

Molten Fayalite Modification Using Intrinsic Latent Slag Heat During Pouring

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Abstract: In this study, a synergistic internal modification method based on $\text{Na}_2\text{CO}_3 + \text{CaCO}_3$ was proposed for processing liquid copper smelting slag. The process is carried out based on very low-carbon technology at temperatures of 1180-1280 °C, directly at the stage of pouring the slag into the bowl, eliminating the traditional slow cooling and grinding stages. Na_2O and CaO , formed as a result of the thermal decomposition of carbonates, depolymerize the silicate chain, break down the structure of fayalite (Fe_2SiO_4), and enhance the separation of metal phases. Thermodynamic analysis confirms that reactions occur spontaneously ($\Delta G < 0$). Kinetic results show that the activation energy decreases to $38.7 \text{ kJ} \cdot \text{mol}^{-1}$, and the flotation half-life is ~15 s. Under optimal conditions, the copper recovery rate increases from 62–65 % to 95–98 %. Additionally, viscosity decreases by 40–45 %, and the rheological properties of the slag significantly improves. The proposed method is an energy-efficient, environmentally sustainable, and innovative technology that aligns with the principles of a circular economy.

Keywords — copper slag, $\text{Na}_2\text{CO}_3 + \text{CaCO}_3$, modification, fayalite decomposition, alkali activation, non-bridging oxygen, flotation kinetics, thermodynamic analysis, viscosity, metallurgy, circular economy

1. INTRODUCTION

Copper slags are one of the most important by-products of modern pyrometallurgical processes, with annual global production volumes exceeding 50 million tons. The volume of slag accumulated in the waste storage facilities of Chinese metallurgical enterprises alone exceeds 70 mln. tons. In the metallurgical workshop of the "Almalyk MMC" Copper Smelter, more than 1 million tons of copper slags, containing significant amounts of copper (0.7-2.0 %), gold (0.2-0.4 g/t), silver (3-5 g/t), iron (35-40 %), molybdenum, nickel, cobalt, and rare earth metals (La, Cs, Nd) are formed in the technological chain for producing 150,000 tons of raw copper per year [1].



Fig. 1.1. Almalyk Copper Smelter.

- 1) Waste slag dump storage 2) Metallurgical workshop

Almost 70% of this slag is re-floated at the Copper Enrichment Plant №2. The remaining slag leads to an increase in the accumulation of slag in the tailings pond and the expansion of fertile land areas. Currently, the volume of accumulated slag in the slag dump is about 10 million tons [2]. The concept for expanding production capacities at JSC

"Almalyk MMC" stipulates that by 2030, the volume of gold will reach 50 tons, silver 500 tons, and copper 500,000 tons. These figures indicate a proportional increase in the volume of the resulting slag by 3–3.5 times. Waste is an important secondary resource for the country's economy [3]. Today, Uzbekistan's demand for steel products is 6 million tons, and the volume of secondary scrap metal processed at local ferrous metallurgy and foundry-mechanical enterprises exceeds 2 million tons. The shortage is covered by imported steel products. The cost of imported products, transport and logistics costs, customs and tax payments, exchange rate instability in foreign currencies increase the cost of production. It was concluded that due to the low content of iron in the deposits of Uzbekistan and the complex structure of ore iron (Tebinbulak deposit, Republic of Karakalpakstan, Fe – 16 %; reserves - 1.2 billion tons) [4], the small volume of reserves (Suyun-ata deposit, Parkent district, Fe – 30 %; reserves - 25 million tons), or the location of the deposit in deep layers (Temirkon, Samarkand region - 100 million tons), their processing is currently economically unprofitable. More and more investments, construction projects, mechanical engineering, spare parts for machinery and equipment of enterprises and technological materials require a lot of steel [5].

The main mineral phase of copper slags is fayalite (Fe_2SiO_4), which accounts for approximately 60-70 % of the mineralogical composition of the slag. The fayalite crystal lattice possesses a highly stable silicate structure, within which the aforementioned precious metals are observed to be isomorphically or mechanically trapped. Therefore, the effective extraction of these metals requires the destruction of the fayalite structure or significant modification. However, the high thermodynamic stability of fayalite is one of the main factors complicating this process. In traditional industrial practice, a technology of slow cooling of slag prior to flotation

is applied to achieve a high degree of copper recovery. This approach, in turn, is characterized by high energy consumption, long processing times, and the multi-stage nature of the technological process [6].

Alternative approaches include carbothermal reduction [7], lime-based decomposition (CaO), and alkaline activation [8]. However, each of these methods has certain limitations. In particular, reduction with carbon-containing substances requires a long process (≈ 60 minutes) at temperatures of $1100\text{--}1200^\circ\text{C}$ and high carbon consumption. Although CaO -based systems are thermodynamically favorable, they face significant kinetic obstacles due to the formation of a dense passive layer of the Ca_2SiO_4 type, which sharply reduces the reaction rate.

In this regard, in recent years, internal approaches based on the direct modification of liquid slag have been of great scientific and practical interest. This work proposes a synergistic Na–Ca modification method based on the simultaneous introduction of Na_2CO_3 and CaCO_3 into liquid slag at a temperature of 1250°C . This approach can be implemented without additional energy input by utilizing the internal latent heat of the slag coming out of the smelting furnace [9].

The proposed method has a number of significant advantages:

First, carbonates decompose spontaneously at high temperatures ($\text{Na}_2\text{CO}_3 \approx 851^\circ\text{C}$, $\text{CaCO}_3 \approx 840^\circ\text{C}$) to form active oxides (Na_2O and CaO). This ensures the thermodynamic convenience of the process [10].

Secondly, as a result of the combined action of Na and Ca modifiers, synergistic effects occur, and the decomposition of the fayalite structure is significantly accelerated. Ca^{2+} ions partially displace Fe^{2+} ions at positions in the crystal lattice, leading to the destruction of the silicate structure, while Na^+ ions depolymerize the aluminosilicate network, making the surface properties favorable for flotation.

Thirdly, since the process is carried out at the stage of pouring the slag into the bowl, mixing is ensured through natural convection, and the modification process is completed within a few seconds. This creates a significant technological advantage over traditional hours-long cooling and processing processes.

Furthermore, this method allows for its implementation without deviating from existing technology. Excludes additional pyrometallurgical machines.

