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Studies of Physicochemical Bases and Optimization of Environmentally Safe Technology of Lead Production Waste Recycling

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ABSTRACT

Physicochemical research of peculiarities of technogenic metallurgical wastes and mathematical optimization of ecologically safe technology of their processing are of great practical importance for solving ecological problems of the region. The aim and the main direction of the research are connected with the study of physical and chemical bases of the organization of the technology of waste recycling with separation of valuable metals in the form of their chlorides and simultaneous production of agloporite. Peculiarities of phase and mineralogical composition of raw materials and chloride roasting products were studied by means of modern devices: Q-1500D derivatograph, X-ray diffractometer Panalytical X'PERT, scanning electron microscope JSM-6490LV JOEL. Studies have shown that solid metallurgical waste is characterized by the presence of non-ferrous metals Fe, Ti, Pb, Cu, Zn, and the microstructure is characterized by the presence of silicate, aluminosilicate and ferrite minerals. Using the method of mathematical design with the application of Stuyudent's criteria and Fisher's equation, the adequacy of the obtained roasting results was established, providing the degree of extraction up to 86–98%, at the temperature of 1100 °C. The microstructure of the roasted products of the waste mixture with clay binder and calcium chloride is characterized by the predominance of calcium ferrites, silicon ferrites and aluminosilicate minerals. The obtained results of the study of the peculiarities of the physical and chemical bases and the optimization of the safe technology are of practical importance for the solution of the ecological problem of utilization of technogenic wastes with obtaining of valuable products.

Keywords: waste slag; chlorination; thermodynamics; utilization; optimization; refactory clays; agloporite.

INTRODUCTION

The safety of the environment has become an important aspect of human activity. A special place in the solution of environmental problems in the world is occupied by the issues of utilization of metallurgical waste slag in recent years [Umanec et al., 2002; Ati-Hellal et al., 2021; Rastmanesh et al., 2018; Information bulletin, 2021].

There are more and more sources of emission of harmful substances into the environment of the region with the growth of production activities of large and small enterprises, chemical, petrochemical, ferroalloy, textile products. The health of the people of Southern Kazakhstan region is deteriorating with the growth of environmental degradation. This is an ecological, economic and social problem for the region and the whole country [Government Decree, 2018; Abilmagzhanov et al., 2022].

The actual problem in Turkestan region is accumulation of heavy metals in soils and their influence on environmental components. The accumulation is mainly characteristic for the areas of residential settlements, as well as for the areas of growing crops [Environmental Code, 2021].

It is necessary to solve the problems of introduction of new available technologies that neutralize the negative effects of slag waste on the environment, due to methods of utilization or production of slag with desired properties for their further use in production at present, taking into account the current requirements of the Environmental Code of Kazakhstan [GOST, 2010].

Residual metals in slags have the ability to be transferred along the food chain from small to large organisms. Thus, lead accumulates in the soil, is adsorbed by organic matter, and is transferred to humans through the food chain [Moiseenko, 2017; Moiseenko, 2019; Tiwari et al., 2012; Tiwari et al., 2012].

Zinc and cadmium accumulate in the soil, and they are fixed in the humus layer [Wang et al., 2015]. The presence of Zn, Cd, etc. has a negative impact on the soil compared to lead. The penetration of any metals into the food chain is an important public health problem. it contributes to the ingress of harmful toxic metals through the soil and the plant into the human body [Vitosevic et al., 2007].

All these points are the problem of the metallurgical industry in the relationship of nature and living organisms [Kapatsyna et al., 2012; Pooladi et al., 2020].

The analysis of literature sources has shown that in Turkestan region, the of environmental problems solution is closely with the disposal and processing of lead slag. Currently, lead recycling with the production of valuable components from slags and the extraction of useful material from waste rock have not been introduced into production [Pazylova et al., 2020].

Solid waste contains non-ferrous metals and their compounds that can be used as secondary raw materials. Recycling produces economically viable raw materials [Tleuova et al., 2014].

In this regard, there are known studies of the kinetic regularities of complex wasteless processing of metallurgical wastes with obtaining non-ferrous metal chlorides and cement clinker with confirmation in industrial approbation of the proposed technology [Tleuova, 2010; Tleuova, 2010].

