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COMPLETE RECYCLING OF COPPER SMELTING SLAG DUMPS WITH ZINC OXIDE RECOVERY AND PRODUCTION OF CAST IRON AND CERAMIC PRODUCTS

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Abstract. The study proposes a zero-waste pyrometallurgical technology for the comprehensive recycling of copper smelting slag dumps to extract valuable components and obtain marketable products. Thermodynamic modelling in the temperature range of 600–1750°C confirmed the feasibility of producing three target products: zinc oxide, iron-carbon alloy, and silicate slag. Experiments demonstrated that using thermal coal instead of scarce coke as a reducing agent achieves a high degree of iron recovery, forming metallic nodules of 20–50 µm. Subsequent melting of reduced briquettes yields cast iron or ferrosilicon suitable for foundry applications. The resulting metal contains copper and sulfur, limiting its use in high-grade metallurgy but making it suitable for producing grinding cast iron balls with hardness up to 59 HRC, corresponding to class IV per GOST. The slag phase is processed into proppants and construction aggregates. A technological scheme of a microplant is proposed, ensuring integrated slag processing with minimal capital and operational costs. The development is supported by the Ural Scientific and Educational Center and aligns with the priorities of resource conservation, environmental safety, and import substitution in the metallurgical industry.

Key words: copper smelting slags, pyrometallurgical processing, zinc oxide capture, iron recovery, cast iron products, ceramic products, micro-factories, waste-free technologies

Introduction

Copper smelting production is accompanied by the formation of significant amounts of slag containing residual quantities of non-ferrous and ferrous metals, as well as oxide compounds with potential for secondary use. In particular, dump slags retain considerable amounts of iron, zinc, copper, silicon, aluminum, and other components. Despite the accumulated volume of these technogenic wastes, effective technologies for their complete processing, ensuring the extraction of all valuable components and the safe disposal of residual phases, are implemented only to a limited extent in practice.

Traditional approaches to the processing of copper smelting slags involve only the partial extraction of metals, while the residual slag is sent for further disposal or temporary storage, leading to resource losses and environmental pollution. Considering the increasing demands for environmental safety and resource conservation, the development of a zero-waste technology for processing copper smelting slags, aimed at the comprehensive utilization of all components, is a highly relevant task.

The aim of this study is to develop a rational pyrometallurgical technology for processing copper smelting slags with the extraction of zinc, the reduction of iron, and the subsequent use of the residual slag in the production of construction ceramic products. It is proposed to organize micro-scale production that does not require significant capital investments and ensures the production of marketable products.

In regions with a developed non-ferrous metallurgy industry, there is a large amount of copper smelting slag accumulated in dumps, the total mass of which can hardly be accurately determined. According to estimates, copper smelting enterprises in Russia have accumulated over 110 million tons of slag. For instance, around the city of Karabash in the Chelyabinsk region alone, approximately 30 million tons of industrial waste are stored, containing around 40%, or about 10 million tons, of iron. Storing such waste not only requires vast areas but also has a negative impact on the environment. Furthermore, significant funds are spent on maintaining the dumps and paying environmental taxes, which underscores the relevance of their rational utilization [1]. Currently, there are no fully developed methods for recycling copper smelting slags. However, several underdeveloped approaches are actively studied and applied in some industrial technologies [2].

Copper smelting slag mainly consists of oxides of iron, silicon, calcium, and aluminum. In smaller amounts, it contains copper, zinc, selenium, arsenic, and several other elements. Among these, iron has the highest value due to its quantity. Zinc is the second most valuable component in the slag. While there is not enough raw materials to meet the growing demand for zinc in Russian industry, copper smelting slag contains about 2.5% zinc [3].

The technology for processing any complex material should aim at extracting all valuable components to conserve resources and increase production efficiency with minimal costs for concentrate preparation. Using thermal coal as the reducing agent instead of scarce coke in the reduction of iron is more efficient. Therefore, a potential solution for recycling copper smelting slag is the establishment of small-scale production (a micro-plant) for extracting zinc and iron from the slag while simultaneously utilizing the remaining components to produce valuable commercial products [4–5].

The objective of this study is the development of a rational technological scheme for processing copper smelting slag obtaining commercially viable products.

Materials and methods of research

Copper smelting slags collected from the dumps of metallurgical enterprises in the Ural region were used as the initial raw material. The chemical composition of the slags was determined using X-ray fluorescence analysis (XRF) and confirmed by inductively coupled plasma mass spectrometry (ICP-MS). The main components of the investigated slags were oxides of Fe, Si, Al, and Mg, as well as residual amounts of Cu and Zn.

