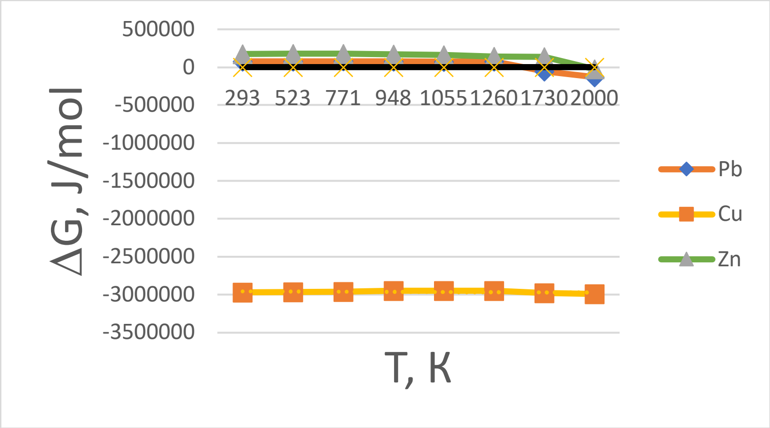

Fig.-4: The Effect of Temperature (T) on the Change in the Gibbs Energy (ΔG) of Reactions 4-6

$PbO+NiO+Fe_2O_3+2CaCl_2=PbCl_2+NiCl_2+2CaO\cdot Fe_2O_3$ (4)

$CuO+NiO+Fe_2O_3+2CaCl_2=CuCl_2+NiCl_2+2CaO\cdot Fe_2O_3$ (5)

$ZnO+2NiO+Fe_2O_3+2CaCl_2=ZnCl_2+2NiCl_2+2CaO\cdot Fe_2O_3$ (6)

An analysis of the obtained dependence of the change in the Gibbs energy showed that the thermodynamic probability of the studied reactions occurring is impossible, as evidenced by positive values up to 1800K. Only at a temperature of 2000K, the joint chlorination of nickel and zinc oxides in the presence of iron oxide has a negative value of -23987.75 J/mol. Laboratory studies of chlorinated roasting of waste slag mixed with refractory clay and calcium chloride were carried out at the facility shown in Fig.-5.

The installation for chlorinating roasting of waste slags consists of a tubular electric furnace (1), which allows heating up to 1000-1200^{0}C, to control the temperature, the furnace is equipped with a chromel-alumel thermocouple (2), a millivolt meter (3), the set temperature is maintained by a thermostat - a thermal relay (4), in the center of the furnace there is a reaction porcelain tube (5), in which a boat (6) with a sample is placed. Exhaust gases are absorbed by absorbers 7 and 8, and the purified gases are sent to chamber 9 for the last cleaning.

The results obtained after firing are presented in Table-3. To reduce the number of experiments, we used a rotatable design of the experiment. To build rotatable central compositional plans, the so-called "star shoulder" (shoulder of star points) is used. For two factors, the value of the "star shoulder" φ=1.414 (on the coded scale). Temperature and duration of the process were independent factors.

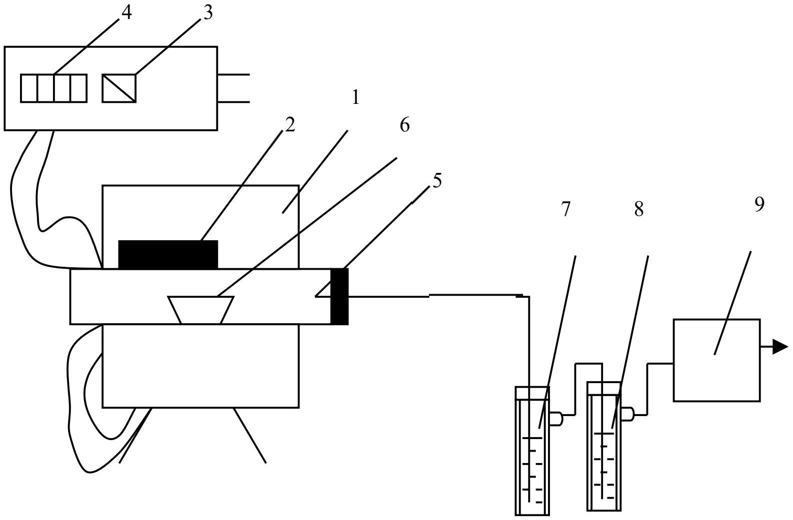

Fig.-5: Scheme of the Installation For Chlorinating Roasting: 1 - Tubular Furnace, 2 - Chromel-Alumel Thermocouple, 3 - Millivoltmeter, 4 - Thermostat, 5 - Reaction Porcelain Tube, 6 - Boat, 7.8 - Absorber, 9 - Chamber