2. MATERIALS AND METHODS

2.1 Research objects

The object of the research work was a mixture of copper slags from the Vanyukov, Oxygen-flame and Refractory smelting furnaces of the copper smelting plant "Almalyk MMC," calcined soda and limestone as reagents. Experimental work was carried out on equipment in the laboratories of the Almalyk State Technical Institute.



Fig. 2.1.1. Sample of solid slag from the dump of Copper Smelter "Almalyk MMC" JSC

The complex of analytical studies included the use of modern instrumental methods: X-ray fluorescence analysis (XRF) to determine chemical composition, X-ray diffraction analysis (XRD) was used to determine phase composition, as well as scanning electron microscopy (SEM) and light-emitting electron microscopy (TEM) to study the morphology and microstructure of the studied slag.

Analytical studies of the samples were conducted using X-ray fluorescence analysis (XRF), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), and radiation electron microscopy (TEM). The light microscopy method was used to obtain an overview of the structure, porosity, and sulfide distribution of the samples, as well as to prepare for studies using a scanning microscope. For these studies, the Olympus GX71F-5 microscope was used (Fig. 2.1.2), equipped with a microstructure photography system with a magnification of 12.5 to 1000 times and high image quality.



Fig. 2.1.2. Olympus GX71F-5 light microscope

The study of the alloy structure was conducted using a TESCAN VEGA LMH scanning electron microscope with a LaB_6 cathode (SEM) and an Oxford Instruments Advanced AZtecEnergy X-ray energy dispersion microanalysis system (Fig. 2.1.3).



Fig. 2.1.3. Scanning electron microscope.



Fig. 2.1.4. TESCAN VEGA LMH electron scanning microscope with LaB6 cathode and Oxford Instruments Advanced AZtecEnergy X-ray energy dispersion microanalysis system.

Laboratory studies using the alkaline activating decomposition method were conducted in the SX2-9-17TP Muffle furnace. When using the internal latent heat of copper slag, the temperature was maintained within the range of 1200–1300°C. The electric furnace casing is equipped with two-layer forced-air cooling.



Fig. 2.1.5. SX2-9-17TP muffle furnace. Maximum temp. is 1700°C, operating temp. is 1600°C.

2.2 Initial Analyses

Table 2.2.1 demonstrates the elemental composition according to the results of the XRF analysis of a sample of copper slag mixed in equal proportions from Vanyukov, Flash smelting and Reverberatory smelting furnaces.

Table 2.2.1. Elemental composition of slag sample

№	Element	Quantity, %	№	Element	Quantity, %
1	Cl	0.0311	14	Cu	1.47
2	Na	2.70	15	Zn	2.71
3	Mg	0.888	16	As	0.0350
4	Al	3.78	17	Rb	0.0184
5	Si	19.0	18	Sr	0.0219
6	S	0.943	19	Y	0.0078
7	K	2.92	20	Zr	0.396
8	Ca	1.91	21	Mo	0.455
9	Ti	0.283	22	Sb	0.111
10	Cr	0.0130	23	Ba	0.182
11	Mn	0.170	24	Pb	0.602
12	Fe	61.2	25	Ac	0.0352
13	Co	0.138			

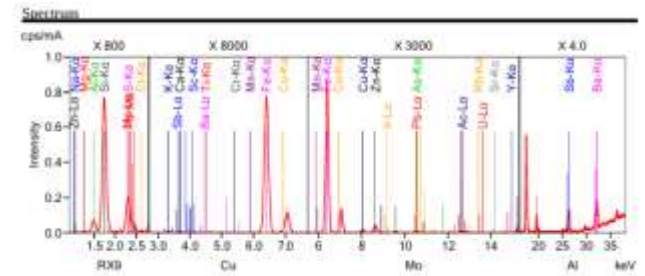


Fig. 2.2.1. Corresponding spectrogram of elemental composition based on the results of XRF analysis of a copper slag sample.

The sample preparation methodology included standard procedures for material selection, grinding, and averaging. The analysis was conducted without preliminary chemical decomposition, which allowed for the preservation of the sample's original structure and the acquisition of reliable data on its composition.

The results show that, iron and silicon form the main matrix of the slag, besides non-ferrous metals (Cu, Zn) are present in residual quantities and also indicating the loss of metals during smelting;

- The presence of Pb, As, Sb, and other elements indicates the potential environmental hazard of the slag.

The slag under study is a complex multi-component system that requires an integrated approach to processing [11].

XRF analyses. The determination of the chemical and oxide composition of copper slag using the Rigaku NEX CG analyzer (Figs. 1.1 and 1.2) is based on the X-ray fluorescence analysis (XRF) method, i.e., its energy-dispersion type (EDXRF). This method allows for the direct determination of the elemental composition of the sample, after which the data obtained via software are converted into the corresponding stoichiometric oxide forms (e.g., FeO, Fe₃O₄, etc.). Therefore, the results obtained for copper slag are classified as elemental and oxide analysis performed using the XRF method.

Table 2.2.2. Oxide composition of the copper slag sample according to XRF analysis results.

№	Compound	Quantity, %	№	Compound	Quantity, %
1	Cl	0.0218	15	Co ₂ O ₃	0.110
2	Ac	0.0186	16	CuO	0.999
3	Na ₂ O	3.03	17	ZnO	1.82
4	MgO	1.06	18	As ₂ O ₃	0.0248
5	Al ₂ O ₃	5.06	19	Rb ₂ O	0.0107
6	SiO ₂	28.2	20	SrO	0.0138
7	SO ₃	1.71	21	Y ₂ O ₃	0.0052
8	K ₂ O	2.27	22	ZrO ₂	0.286
9	CaO	1.70	23	MoO ₃	0.365
10	Sc ₂ O ₃	ND	24	Sb ₂ O ₃	0.0717
11	TiO ₂	0.299	25	BaO	0.111
12	Cr ₂ O ₃	0.0116	26	Ir ₂ O ₃	(0.0079)
13	MnO	0.134	27	PbO	0.346
14	Fe ₂ O ₃	52.3	28	U ₃ O ₈	(0.0015)

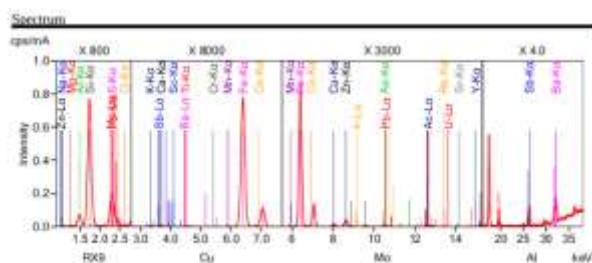


Fig. 2.2.2. Corresponding spectrogram of the oxide composition of a copper slag sample based on XRF analysis results.