Thermodynamic modeling of the reduction smelting processes and zinc behavior during heating was carried out using the HSC Chemistry 10.0 software (Outotec, Finland). The modeling covered a temperature range from 600 to 1750 °C and included various options for the gas atmosphere (reducing and oxidizing) as well as types of reductants (thermal coal, coke, and charcoal).

Experimental smelting was carried out in laboratory crucible furnaces of both open and closed types. Thermal coal with a high volatile matter content was used as the reductant. The temperature regime was maintained in the range of 1400–1550 °C. After smelting, the samples were subjected to phase analysis using X-ray diffraction (XRD), as well as metallographic analysis to evaluate the structure of the obtained alloys.

Zinc released during smelting was captured in the form of oxide on cold condensation surfaces. The resulting residual slag was used to produce pressed and fired ceramic samples, which were tested for strength and water resistance in accordance with GOST 530–2012.

Results and its discussion

1. Results of Thermodynamic Modeling.

To develop a processing scheme for copper smelting slag at the initial research stage, it was necessary to determine the thermodynamic conditions for iron and zinc reduction in order to ensure the rational utilization of the slags. For this purpose, thermodynamic modeling was carried out using the Terra software package. As a result of the thermodynamic modeling, it was established that when the amount of carbon corresponds to the stoichiometry required for iron reduction, within the temperature range of 650–1250 °C, all the iron in the modeled system is present in the metallic phase, while all sulfur is bound in compounds such as CaS and Cu_2S. Concentrations of primary slag phases such as magnetite, fayalite, and pyroxene are absent in this temperature range under a reducing atmosphere, as they decompose at lower temperatures. With an increased carbon concentration exceeding the stoichiometric requirement, and at a temperature rise up to 1750 °C, metallic silicon begins to form in the system, accompanied by a decrease in the concentration of silicon oxides (Figure 1).

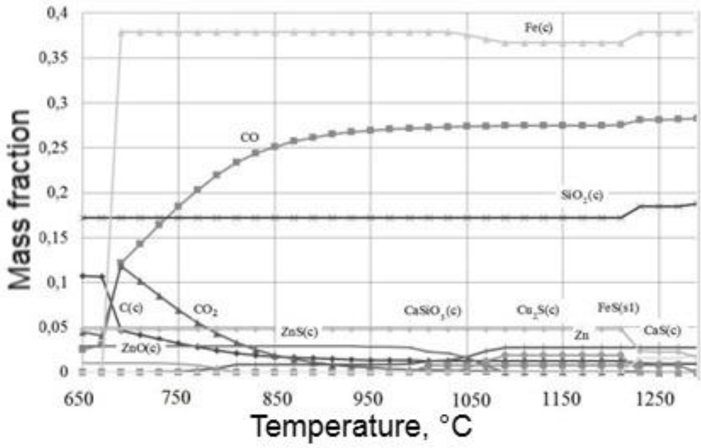

Figure 1. Composition of the system depending on temperature under stoichiometric carbon conditions for the reduction of iron and zinc.

2. Results of Zinc Oxide Extraction.

Zinc extraction was carried out in a laboratory arc furnace with a graphite electrode, which also served as a collector for zinc. Due to the complexity of temperature measurement, it was only measured before tapping and averaged around 1600 °C. The smelting process lasted no more than 60 minutes, including furnace startup. As a result, zinc oxide was deposited on the electrode in the form of a loose white powder. Upon contact with skin, it smears into a gel-like substance. Chemically, the powder mainly consists of zinc oxide, but also contains iron and silicon oxides.

Results of Reduction Roasting and Pyrometallurgical Separation of the Reduction Products.

Thermal coal was used as the reducing agent for iron from slag components. Reduction was performed either using a mixture of slag and reducer powders (<1 mm particle size) or briquettes pressed from this mixture. The reduction process was conducted in a Tamman furnace. The reduction temperature was 30–50 °C below the slag melting point. After holding the mixture at 980 °C for 1 hour, iron nuggets measuring 5–20 µm were observed, containing 1.5–2.0% copper but free of sulfur. As a result of the reduction, magnetite in the slag disappeared.

The rate of iron reduction in briquetted samples was 3–4 times higher than in the mechanical mixture. For example, after 1 hour of holding at 1020 °C, the iron content in the oxide phase dropped to 10%, and the nugget size increased to 20–50 µm. However, further increasing the holding time did not lead to further reduction in iron content in the oxide phase.