The works of the authors [Badirova et al., 2005; Shevko et al., 2006] present the results of thermodynamic studies of chlorination of rare and non-ferrous metals using the software system "Astra-4" on the possibility of reactions with the formation of inorganic chlorides, as well as the equilibrium distribution of elements and compounds in the working mixture under heat treatment.

Our research suggests waste-free recycling of both waste slag, with separation of residual non-ferrous metals and obtaining commodity products, demanded in the construction industry. The research tasks are to study the composition of solid metallurgical wastes; to process and analyze their composition; to carry out physical and chemical analyses of initial raw materials and final products; to establish the hazard class according to ecotoxicity indicators of metallurgical wastes and composite materials obtained from them; to mathematically plan the process of metal extraction.

The generalized analysis of hazard class of dumped lead slag according to classification of chemical substances labeling GHS-GHG was carried out. A utility model patent was obtained based on the results of the research [Tleuov et al. 2023].

MATERIALS AND METHODS

The objects of the study are waste metallurgical slags, technical calcium chloride and local aluminosilicate ores. the proposed method for integrated processing of slags with release of residual metals in the form of their chlorides is a chloride-burner. Temperature influence on the composition of charge from the initial materials was studied on derivatagraffe at 1000 °C. Diffractometer Pananalytical was used to analyze the initial and final phase composition of the product (DTA).

The scanning electron microscoperam equipped with an energy dispersive microanalysis system INCA Energy 350 was used to study the elemental composition and microstructure of the initial and final products.

One of the effective methods of processing tailings, waste metallurgical slags is chloride-burning, which provides, using calcium chloride and correcting additives, extraction of inorganic chloride concentrate and building materials [Tleuov et al., 2023].

The hazard class of lead slag was calculated according to the methodology for calculating the hazard class of the "GHS system" [Methodology, 2013].

The passport of lead slag as a hazardous waste was made according to the waste classifier [The list of wastes, 2007].

The method of mathematical planning of the flagship product of the STATISTICA 10 statistical analysis system used to ensure the efficiency of research on chlorination of heavy metals [Ismailov, 2006]. The results of thermodynamic studies of reactions of combined chlorination of metals in the presence of impurity components characteristic of the composition of the waste slag by the change in Gibbs free energy (ΔG), enthalpy and entropy were obtained using the Finnish program Outkumpys HSC Chemistry 5.1.

Significance of the regression equation coefficients was assessed using Student's test. The adequacy of the regression equation was checked by Fisher's criterion [Naboychenko et al., 2005].

RESULTS AND DISCUSSION

The slag from lead production is classified as a mixture of Hazard Class 5 (because the main components according to the criterion "when ingested" are attributed to this class) applying the principles of interpolation according to the GHS methodology. According to the summation method (the classified components) is also classified as a mixture of Hazard Class 5 (since three components have Hazard Class 5 and one component has Hazard Class 4). Summarizing the data of the above methods, the lead slag production slag belongs to hazard class 5.

Lead slag has the same, invariable structure and is a glassy material of orthosilicate composition with typical features of Portland cement clinker. The slag is insoluble in water and is not a fire hazard. Full waste code is N100870//Q8//WS5//C10+13+15+27//H00//D5//A223//AB010. The waste belongs to the amber hazard level. slag from lead-zinc production refers to waste for disposal in class 1 landfills (landfills for hazardous waste).

The results of the analyses of the original waste slag and refractory clay Turkestan region, located in the southeastern part of Sairam district are below (Table 1).

Lead slag has the following average composition: Lead (Pb) 2.2%, Calcium oxide (CaO) 19.0%, Silicon oxide (SiO_2) 23.0%, Iron (FeO) 30.0% and other components (copper, zinc, sulfur) 25.8%.

Analysis of the results of X-ray phase (RFA) analysis of spent slag samples taken at the bottom of the repository at a depth of 20 cm showed changes related to the formation of the phase transition of a number of helenite crystals (Figure 1, Table 2).