Copper slags are primarily composed of iron-silicate phases, primarily fayalite (Fe_2SiO_4) and the vitreous amorphous phase. The structure of slag is usually vitreous or fine-crystalline, which is due to the rapid cooling of the melt. Particle morphology is characterized by an angular shape with a rough surface, as well as the presence of pores and inclusions of metallic copper or sulfide phases.

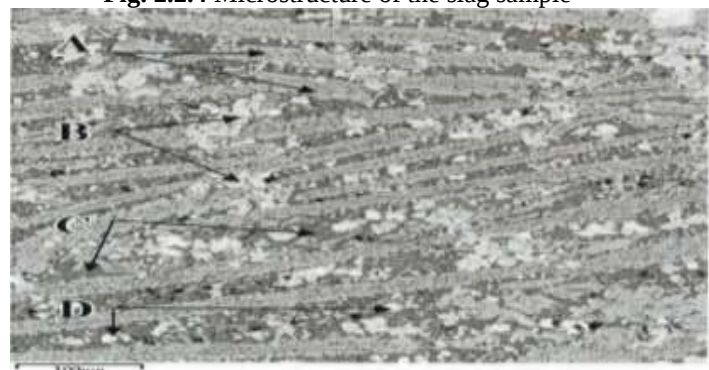
The granulometric composition of copper slags varies within a wide range depending on the cooling method (water granulation or air cooling), ranging from dust particles to fractions of several millimeters or larger. During aqueous granulation, smaller, glassy particles are formed, while during slow cooling, large crystalline aggregates are formed [12]. Thus, the investigated copper slag consists of an iron silicate system with a predominance of Fe and Si oxides and the presence of residual copper and its associated non-ferrous and rare metals, making it a promising object for further processing and the complex extraction of valuable components [13].



Fig. 2.2.3 - Sample of slag VF, FSF Inco and RF from the landfill



Fig. 2.2.4 Microstructure of the slag sample



Phases in the sample: A - Fayalite; B-Geshteinite; C- Almandine; D-Pyrrhotin

Fig. 2.2.5. Phase distribution in the thin section of the test sample

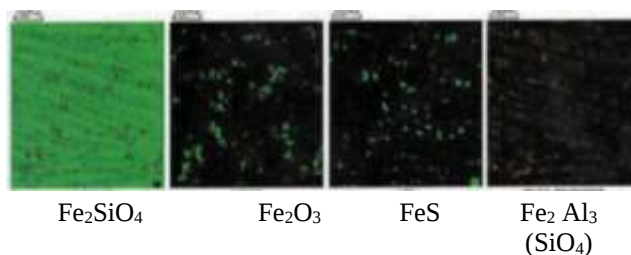


Fig. 2.2.5. Distribution of the elemental composition in the thin section of the spectrum sample.

According to X-ray fluorescence analysis, the copper content in the sample was 0.6449 % (error $\pm \Delta 0.0096\%$). Titrimetric studies showed a copper content of 0.7998 % (error $\pm \Delta 0.0119\%$). The copper content in the sample does not exceed 1.08% of the value of the slag sample in the corresponding waste.



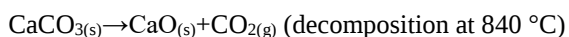
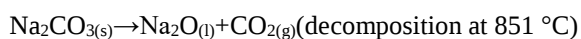
Fig. 2.2.6. Distribution of the elemental composition in the spectrum in the thin section of slag sample

2.3. Objectives of the research

High-temperature The main objectives of this study are:

- assessment of the thermodynamic and kinetic possibilities of the combined application of Na_2CO_3 and CaCO_3 in a liquid slag medium at 1250 °C;
- studying the kinetic mechanisms of fayalite decomposition in the bicarbonate system;
- determining the advantages of the proposed approach by comparing it with traditional modification methods;
- quantitative assessment of changes in viscosity and other physicochemical properties;
- studying the degree of grinding and crushing of the treated slag;
- analysis of the efficiency of the flotation process after modification.

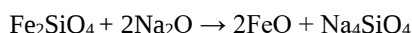
Thermodynamic calculations made use of Gibbs free energy minimization using built-in databases. The decomposition of carbonates of the combined alkaline activating modifier occurs in the following reaction:



The decomposition of fayalite by CaO formed from the initial decomposition occurs based on the following reaction:



fayalite decomposition reaction by Na_2O :



The Gibbs free energy change (ΔG) was calculated as follows:

$$\Delta G = \Delta H - T\Delta S$$

The equilibrium constants were determined as follows:

$$\Delta G^\circ = -RT \ln K$$

2.4. Kinetic analysis approach

Kinetic analysis used the Arrhenius equation:

$$k = A \exp \left(-\frac{E_a}{RT} \right)$$

The shrinkage shell model was adapted for liquid-solid reactions with modifiers simultaneously. The speed control stages were determined by analyzing the conversion fraction (α) and time (t) graphs.

2.5. Methods of Data Synthesis

The quantitative data obtained from the reviewed studies were synthesized using meta-analysis techniques. The reduction in viscosity, improvement in flotation enrichment indicators, and reduction in operating time were calculated at average values throughout the studies. Statistical significance was estimated using standard error calculations. Content of raw copper slag (%):

3. RESULTS

3.1. Thermodynamic possibility of modification using a dicarbonate alkali

Thermodynamic analysis confirms that the simultaneous addition of Na_2CO_3 and CaCO_3 to liquid slag at 1250°C is highly beneficial [14]. Both carbonates decompose spontaneously at temperatures well below 1250°C:



Combined fayalite decomposition reactions show that the simultaneous presence of both modifiers creates additional thermodynamic driving force through synergistic interactions, with a combined ΔG of about $-210 \text{ kJ} \cdot \text{mol}^{-1}$.

3.2. Kinetic Analysis Results

Kinetic studies reveal that the bicarbonate modification has a complex multi-stage kinetics.