A key distinction of the briquetted samples emerged during melting in a corundum crucible for separating metal from slag. When heated to 1500 °C, intensive gas release indicated continued active reduction. After melting, the iron content in the slag dropped below 1%, and the metal began to contain silicon (0.7%). The potential for additional iron reduction and partial silicon reduction during melting is attributed to residual carbon particles in the reduced briquettes.

When melting the pre-reduced briquettes in a graphite crucible, cast iron instead of pure iron can be obtained. Further increasing the temperature and holding time allows for the production of ferrosilicon containing 10–13% silicon. As the metal composition transitions from steel to cast iron and then to ferrosilicon, the sulfur content significantly decreases. Initially, the metal contains about 2% sulfur immediately after melting, while cast iron contains about 1%, and ferrosilicon with 12% silicon contains only ~0.1% sulfur. Sulfur can be removed during ladle treatment of the molten iron. Copper, however, cannot be economically removed, so the resulting metal can be used for producing foundry-grade cast iron, where copper content is not regulated, or copper-alloyed steels.

4. Production of Cast Iron and Steel Products.

For establishing a plant to process copper smelting slag, the production of finished metal goods should be organized. However, the extracted metal contains copper. Therefore, the authors consider a rational direction to be the production of cast iron grinding balls, as wear-resistant white cast irons used for grinding balls typically contain around 1.5 wt% copper.

To produce white wear-resistant cast iron for grinding balls from copper slag, preliminary thermodynamic modeling was conducted to predict alloy composition (copper and silicon) by adjusting the carbon-iron phase diagram. The Thermo-Calc software package was used for modeling. The results showed that copper additions alter the solubility of carbon in austenite. Adding 3.5% silicon, while maintaining 1 wt% copper in the melt, increases the ferrite region due to silicon's solubility in ferrite and reduces carbon solubility in austenite, shifting the eutectic point of ledeburite from 4.3 to 3.2 wt% carbon.

Based on the thermodynamic modeling results, the target composition for producing eutectic cast iron was determined as 3.2 wt% carbon, 3.5 wt% silicon, and 1 wt% copper. Using this predicted composition, laboratory experiments were conducted to produce grinding balls. The chosen production method was permanent mold casting. However, this method failed to produce white cast iron due to insufficient heat extraction.

In industrial settings, white cast iron is typically produced with the addition of "whitening" elements such as chromium and manganese. However, these alloying elements significantly increase the cost of grinding balls. Additionally, sulfur in the metal extracted from copper slag requires further processing for removal. Therefore, additional experiments were conducted to study the effect of sulfur on white cast iron formation. These experiments revealed that increasing sulfur content to 1 wt% enhances the whitening of grey cast iron from 2% to 95%.

Based on these findings, grinding balls were produced with a hardness of 59 HRC (Rockwell), which corresponds to Class IV hardness per GOST 7524 «Steel Grinding Balls for Ball Mills» and ST RK 2310-2013 «Cast Iron Grinding Balls». Drop tests from a height of 4 meters onto a cast iron plate revealed no cracks or dents.

Thus, a high sulfur content (1%) did not negatively affect the mechanical properties of the cast iron. The presence of 1% copper, dissolved in the ferrite phase, improves the ductility of the metal and the overall properties of the products. Based on these studies, a technology for industrial production of cast iron for grinding media was developed, and a set of standard production equipment was selected (manufacturer: Shanghai Minggong Heavy Equipment Co., Ltd).