The X-ray picture of the dumped lead slag is characterized by a high-intensive diffraction

Table 1. Content of basic and impurity contents

Component	Zn	Pb	Cu	Al_2O_3	MgO	SiO_2	Fe_2O_3	Cr_2O_3	CaO	K_2O	Na_2O	Ni	Others
Slag	1.86	2.07	0.64	-	-	28.78	39.44	-	24.5	-	0.2	0.13	2.15
Clay	-	-	-	20.46	1.41	59.86	6.15	-	1.32	2.8	0.26		7.6

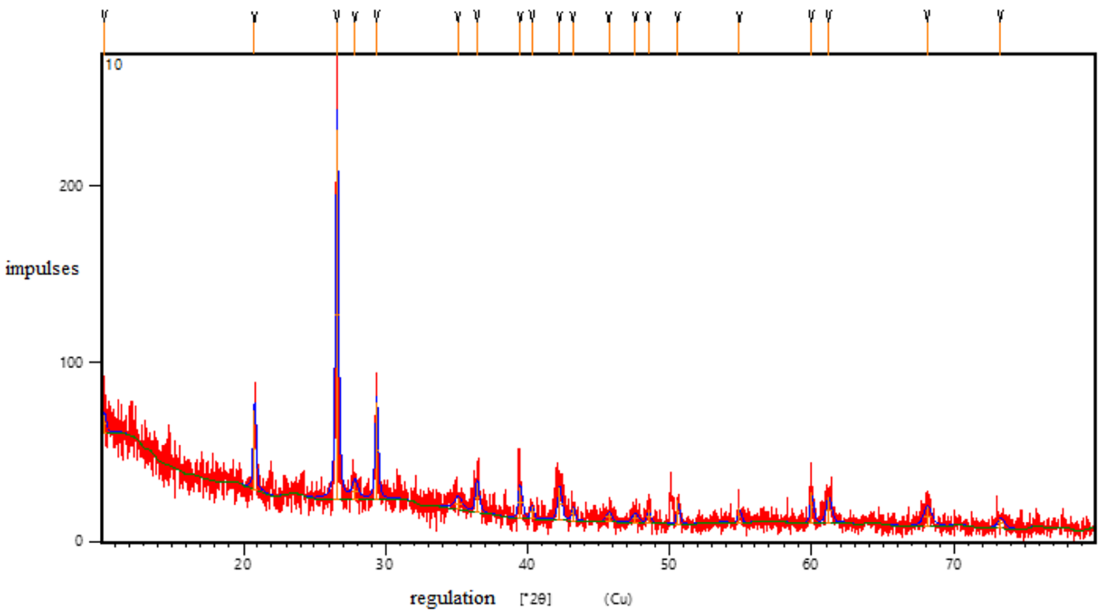

Figure 1. RFA results of waste slag

Table 2. RFA results of waste slag

Regulation [°2θ]	Height [pulse]	FWHM left [°2θ]	Lattice spacing [Å]	Relative interval [%]
10.2008	10.45	0.3149	8.67185	5.02
20.7932	45.05	0.2362	4.27205	21.65
26.5784	208.09	0.2362	3.35385	100.00
27.8369	9.45	0.4723	3.20502	4.54
29.3633	55.07	0.2362	3.04180	26.46
35.0932	6.81	0.6298	2.55716	3.27
36.4415	16.75	0.3149	2.46559	8.05
39.4610	18.05	0.3149	2.28361	8.67
40.3019	7.25	0.2362	2.23788	3.48

peak, 3.35, 2.1, 1.98A° characteristic of the fayalite phase, and also peaks of average intensity with d equal to 3.04, 2.28, 1.87 corresponding to larnite phase. The non-intensive diffraction peaks with d equal to 2.46, 2.23, and 2.09 are characteristic of the pyrite phase of fayalite.

The DTA results of the initial sample of the waste lead slag is resulted in Figure 2. The results of differential thermal analysis of the slag sample does not have pronounced endo-effects in the temperature region under study. Intense exo-effects are observed in the region of 300 °C, 400 °C and 500 °C and at 750-780 °C an intensive peak of exo-effect is observed. These exo-effects are apparently characteristic of the burnout of volatile impurities and sulfur-containing iron compounds.