Table 3.2.1. Activation energy comparison

No	Method	Activation energy ($\text{kJ} \cdot \text{mol}^{-1}$)	At 1250°C
1	$\text{Na}_2\text{CO}_3 + \text{CaCO}_3$	38,7	15 seconds
2	Na_2CO_3 only	45,3	22 seconds
3	CaO only	52,8	35 seconds
4	Lime decomposition	85-120	>60 seconds
5	Carbothermic reduction	95-110	60 minutes

The reduced activation energy ($38.7 \text{ kJ} \cdot \text{mol}^{-1}$) for the two-carbonate modification indicates a synergistic kinetic improvement. 15 seconds represents a reduction of 60% from Na_2CO_3 and 97% from carbon reduction.

Mechanistic indications for CaO-fayalite interaction:

Recent mechanistic studies confirm that CaO accelerates the decomposition of fayalite through ion-exchange-like processes. At high temperatures, CaO dissociates into Ca (II) and Ca-waved $\text{Ca}_{1-\gamma}\text{O}$. In the second position of Fe_2SiO_4 , where the metal is located, Fe (II) is replaced by Ca (II), forming $[(\text{Fe}_{2-x}\text{Ca}_x)\text{SiO}_4] \cdot x \text{ Fe (II)}$. In the

substituted Fe (II) $\text{Ca}_{1-\gamma}\text{O}$, Ca takes the place of the vacancy and forms $(\text{Ca}_{1-\gamma}\text{Fe (II)} \gamma) \text{O}$. The disproportionation of Fe (II) and the addition of CaO-SiO_2 form compounds Fe_2O_3 , Fe_3O_4 , and CaSiO_3 . This mechanism explains why CaO significantly improves iron recovery from copper slag compared to other modifiers [15].

In the complex modification system based on $\text{Na}_2\text{CO}_3+\text{CaCO}_3$, the kinetics of copper fayalite slag decomposition are carried out through the mechanism of high-temperature heterogeneous reactions. The main kinetic stages of the process are associated with the thermal dissociation of carbonates, the formation of active oxides, the depolymerization of the silicate structure, and ion diffusion [16]. Initially, under the influence of high temperatures, CaCO_3 and partially Na_2CO_3 decompose to form active components CaO and Na_2O . The release of the resulting CO_2 gas creates a micropore inside the slag, increasing mass transfer and diffusion rates [1]. This causes kinetic acceleration at the initial stage of the reaction. During the process, Ca^{2+} and Na^+ ions diffuse into the fayalite structure, leading to the weakening of Fe–O–Si bonds.

From a kinetic perspective, the process is initially controlled by a chemical reaction, while diffusion control prevails in subsequent stages. In particular, the decrease in slag viscosity resulting from the depolymerization of the silicate network increases ion mobility and significantly increases the overall reaction rate.

The rate of the process can be described by the Arrhenius equation:

$$k=Ae^{-E_a/RT}$$

where:

k is the reaction rate constant;

A is the frequency factor;

E_a is the activation energy;

R is the universal gas constant;

T is the absolute temperature.

At a temperature of 1250°C , an effective reduction in activation energy is observed due to the high thermal activity of the system. The breaking of silicate bonds by Na_2O and the destabilization of the fayalite structure by CaO reduce the energy barrier of the reaction. Therefore, in a complex modification system, the reaction rate is significantly higher than with individual modifiers.

According to kinetic observations, the bulk of the modification occurs within the first 15–30 seconds. This condition is explained by the decomposition rate of carbonates at high temperatures, accelerated ion diffusion, and a decrease in viscosity. The fact that the degree of Fayalite decomposition reaches values above 90% confirms the kinetic efficiency of the process.

Kinetic improvement is also observed during the flotation stage. After modification, the bonds between mineral particles weaken and the emergence of copper-containing phases becomes easier. As a result, the half-life of the flotation kinetics is reduced to about 15 s, which is a significant advantage over traditional systems. The advantages of adding the modifier $\text{Na}_2\text{CO}_3+\text{CaCO}_3$ at 1250°C were demonstrated.

Table 3.2.1. Energy efficiency comparison

№	Parameter	$\text{Na}_2\text{CO}_3+\text{CaCO}_3$ internal	Carbother reduction	Decompos by CaO	Acidic leach
1	Temp.	1250°C (spontaneous reaction)	$1100-1200^\circ\text{C}$	1200°C	100°C
2	Additional energy	No (internal latent heat)	High (carbon)	Medium	Medium (acid + heat)
3	Working hours	15-30 seconds	60 minutes	> 60 seconds	Several hours
4	CO_2 emissions	Low, (from carbonate breakdown)	Carbon oxidation	Low	Low
5	Auxiliary equipment	Mechanical device (Bunker, screw)	Pipe rotary furnace	Not required	Reactor

Overall, the $\text{Na}_2\text{CO}_3+\text{CaCO}_3$ complex system significantly activates the processes of diffusion, mass transfer, and phase transformation, accelerating the decomposition kinetics of copper fayalite slags. The use of the liquid slag's own internal latent heat eliminates the need for additional heating, and the addition of carbonate to the process reactions within the modifier provides an energy advantage. Unlike lime decomposition, which is practically stopped after 60 seconds due to the formation of a Ca_2SiO_4 coating, bicarbonate modification achieves 90-95% fayalite decomposition within 30 seconds. Carbonate decomposition releases gases (CO_2), which creates stirring effects, improves mixing, and prevents the formation of a passivating layer. At the same time, in the practice of pouring liquid hot slag into a bowl on an industrial scale and mixing the modifier at the same time, the uniform and flow-through pouring of the slag is of great importance in terms of technical safety.

3.3. Improving the extraction of additional metals

$\text{Na}_2\text{CO}_3+\text{CaCO}_3$ alters the Fe_2SiO_4 phase, releasing fine-dispersed precious metals by disrupting the structure of the outer layer surrounding them. During flotation enrichment (600 g/t Na_2CO_3 + 300 g/t potash) [18], copper recovery reached 98.07% and the copper content in the concentrate reached 36.13 %. When combined with mechanical activation, sodium carbonate improves flotation for copper recovery from copper slag. The Na_2SiO_3 formed in the treated slag can be filtered and sent for the production of liquid glass after washing [19].

3.4. Impact of slag modification

Viscosity Reduction. The bicarbonate modification significantly reduces the viscosity of the liquid slag.