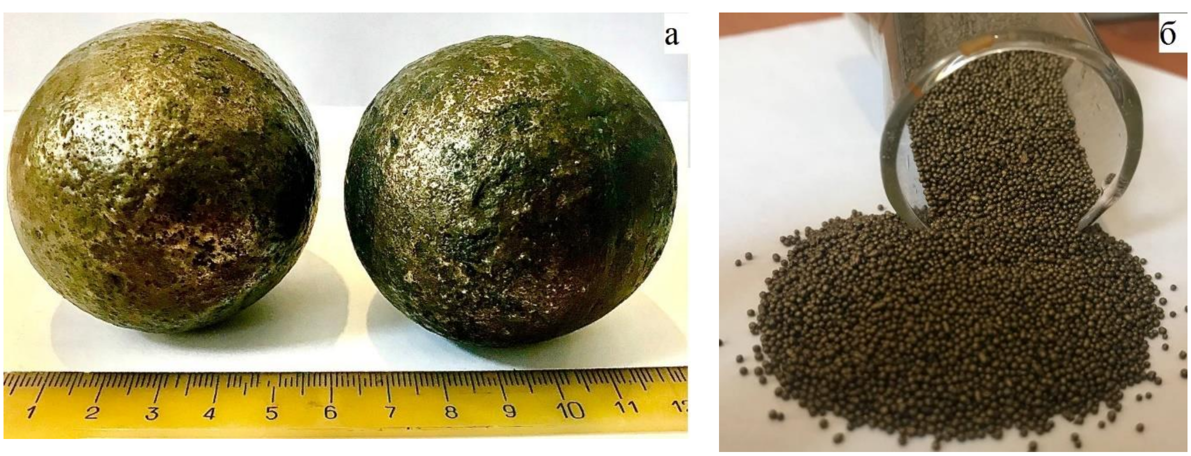

Figure 2. Experimental samples of grinding balls (a) and proppants (b).

5. Utilization of Smelting Slags.

A simple and effective technology has been developed for the production of proppants based on smelting slags. The batch for proppants consists of a mixture containing approximately 50% slag, with the addition of quartzite and aluminum oxide-containing waste. The technological process includes melting the slag with additives, centrifugal spraying to form granules of a specified size range, thermal treatment, and separation.

Slags with a wide range of chemical compositions can be used as raw material; however, slags with low iron oxide content and a high silica content are preferred.

Proppant samples have been produced that meet all the requirements of GOST R 54571-2011 «Magnesia-Quartz Proppants.»

The crush resistance of the proppants complies with American standards of 5,000, 7,500, 10,000, and 12,500 psi.

Acid solubility in hydrochloric acid solution is less than 1%, and in a mixture of hydrochloric and hydrofluoric acids it is less than 10%, which meets regulatory requirements.

Other steelmaking slags, with relatively low iron oxide content, can be granulated and used as sand in the construction industry, particularly as aggregates for concrete.

Based on the obtained results, a general technological scheme for the processing of copper smelting slags and sludges is proposed. The scheme includes the extraction of iron—the most valuable component—for the production of high-demand metallic products, along with the recovery of zinc and deep processing of slags to produce proppants for the oil and gas industry and sand for construction.

The initial slag is dried, mixed with pre-ground reducing agent and binder. The resulting mixture is then briquetted or pelletized. The briquettes are dried and fed into a rotary kiln, where they are heated in a reducing atmosphere at temperatures ensuring maximum iron reduction. Zinc oxides are captured from the exhaust gases of the rotary kiln.

The hot reduced products are directed into an arc furnace. In the arc furnace, cast iron is produced from the reduced materials for casting grinding media. The slag formed during melting in the arc furnace is chemically adjusted and then atomized to produce granules, which are used as proppants.

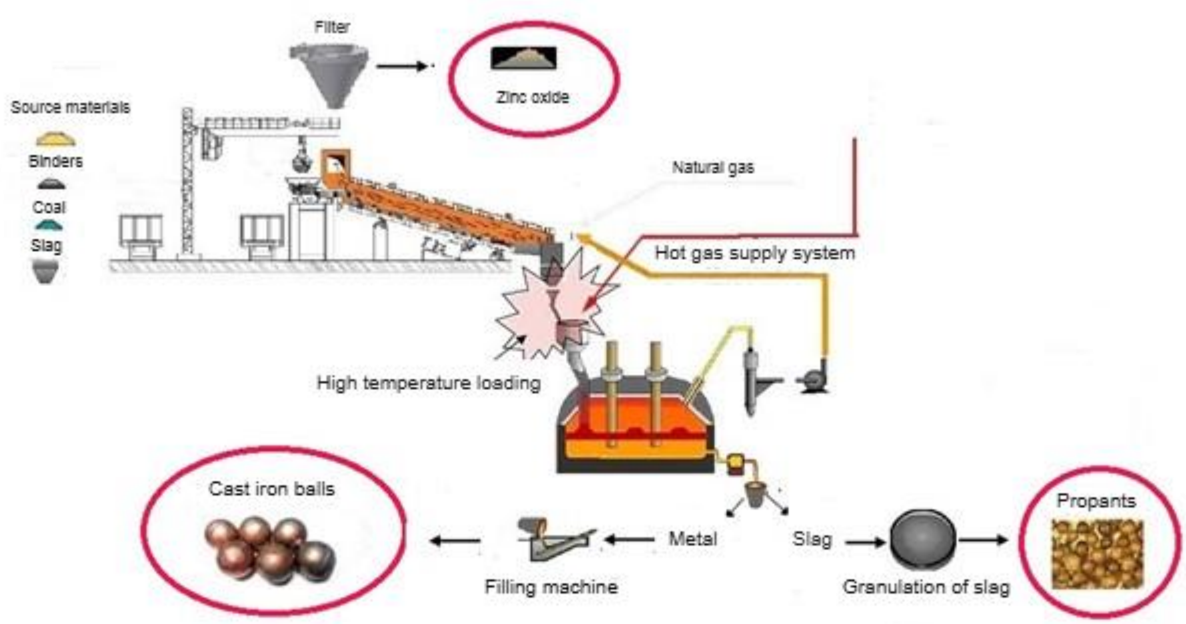

Figure 3. Technological scheme for the processing of copper smelting slags.