The analysis of the microstructure of the averaged sample is shown in Figure 3. In the general structure of dumped slag surface is also characterized by the presence of helenite crystals. Around the aluminosilicate crystals there are small rounded forms of monosilicate and calcium ferrite crystals.

The OutKumpysHSCChemistry-5.1 software package was used to study the possibility of chloride burning for extraction of residual content of non-ferrous metals.

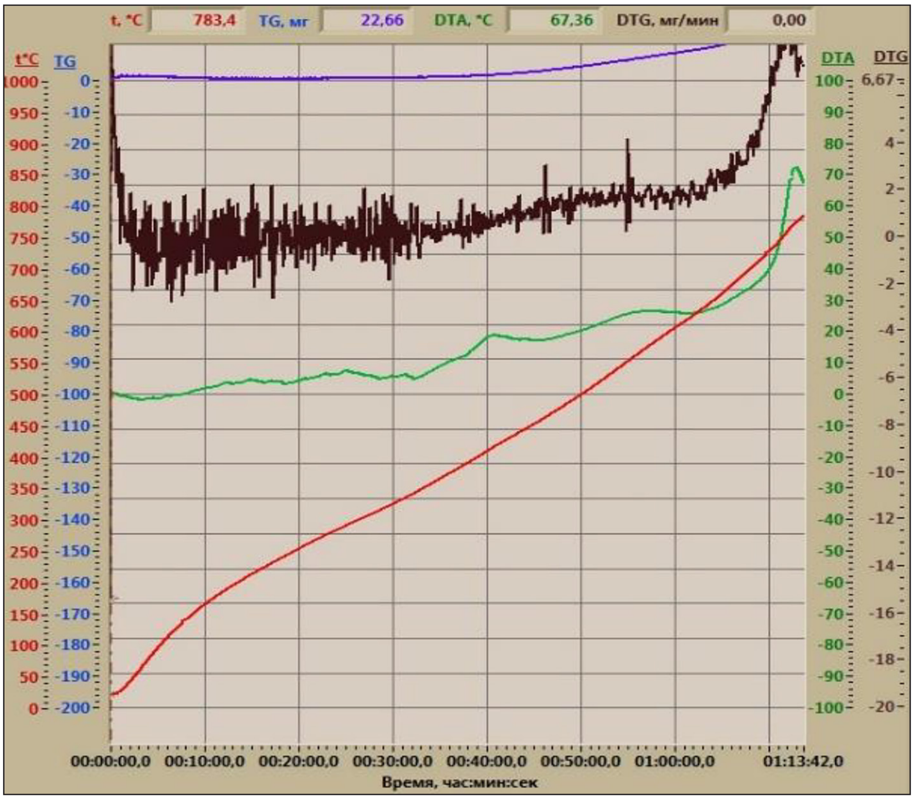

Figure 2. DTA of waste lead slag

Elements	Weight, %
Mg	1.47
Al	3.01
Si	22.11
Pb	0.47
S	0.13
K	0.91
Ca	12.47
Ti	0.57
Mn	0.50
Fe	28.2
Cu	0.11
Zn	0.82
Totally	100.00

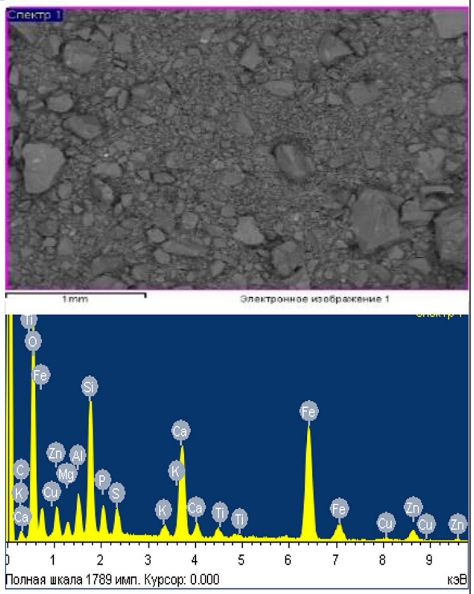

Figure 3. Elements and structure of minerals from dumped slags

Possible reactions in the calcium chloride and clay component slag burning were calculated by changing the thermodynamic indices of the reaction components:

$$PbO + Cr_2O_3 + Al_2O_3 + 4CaCl_2 = \\ = PbCl_2 + 2CrCl_3 + 4CaO \cdot Al_2O_3 \quad (1)$$

$$CuO + Cr_2O_3 + Al_2O_3 + 4CaCl_2 = \\ = CuCl_2 + 2CrCl_3 + 4CaO \cdot Al_2O_3 \quad (2)$$

$$ZnO + Cr_2O_3 + Al_2O_3 + 4CaCl_2 = \\ = ZnCl_2 + 2CrCl_3 + 4CaO \cdot Al_2O_3 \quad (3)$$

$$PbO + Cr_2O_3 + 2SiO_2 + 4CaCl_2 = \\ = PbCl_2 + 2CrCl_3 + 2(2CaO \cdot SiO_2) \quad (4)$$

$$CuO + Cr_2O_3 + 2SiO_2 + 4CaCl_2 = \\ = CuCl_2 + 2CrCl_3 + 2(2CaO \cdot SiO_2) \quad (5)$$

$$ZnO + Cr_2O_3 + 2SiO_2 + 4CaCl_2 = \\ = ZnCl_2 + 2CrCl_3 + 2(2CaO \cdot SiO_2) \quad (6)$$

Earlier researches on thermodynamic modeling of systems Cr_2O_3-6HCl and Cr_2O_3-$3Cl_2$ with use of program complex Astra-4 in the temperature range 298–1500 K and pressures 0.04–0.101 MPa have been conducted. As a result of studies it was found that the equilibrium degree of distribution of elements and compounds reaches the high-temperature region of formation of $CrCl_3$ at