The decrease in slag viscosity is represented by the following exponential relationship: $\eta=\eta_0 \exp(-k \cdot C_{\text{total}})$ where:

η is the viscosity of the modified slag;

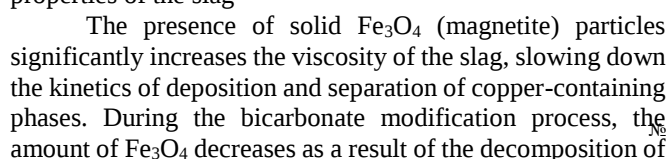
η_0 is the initial viscosity;

k is the modification coefficient;

$C_{\text{(total)}}$ is the total concentration of added carbonate modifiers.

Table 3.4.1. Influence of various doses of modifiers on slag viscosity

Secondly, an increase in the CaO content increases the basicity of the slag and reduces the degree of polymerization of the silicate solution. This increases ion mobility and improves the rheological properties of the liquid phase. Additionally, the modification of $\text{Na}_2\text{CO}_3 + \text{CaCO}_3$ significantly reduces the melting point of the slag. In particular, when adding a total of 3 % of the modifier, a decrease in the liquid state temperature from 1205°C to 1135 °C is observed. This increases the thermodynamic and technological efficiency of the smelting process. To reduce the temperature of the slag melt inside the Vanyukov furnace of the copper smelting plant from operating 1250 °C to 1200 °C, increasing the CaO content in the slag from 2.2 % to 2.8 % (by adding additional limestone from a separate hopper to the charge, at a rate of 500-600 kg/h per 1% of the loaded charge volume) prevented the corrosion of the furnace lining and extended the inter-repair period from 1 to 2 years [22].



For this reason, it is technologically expedient to incorporate modifiers into the loaded charge and use them at the stage of slag removal from the furnace and pouring, rather than during the smelting process itself [28]. This approach ensures structural softening and a decrease in the viscosity of the slag during the cooling process, particularly in the interval up to the eutectic solidification point. As a result, the separation of copper-containing phases is improved, the technological properties of the slag are optimized, and the negative impact on the furnace lining is minimized [28].

Furthermore, the reduction and liberation of iron from the fayalite lattice facilitate the formation of metallic iron (Fe^0). Compared with fayalite and magnetite, metallic iron exhibits lower brittleness and greater plastic deformability, thereby reducing the overall abrasiveness of the modified slag. The destruction of the dense fayalite matrix also increases the number of microcracks and structural defects, resulting in improved grindability and lower comminution energy requirements.

Phase	Chemical formula	Mohs hardness	Relative abrasiveness	Effect on grinding
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1	Fayalite	Fe ₂ SiO ₄	6,5-7,0	Very high	Increase energy consumption
2	Magnetite	Fe ₃ O ₄	5,5-6,5	High	Difficult to grind
3	Wustite	FeO	4,5-5,0	Moderate	Intermediate behavior
4	Metallic iron	Fe ⁰	4,0-4,5	Low	Improves grindability
5	Ca-Na silicates	CaSiO ₃ , Na ₂ SiO ₃	3,5-5,0	Low	Facilitates particle breakage

From a mineral processing perspective, the conversion of hard fayalite-rich phases into softer calcium-sodium silicates and metallic iron is expected to decrease the Bond Work Index and enhance crushing efficiency. In addition, the reduction in abrasive mineral phases minimizes wear of grinding media and milling liners. Therefore, the Na₂CO₃+CaCO₃ composite modification not only promotes fayalite decomposition and iron recovery but also improves the mechanical properties of the slag, making subsequent grinding, magnetic separation, and beneficiation processes more energy-efficient and economically favorable [29].

The modification of Na₂CO₃+CaCO₃ produces several useful transformations. The properties of the liquid slag play an important role in separating the fabric from the slag during the smelting of copper charge. Modification improves physicochemical properties such as viscosity, electrical conductivity, density, and surface tension [30].

Table 3.5.2. Comparison of untreated and modified slags

No	Specificity	Untreated slag	Modified (3% each)	Change
1	Liquid temperature	1205°C	1135°C	-70°C
2	Density (g·sm ⁻³)	3,8-4,0	3,5-3,7	-8%
3	Surface tension (mN·m ⁻¹)	450-480	380-410	-15%
4	Electrical conductivity (S·m ⁻¹)	0,8-1,0	1,2-1,5	+50%
5	Flow index	65-70	85-90	+29%

Two-carbonate modified slag demonstrated significantly improved flotation results.

3.6. Mechanisms of flotation improvement

The mechanism for improving the flotation process is carried out through several interconnected synergistic physicochemical interactions. The use of Na₂CO₃ in this process acts as a complex modifier that alters the properties of mineral surfaces.

First, a modification of the surface energy is observed. In the presence of Na₂CO₃, the surface energy of copper slag particles changes, which increases the probability of separation (liberation) between chalcocite and gangue mineral particles and creates favorable conditions for selective flotation.

Secondly, a surface cleaning effect occurs. Sodium carbonate partially dissolves or weakens the oxide films on the surface of mineral particles, ensuring the opening of active mineral surfaces. This improves the adsorption of collector reagents (e.g., khantats) [31].

Third, controlled oxidation processes play an important role. Partial oxidation of the chalcocite (Cu₂S) surface increases its flotation activity and enhances its hydrophobic properties.

Table 3.6.1. Performance indicators for the re-flotation of treated slag

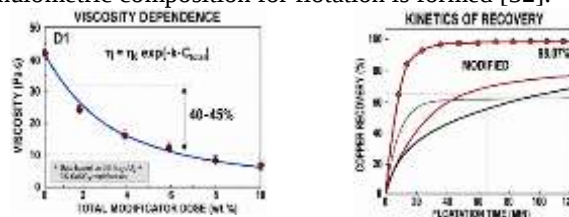
No	Parameter	Untreated slag	Na ₂ CO ₃ +CaCO ₃ modified	Improvement
1	Copper recovery (%)	62-65	95-98	+50%
2	Cu in concentrate (%)	18-20	34-36	+80%
3	Recovery efficiency (%)	45-48	82-85	+80%
4	Flotation time (min)	12-15	6-8	-47%
5	Reagent consumption (g/t)	500-600	300-400	-33%

Under optimal conditions (600 g/t of Na₂CO₃ + 300 g/t of potash), the reduction efficiency reaches 98.07% and the concentration level reaches 36.13 %.

Fourthly, a stabilization of the pulp medium is observed. The addition of Na₂CO₃ regulates the chemical stability and ionic strength of the sludge, improving the kinetic parameters of the flotation process.

Fifthly, the decomposition of the fayalite structure occurs in the presence of CaO, which enhances the release of copper minerals trapped in the silicate matrix.