As a result of mathematical processing of the experimental results, the coefficients b of the regression equation was determined, which describes the object under study in the form:

$$\alpha_R = b_0 + b_1 \cdot X_1 + b_2 \cdot X_2 + b_{11} \cdot X_1^2 + b_{22} \cdot X_2^2 + b_{12} \cdot X_1 \cdot X_2 \qquad (7)$$

Where α_R is the calculated value of the output.

The assessment of the significance of the coefficients of the regression equation was carried out using the Student's t-test. The adequacy of the regression equation was checked using the Fisher criterion. [10]

As the target output variables, the following were chosen: the degree of chloride sublimation of the metal Zn, Pb, and the physical properties of the cinder. The independent parameters were the content of slag, calcium chloride, and clay. The ranges of factors are shown in Table-3. The plan and results of the experiments are shown in Table-4.

The method of processing the results of experiments was used.[11,12] To automate the processing of the results, a special program for a personal computer based on the MS Excel system was developed, which is used in the environment of the Windows system. This made it possible to obtain almost instantly all the necessary calculation results during processing and to ensure the search for optimal modes of the process.

Table-3: Initial Data for Planning Experiments

Levels and intervals of variation of variables	Coded look			Natural look		
	x_1	x_2	x_3	Slag, m.h.	Calcium chloride, m.h.	Clay, m.h.
Main level	0	0	0	85	6	9
Variation interval	Δ	Δ	Δ	2	2	4
Upper level	+1	+1	+1	86	8	5
Lower level	-1	-1	-1	80	4	9
Upper Star Shoulder	+1.682	+1.682	+1.682	83.318	8.182	9
Lower Star Shoulder	-1.682	-1.682	-1.682	78.318	6.318	3.318

Table-4: Design and Results of Experiments on Lead Chloride Distillation

No.	Coded look			Natural look			$\alpha_{exponential}$, %	$\alpha_{estimated}$, %
	x_1	x_2	x_3	Slag, m.h.	Calcium chloride, m.h.	Clay, m.h.		
1	+1	+1	+1	84	6	9	91.5	93.6
2	-1	+1	+1	82	6	9	83.5	87.5

3	+1	-1	+1	84	3	9	89.1	93.42
4	–1	-1	+1	82	3	9	77.9	89.46
5	+1	+1	-1	84	7	5	87.6	79.00
6	-1	+1	-1	82	7	5	80.5	83.15
7	+1	-1	-1	84	3	5	80.6	80.57
8	-1	-1	-1	82	3	5	83.0	89.86
9	+1.682	0	0	86	5	9	91.3	92.47
10	-1.682	0	0	78	5	9	90.3	89.22
11	0	+1.682	0	86	8.4	9	90.8	92.79
12	0	-1.682	0	78	1.6	9	90.5	89.56
13	0	0	+1.682	78	5	11	85.7	77.41
14	0	0	-1.682	78	5	4	80.5	80.83
15	0	0	0	78	5	9	83.9	79.06
16	0	0	0	78	5	9	83.5	79.06
17	0	0	0	78	5	9	90.9	79.06
18	0	0	0	78	5	9	89.9	79.06
19	0	0	0	78	5	9	82.2	79.06
20	0	0	0	78	5	9	88.1	79.06

The significance of the coefficients of the equation was checked using Student's t-test. The use of the Fisher criterion confirmed the adequacy of the resulting equation.

In coded form, the regression equation looks like this:

$$\alpha_{Pb}=85{,}06+2{,}45\cdot X_1+0\cdot X_2+2{,}55\cdot X_3+1{,}87\cdot X_1^2+1{,}81\cdot X_2^2+0\cdot X_3^2+0\cdot X_1\cdot X_2+0\cdot X_1\cdot X_3+2{,}94\cdot X_2\cdot X_3 \quad (8)$$

Which, after screening out independent coefficients according to the Student's criterion, takes the form:

$$\alpha_{Pb}=85{,}06+2{,}45\cdot X_1+2{,}55\cdot X_3+1{,}87\cdot X_1^2+1{,}81\cdot X_2^2+2{,}94\cdot X_2\cdot X_3 \quad (9)$$

The results of mathematical modeling of the dependence of nickel chloride sublimation on the charge composition are shown in Fig.-6 and 7.