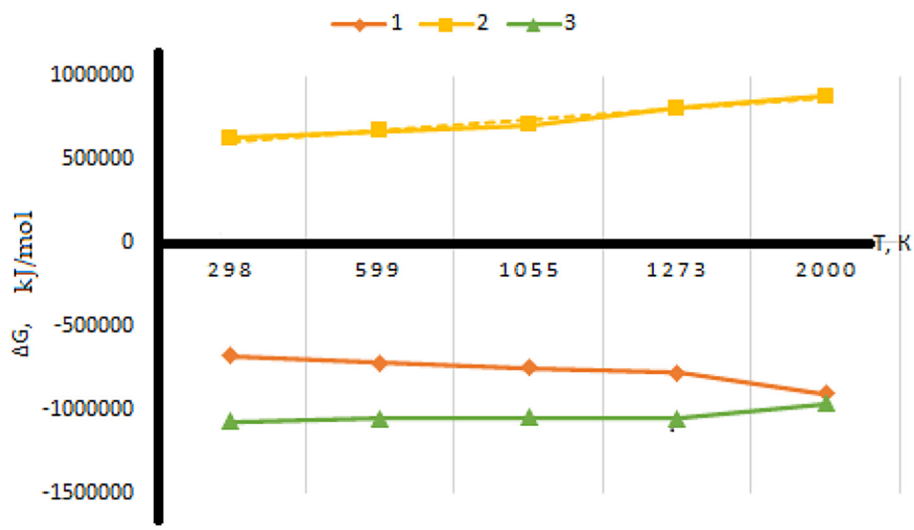

Figure 4. Change of thermodynamic indices of the reaction of the system 1-3

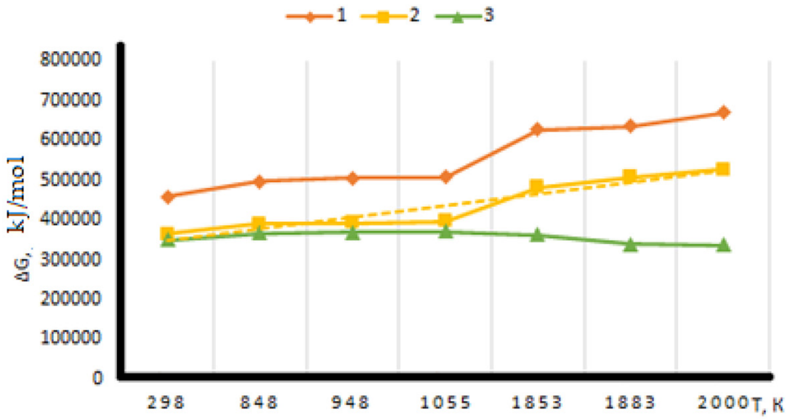

Figure 5. Change of thermodynamic indices of the reaction of the system 4-6

98–99%. With increasing pressure up to 0.101 MPa is characterized by negligible formation of $CrClO_2$ and $CrCl_2$ [28].

Graphical dependence of joint chlorination reactions of chromium, zinc, lead and copper oxides in the presence of aluminum oxide in the temperature range 298–2000 K is shown in Figure 4.

Analysis of the obtained Gibbs energy dependences on T showed that in the investigated area joint chlorination is possible only for chromium oxide in the presence of impurities. This is evidenced by the negative values ΔG from -674.686 to -878.718 kJ/mol PbO-Cr_2O_3-Al_2O_3 and from -255.517 to 964.538 kJ/mol ZnO-Cr_2O_3-Al_2O_3. these reactions are not possible at high temperatures.

The graphical dependence of the Gibbs energy change on the temperature of co-chlorination of chromium, zinc, lead and copper oxides in the presence of silicon oxide is shown in Figure 5.

Analysis of the obtained graphical dependences ΔG on the temperature showed that in the range 298–2000 K they have positive values. This indicates the thermodynamic impossibility of these reactions in the presence of excess silica.

For experimental researches we chose the slag after fuming of lead manufacture, with the following composition, wt. %: PbO-1,2; ZnO-5,12; CuO-1,45; CaO-19,45; Al_2O_3-5,46; Fe_2O_3-30,0; SiO_2-23,43. The total content of Cd, Ni, Cr, Mo is 3–4,5%.

Conditions for obtaining the granules is as follows: formed mass, contains waste slag of lead production, technical calcium chloride and bentonite clay, in a ratio of 100:10:6.

The samples were dried to a moisture content of 1.0–1.5% wt. to obtain pellets. Grinded in a ball mill to a particle size of 150 microns. Then the charge composition was thoroughly mixed, then pelletized in a pan pelletizer with a diameter of 7–12 mm. The dried pellets were burned in a tube furnace at 800–1100 °C for 60 minutes. The cooled pellets were crushed and analyzed for their content of non-ferrous metal chlorides.

There are used rototable planning of the experiment to study the mechanism of chloride distillation and to establish the effect of temperature

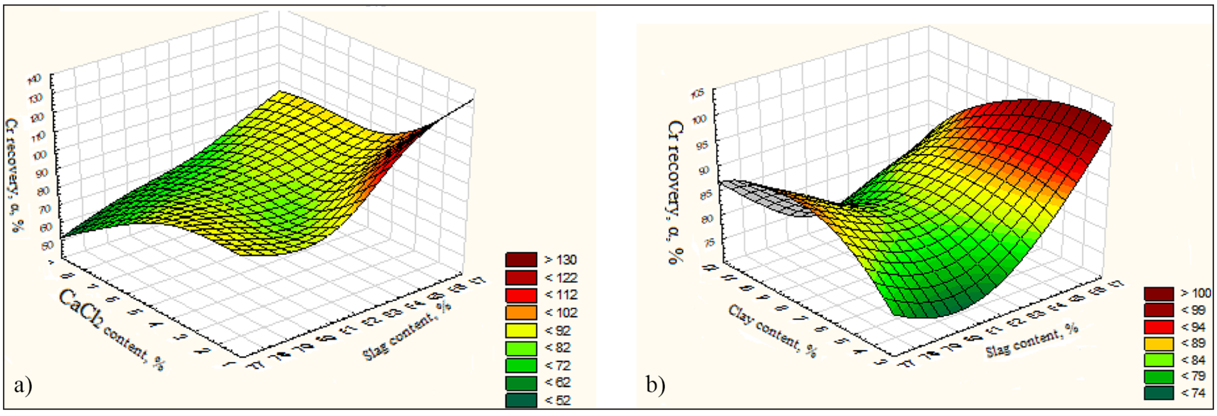

Figure 6. volumetric chart of chromium extraction from the working system

Elements	Weight, %
Mg	1.47
Al	3.01
Si	25.11
Pb	0.47
S	0.13
K	0.91
Ca	12.47
Ti	0.57
Mn	0.50
Fe	21.2
Cu	0.11
Zn	0.82
Totally	100.00