Sixth, the degree of particle liberation increases. As a result of cooling and reducing the viscosity of the solution, the separation of crystalline phases improves, and an optimal granulometric composition for flotation is formed [32].



The flotation process kinetically approaches the first-order model, i.e., the separation rate is proportional to the existing mineral concentration. The addition of Na₂CO₃ significantly accelerates this kinetics, increasing the overall extraction efficiency.



Fig. 3.6.1. Processed liquid copper slag.



Fig. 3.6.2. Alkaline-modified copper slag.

When used in combination with mechanical activation, synergistic effects are further enhanced. The introduction of Na_2CO_3 prior to wet grinding stimulates the formation of interparticle microdefects and enhances the weakening of the interface between the chalcocite and gangue phases. As a result, higher selectivity and flotation efficiency are ensured compared to traditional grinding methods.

DISCUSSION

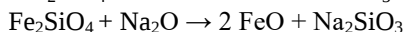
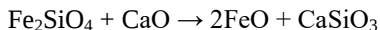
4.1. Thermodynamic and Kinetic Indicators

Thermodynamic assessments showed that the decomposition of CaCO_3 at a temperature of 1250 °C is thermodynamically strongly spontaneous, with a Gibbs free energy value of approximately $\Delta G^\circ \approx -63$ kJ/mol. Although Na_2CO_3 is relatively stable in its pure state, it is thermodynamically activated due to silicate-forming reactions in a silicate slag medium. As a result, the $\text{Na}_2\text{CO}_3 + \text{CaCO}_3$ complex system shifts the total Gibbs free energy of the fayalite modification process toward negative values, confirming the thermodynamic feasibility of the proposed modification method at 1250°C [33].

The main decomposition reactions of carbonates are expressed as follows:



At 1250 °C, $\Delta G < 0$ for these reactions, which ensures their complete and spontaneous decomposition. As a result, active oxides (Na_2O and CaO) are formed in the system, which play an important role in the structural reorganization of the slag phase. Interaction with the fayalite system. The resulting oxides react with the fayalite (Fe_2SiO_4) system in the following direction:



As a result of these reactions, the decomposition of the fayalite structure intensifies, the silicate network undergoes depolymerization, and free FeO phases are formed. This significantly improves the rheological properties of the slag.

4.2. Thermodynamic stability and ΔG analysis

For the overall process, the change in Gibbs energy is expressed as follows:

$$\Delta G = \Delta H - T\Delta S$$

at the temperature 1250 °C:

ΔH — decreases due to carbonate degradation and silicate reactions

$T\Delta S$ — gas phase (CO_2 release) significantly increases.

As a result, $\Delta G < 0$ and the system develops in a thermodynamically stable direction

4.3. Physicochemical scientific analysis

The effectiveness of the two-carbonate modification is explained by the following main factors:

The increase in entropy due to CO_2 release and the formation of the gas phase increased the disorder of the system. With the formation of active oxides (Na_2O , CaO), they depolymerized the silicate network. After the decomposition of the fayalite phase, the Fe–Si bonds weakened, free FeO was released, and ultimately, mass transfer and phase separation accelerated following an increase in the liquid phase fraction.

The kinetic advantage of the reaction is evident. A decrease in activation energy ($38.7 \text{ kJ} \cdot \text{mol}^{-1}$) compared to individual modifiers confirms the presence of a synergistic effect. The use of liquid slag as a reactive medium has a higher reactivity compared to the solid phase Fe_2SiO_4 , which significantly reduces heat loss. The half-life of the process ($t_{1/2}$) was 15 s, which showed a significantly faster kinetics than alternative methods. At a temperature of 1250 °C, the $\text{Na}_2\text{CO}_3 + \text{CaCO}_3$ system is fully thermodynamically activated, and the oxides formed as a result of the spontaneous decomposition of carbonates significantly alter the slag structure. This process culminated in the decomposition of the fayalite, the depolymerization of the silicate network, and an improvement in overall rheological properties [34].

4.4. Comparative analysis using single-modifier approaches

The two-carbonate ($\text{Na}_2\text{CO}_3 + \text{CaCO}_3$) modification system demonstrates significant kinetic and rheological advantages compared to traditional single-modifier approaches. When NaOH is applied at a concentration of 3%, a reduction in slag viscosity of approximately 35–40 % is observed. However, this system has a number of technological limitations, and the high hygroscopicity and strong corrosive properties of NaOH complicate its storage and dosing. The relatively low stability of the process and the half-life ($t_{1/2}$) ≈ 22 s, and the most important factor, the sale of NaOH in the raw material market, require economically sound calculations when choosing it as a reagent, the highest efficiency in the complex extraction of metals. For comparison, in the $\text{Na}_2\text{CO}_3 + \text{CaCO}_3$ two-carbonate system, a reduction in viscosity of up to 40–45 % is observed when applying a total of 6 % (3 % each), and the process kinetics are significantly accelerated ($t_{1/2} \approx 15$ s) [35].

When using only CaO, the viscosity of the slag decreases by 25-30 %. However, this approach is characterized by the following limitations;

- The formation of a passive layer (coating) of the type Ca_2SiO_4 by CaO in the silicate system limits the depth of the reaction, which slows down mass transfer and reduces the efficiency of modification;
- The formation of Ca_2SiO_4 increases the hardness of the slag. It complicates its subsequent threshing.

However, the activation energy of CaO is high, amounting to $E_a = 52,8 \text{ kJ}\cdot\text{mol}^{-1}$. The proposed dual reagent modifier $\text{Na}_2\text{CO}_3 + \text{CaCO}_3$ system effectively depolymerizes the silicate network via Na^+ ions, eliminating the problem of passivation (Ca_2SiO_4 coating) characteristic of CaO. As a result, the structure is constantly renewed, the reaction surface remains exposed, and the intensity of mass transfer increases. Therefore, the activation energy in this system decreases significantly and equals $E_a = 52,8 \text{ kJ}\cdot\text{mol}^{-1}$, which confirms the high kinetic efficiency of the process.