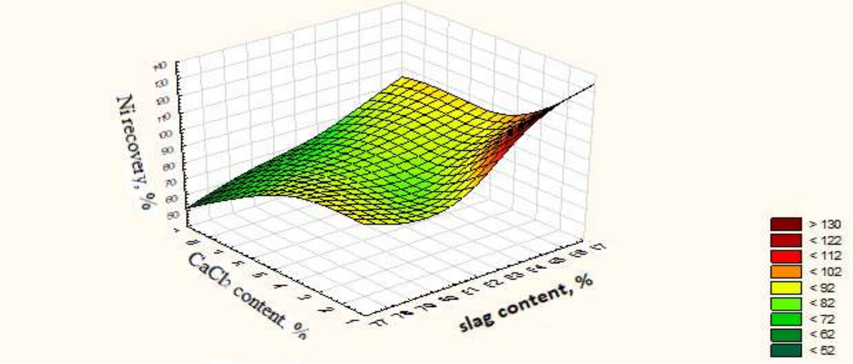

Fig.-6: Three-dimensional Graph of the Dependence of the Degree of Nickel Extraction on the Content of Slag and Calcium Chloride

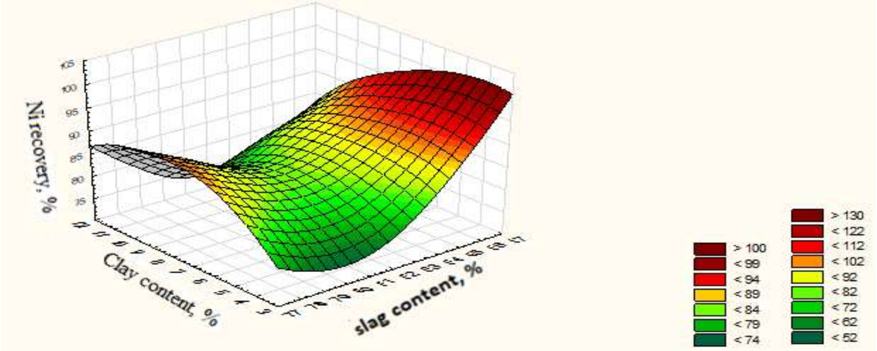

Fig.-7: Three-Dimensional Graph of the Dependence of the Degree of Extraction of Nickel on the Content of Slag and the Addition af a Clay Component

An analysis of the three-dimensional dependences of the degree of nickel extraction on the content of slag and calcium chloride showed that the maximum degree of extraction above 94% is achieved with a slag content of 87% and the addition of calcium chloride up to 8%.

Similarly, the dependence of the degree of nickel extraction on the content of the introduced clay component was revealed. The maximum degree of extraction above 95% is achieved with a slag content of 87% and the addition of a clay component up to 12%. Thus, the obtained results of mathematical planning make it possible to reduce the number of experiments and determine the technological parameters of the process of extracting associated non-ferrous and refractory metals.

CONCLUSION

The predominance of the iron-containing phase of fayalite and calcium monociliate was established as a result of physical and chemical analyzes of the initial dump slag. There are also clear structural diffraction peaks characteristic of metals - Zn, Cu, Ni, Ti and not intense peaks of Mn, Ba, K, S. Microstructural analysis of the waste slag confirmed the detected phases. Thermodynamic studies on the change in the Gibbs energy have established the probability of the reactions of joint chlorination of Pb, Zn, Cu, and Ni in the presence of iron oxide and aluminum only in the high-temperature region. Mathematical optimization of the process of nickel chlorination in the composition of the slag along with lead, zinc, and copper with the verification of the significance of the coefficients of the regression equation by the Student's criterion and the adequacy of the resulting equation by the Fisher criterion established the maximum degree of extraction of 94% with a slag content of 87% and calcium chloride of 8%. Experimental and theoretical indicators of the degree of extraction of metals obtained on the basis of a comparison of the value of the Student's coefficient and Fisher's criteria made it possible to determine the ratios of the components that ensure the maximum extraction of metals into chlorides.

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