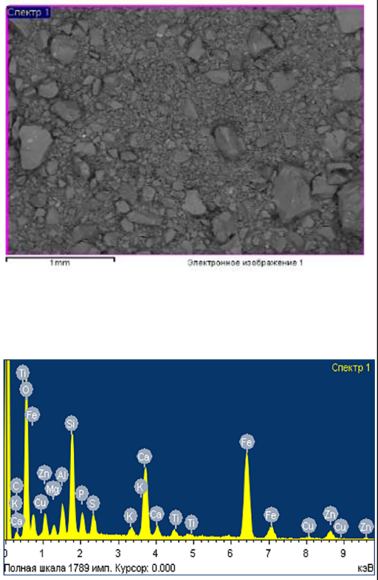

Figure 7. Analysis of the microstructure of firing products from lead slags and refractory clay

and the ratio of components on the chlorination process in the initial firing period, with a reduction in the number of experiments. The results of the three-dimensional mathematical modeling showed on Figure 6.

The degree of extraction of chromium reaches 94.5% at the content of slag - calcium chloride - clay component 80:12:8.

optimization makes it possible to determine technical parameters with less consumption of materials and reagents. The results of study of product microstructure after chloride firing at temperature 1000 °C and duration 60 min of lead slag with addition of 10% refractory clay from Sairam deposit are given in Figure 7.

The surface of the studied sample is characterized by the predominance of minerals of ferrite composition. This is evidenced by the solid dark surface characterizing a large mass of calcium ferrite and silicon ferrite minerals. A minor part of the crystals of calcium aluminates and silicates are represented as vague irregular structures of light gray-colored small piles of minerals.

The analysis of information sources has shown that in the south of Kazakhstan, the solution of environmental problems is associated with the utilization and processing of technogenic metallurgical waste, which has a negative impact on the environment.

Solid wastes from lead are characterized by a residual content of non-ferrous metals, which can be extracted and used as secondary raw materials.

Physico-chemical methods of analysis established the peculiarities of the mineral and metallic part of the waste slag and refractory clay used as a binding component.Analysis of the microstructure of the slag is characterized by the predominance of iron-bearing minerals fayalite and calcium ferrite. The X-ray phase analysis of the slag is characterized by the presence of nonferrous metals Fe, Ti, Pb, Cu, Zn.

To reduce the experiments the method of optimization of experiments planning by Student's criterion was used which allowed to determine the effect of temperature and clay component addition on the degree of chromium extraction. Under laboratory conditions the degree of chloride distillation of Zn, Pb, Cu, Cr, Ni, Mo is achieved in the range of 86-98%.

CONCLUSIONS

The phase composition, microstructure and elemental composition were determined on the basis of physical and chemical analyses of waste metallurgical slag using INCA Energy 350 and a Pananalytical diffractometer. The main phases of slag by intensive diffraction peaks are fayalite and non-intensive diffraction peaks are larnite. Microstructure and elemental composition indicate the presence of minerals gelenite and calcium monosilicate with minor inclusion of calcium ferrite.

The results of thermodynamic studies carried out using the program complex Outkumpys HSC Chemistry 5.1 in the range 298–1500 K showed that in the high-temperature region, the joint chlorination of chromium oxide of lead and zinc is possible in the presence of aluminum oxide.

The results of mathematical planning showed that the degree of extraction of chromium to 94.5% is achieved at a rate of 80% slag, the content of calcium chloride 12% and the addition of clay 8%.

The obtained research results are of important practical importance for determining the technological parameters of chlorination firing in the complex processing of metallurgical waste.

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