Table 4.4.1. Comparative indicators of alkaline decomposition and carbothermal reduction

№	Aspect	$\text{Na}_2\text{CO}_3 + \text{CaCO}_3$ internal	Carbon reduction
1	Time	15-30 seconds	60 minutes
2	Temperature	1250°C (available)	1100-1200°C
3	Carbon demand	No	Theoretical quantity 200%
4	CO ₂ emission	from carbonates	C oxidation, from carbonates
5	Equipment change	Minimal	Significant (furnace)
6	Copper recovery	95-98%	75-82%

4.5. Internal modification approach compared to traditional slow cooling technology

In traditional technologies, a slow cooling stage of the slag is used before the flotation process to achieve high copper recovery. This method is particularly widely used in copper production enterprises in China and Australia. Regardless of the high costs associated with the use of rotating metallurgical containers, which occupy vast areas in the tailings pond, this method has proven to be economically efficient today due to its high metal recovery rates. However, this approach is characterized by high energy consumption and a long process duration. For this reason, many copper smiths are in no hurry to implement this method [35].

The internal latent temperature modification approach eliminates these limitations and provides the following advantages:

- reduces the process duration from hours to ~30 seconds;
- eliminates the cooling-reheating duration (heat exchange);
- increases copper recovery from 62-65 % to 95-98 % for unprocessed slag.

The synergistic mechanism of Na–Ca modification is manifested through several interconnected physicochemical mechanisms. The mechanism of viscosity and structural modification (synergy of CaO and Na_2O) [36]. The interaction of CaO and Na_2O in copper slag systems based on molten fayalite is characterized by significant depolymerization and phase reorganization of the slag structure. These processes drastically change the physicochemical properties of the slag, particularly its viscosity and reactivity.

Calcium oxide (CaO), as a highly basic modifier, disrupts the continuity of the silicate network and kinetically accelerates the decomposition of the fayalite structure (Fe_2SiO_4). Ca^{2+} ions partially isomorphically replace Fe^{2+} ions in the silicate matrix, increasing structural instability. As a result, the recrystallization of iron oxides (Fe_2O_3 and Fe_3O_4) and the formation of the calcium silicate (CaSiO_3) phase are observed. Furthermore, CaO increases the basicity of the slag and reduces the degree of polymerization of the silicate network. This reduces the viscoelastic properties of the solution and accelerates mass transfer processes.

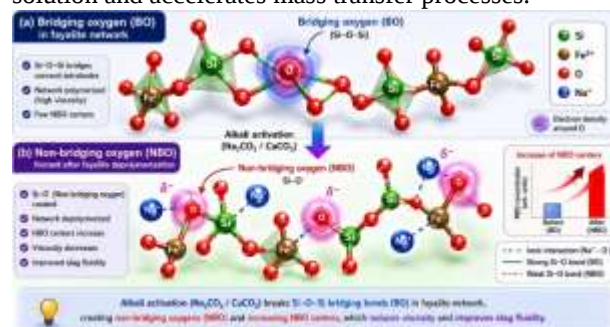


Fig. 4.5.1. The role of ionic and surface-active Na_2O .

Sodium oxide (Na_2O) as a strong depolymerizing modifier weakens the bonds in silicate and aluminosilicate branches. Na^+ ions, acting as network modifiers, disrupt oxygen bridges (bridging oxygen), leading to an increase in free NBO (non-bridging oxygen) centers. This condition is characterized by the "opening" of the slag structure and a significant decrease in viscosity. Additionally, Na_2O reduces particle surface energy, forming the optimal hydrophobic-hydrophilic equilibrium for the flotation process. By increasing the ionic strength of the slurry medium, it improves colloidal stability and accelerates flotation kinetics. Importantly, Na_2O keeps the reactive surfaces exposed by suppressing the formation of passive layers such as Ca_2SiO_4 [11][37].

4.6. Mechanism of synergistic action (CaO– $\text{Na}_2\text{CO}_3/\text{CaCO}_3$ system)

The combined application of CaO (or CaCO_3) and Na_2CO_3 creates complex ionic and phase rearrangement processes within the slag structure. In this system, Ca^{2+} ions ensure phase stability, while Na^+ ions deeply depolymerize the silicate network. As a result, the process of structural decomposition is accelerated, and the rheological resistance

of the solution is sharply reduced. Experimental and thermodynamic assessments showed that

- as a result of the synergistic effect, the degree of fayalite decomposition reached a value exceeding 90 % (70-75 % in individual modifiers);
- viscosity decreases by 40-45 % (25-35 % in individual systems);
- the efficiency of extracting copper, gold, and silver increases to 95-98% (compared to 82-87 %) the kinetic separation time ($t_{1/2}$) is ~ 15 s [33][37].

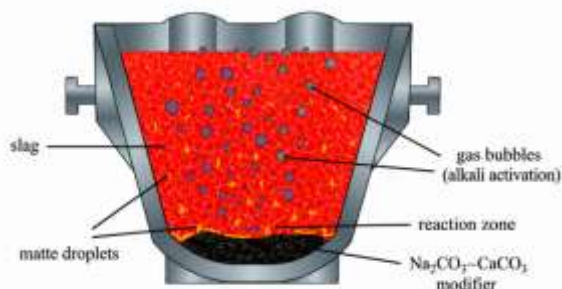


Fig. 4.6.1. Modification of slag by alkaline activation in a ladle.

The decrease in viscosity is associated with the structural reorganization of the silicate network. Na^+ ions act as network modifiers, breaking Si-O-Si bonds to form non-bridging oxygen centers. This leads to the depolymerization of the silicate structure [38].

CaO increases the basicity of the solution and further reduces the degree of silicate polymerization. As a result, ion mobility increases and mass transfer processes accelerate. An increase in thermal energy at 1250°C leads to a significant increase in diffusion coefficients for iron and silicon components [39]. This accelerates the decomposition of the fayalite phase and the formation of new phases (Fe_3O_4 , Fe_2O_3 , CaSiO_3). In iron-rich liquid slag systems, physicochemical parameters such as viscosity, electrical conductivity, density, and surface tension play a decisive role in the efficiency of copper recovery. Internal modification based on $\text{Na}_2\text{CO}_3+\text{CaCO}_3$ eliminates traditional slow cooling technology, providing a high degree of kinetic and technological advantages. As a result, the process is characterized by high selectivity, a short operating time, and maximum metal recovery efficiency.

4.7. Environmental and economic efficiency

1) Sustainability and environmental benefits

The internal modification approach based on $\text{Na}_2\text{CO}_3+\text{CaCO}_3$ is an effective technology with thermodynamic and kinetic foundations for the complete and sustainable utilization of resources during copper slag processing. This method provides the following environmental advantages:

- The volume of waste is significantly reduced as a result of waste reduction and the maximum extraction of metals such as Cu, Ni, Co, and Zn from the slag;

- Energy efficiency: the additional heating requirement is reduced by 60-70 % by utilizing the latent thermal energy of the slag itself;
- Reduced CO_2 emissions: reduced carbon footprint due to lower energy consumption and shorter processing times;
- Circular economy principle: copper slag is no longer a waste, but is treated as a secondary metal resource.

2) Sustainability and environmental benefits

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As final products the company may gain a number of products listed below:

Copper - 7-10 thousand tons/year;

Gold - 400 kg/year;

Silver - 4,000 kg/year, all these three metals (Au, Ag, Cu) are contained in the slag concentrate and added to the charge of smelting furnaces.

Molybdenum - 1500 kg/year, selective molybdenum concentrate is supplied to the Rare Metals Production Workshop.

Directly Reduced Iron (DRI) – 400,000 tons per year. It is supplied to the ferrous metallurgy enterprises of Uzbekistan or to the Central Repair Mechanical Plant for the production of casts and spare parts.

Concentrated REE-containing pulp. Lanthanides will be extracted based on new technology.

De-metallized conditioned slag is sold as a filler for the local cement industry in the amount of 500 thousand tons.

The results obtained confirmed that the complex modification system based on $\text{Na}_2\text{CO}_3-\text{CaCO}_3$ significantly affects the structural and physicochemical properties of the fayalite copper slag. The Na_2O and CaO components formed during the high-temperature decomposition of carbonates during the modification process destabilized the silicate structure of the slag, leading to intensive decomposition of the fayalite phase. As a result, the process not only reduced the total production cost but also increased the efficiency of metal extraction.

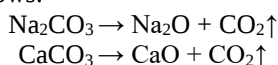
The synergistic effect of Na_2CO_3 and CaCO_3 served as the primary mechanism for the modification. The CaO component primarily accelerated the decomposition of the fayalite (Fe_2SiO_4) structure, causing Ca^{2+} ions to enter into exchange reactions with Fe^{2+} ions. As a result of this process, the formation of Fe_3O_4 , Fe_2O_3 , and CaSiO_3 phases was

observed. At the same time, the increase in slag basicity led to a decrease in the degree of polymerization in the silicate network.

Na₂O broke the Si–O–Si bonds in the silicate structure, intensifying the depolymerization of the system. This led to an increase in the concentration of non-bridging oxygen (NBO) and the activation of diffusion processes. Furthermore, Na₂O reduced particle surface energy, contributing to improved flotation kinetics and limiting the formation of a passive Ca₂SiO₄ layer [41].

As a result of synergistic modification, the degree of fayalite decomposition reached values exceeding 90%, whereas with the use of individual modifiers, this indicator is typically observed at around 70-75 %. At the same time, it was found that the slag viscosity decreased by 40-45 %. The decrease in viscosity increased the rate of mass transfer and interphase diffusion, facilitating the coagulation and separation of metal droplets [42]. As a result, the degree of copper recovery increased to 95-98 %.

Flotation results also confirmed the effectiveness of the modification. In the experiments, the half-flotation time ($t_{1/2}$) was approximately 15 s, indicating significantly faster kinetics compared to traditional NaOH/CaO systems. This is explained by the increased grinding of the modified slag and the weakening of mineral interfacial bonds. Thermodynamic analysis of the process showed spontaneous decomposition of carbonates at a temperature of 1250°C. Reactions are expressed as follows:



The thermodynamic basis of the process can be explained by the Gibbs free energy equation:

$$\Delta G = \Delta H - T\Delta S$$

The release of CO₂ increases the entropy of the system, causing the Gibbs free energy to shift to negative values, allowing the reaction to proceed spontaneously. From a physicochemical perspective, depolymerization of the silicate network, weakening of Fe–Si bonds, and an increase in diffusion coefficients were observed during the modification process. These changes accelerated mass transfer and phase separation, increasing the efficiency of subsequent enrichment stages. Technologically, this approach can be integrated into existing copper smelting systems with minimal structural changes. At the slag casting stage, it is sufficient to apply the modifiers in the temperature range of 1250–1280 °C and mix them using natural convection; the main part of the reaction is completed within 15–30 seconds. As optimal conditions, the use of Na₂CO₃ and CaCO₃ in an amount of 3–5 wt. % and a ratio of 1:1–1:1.5 was deemed appropriate.

Nevertheless, the technology has some limitations. In particular, the additional consumption of carbonate modifiers can increase operational costs. In addition, CO₂ emissions are an important factor from an environmental perspective, but the low energy demand of the process partially compensates for this disadvantage. Therefore, in future research, the study of alternative systems based on K₂CO₃ and MgCO₃, the determination of optimal modifier ratios using artificial

intelligence, and the assessment of the long-term accumulative effects of sodium and calcium are considered important directions.

CONCLUSION

It was established that the technology of internal modification based on Na₂CO₃+CaCO₃ is a highly efficient, energy-saving, and environmentally promising approach to the processing of fayalite copper slags. The research results confirmed that this system has a significant positive impact on the structural state, physicochemical properties, and subsequent enrichment processes of the slag.

As a result of the conducted research, the following main indicators were achieved:

- copper recovery rate increased to 95-98 %;
- energy consumption decreased by 60-70 % compared to traditional slow cooling technologies;
- due to a 40-45 % reduction in slag viscosity, the grinding process accelerated by eliminating the grinding stage;
- the flotation kinetics half-life was approximately 15 s;
- the selectivity and overall efficiency of the flotation process have significantly improved.

It has been established that as a result of the synergistic effect of Na₂CO₃ and CaCO₃, the depolymerization of the fayalite structure intensifies, mass transfer and diffusion processes are accelerated, and the separation of metal phases is facilitated. This increases the technological efficiency of the subsequent grinding, crushing, and flotation stages.

The proposed technology can be considered a promising industrial solution for the gradual replacement of traditional slow cooling methods. This approach serves to implement circular economy principles in copper metallurgy, ensure the integrated processing of industrial waste, and ensure the efficient use of resources.

Furthermore, by implementing the technology, it will be possible to additionally extract critical, noble, and rare metals from waste slags. At the same time, it will be possible to reduce the vast land areas occupied by waste dumps accumulated over the years, reduce the negative impact on the environment, and improve public health. This technology also plays an important role in the formation of an important local mineral raw material base for the ferrous metallurgy and steel industry in Uzbekistan.

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