Conclusion

Thermodynamic modeling conducted in this study demonstrated the feasibility of obtaining three products from copper smelting slag via pyrometallurgical processing in the temperature range of 600–1750 °C:

- zinc,
- iron-carbon-silicon alloys, and
- slag composed mainly of silicon, aluminum, and magnesium oxides.

Experimental work confirmed the possibility of producing cast iron, steel, and iron-silicon alloys, as well as slag with a low iron oxide content and zinc oxide, which forms through oxidation of zinc by oxygen in an oxidative atmosphere during melting in open furnaces.

Based on the results of pyrometallurgical separation of the reduction roasting products, a method is proposed for obtaining grinding media from the metal and proppants from the slag.

A zero-waste, resource-efficient pyrometallurgical processing scheme for copper smelting slag has been developed based on theoretical analysis and experimental results.

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МЫРЫШ ОКСИДІН ЖӘНЕ ШОЙЫН МЕН КЕРАМИКАЛЫҚ БҰЙЫМДАРДЫ АЛА ОТЫРЫП МЫС БАЛҚЫТУ ӨНДІРІСІНІҢ ҮЙІНДІ ҚОЖДАРЫН ТОЛЫҚ ҚАЙТА ӨҢДЕУ

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Аңдатпа. Бұл жұмыста мыс балқыту өндірісінің үйінді шлактарын кешенді қайта өңдеудің қалдықсыз пирометаллургиялық технологиясы ұсынылады, нәтижесінде құнды компоненттер алынып, нарықтық өнімдер өндіріледі. 600–1750°C температура диапазонында жүргізілген термодинамикалық модельдеу мынадай үш мақсатты өнімді алудың мүмкіндігін растады: мырыш оксиді, темір-көміртекті қорытпа және силикатты шлак. Эксперименттерде дефицитті кокс орнына энергетикалық көмірді қалпына келтіруші ретінде қолдану темірді тиімді қалпына келтіруге мүмкіндік беріп, 20–50 мкм мөлшерінде металл түйіршіктерін түзетіні көрсетілді. Қалпына келтірілген брикеттерді балқыту нәтижесінде құйма өндіруге жарамды шойын немесе ферросилиций алынды. Алынған металл құрамында мыс пен күкірт бар, бұл оның жоғары сапалы металлургияда қолданылуын шектейді, бірақ диірмендер үшін 59 HRC қаттылығы бар ұнтақтайтын шойын шарларын шығаруға жарамды. Шлак фазасы пропанттар мен құрылыс толтырғыштарына өңделеді. Минималды капитальдық және операциялық шығындармен шлакты кешенді қайта өңдеуді қамтамасыз ететін микрозаут технологиялық схемасы ұсынылды. Зерттеу Урал ғылыми-білім беру орталығының қолдауымен орындалып, металлургиядағы ресурсты үнемдеу, экологиялық қауіпсіздік және импортты алмастыру басымдықтарына сәйкес келеді.

Түйін сөздер: мыс қождары, пирометаллургиялық өңдеу, мырыш оксидін ұстау, темірді тотықсыздандыру, шойын бұйымдары, керамикалық бұйымдар, микрозауыттар, қалдықсыз технологиялар

ПОЛНАЯ ПЕРЕРАБОТКА ОТВАЛЬНЫХ ШЛАКОВ МЕДЕПЛАВИЛЬНОГО ПРОИЗВОДСТВА С УЛАВЛИВАНИЕМ ОКСИДОВ ЦИНКА, ПОЛУЧЕНИЕМ ЧУГУННЫХ И КЕРАМИЧЕСКИХ ИЗДЕЛИЙ

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Аннотация. В работе предложена безотходная пирометаллургическая технология переработки отвальных шлаков медеплавильного производства с комплексным извлечением ценных компонентов и получением востребованных продуктов. Проведено термодинамическое моделирование в диапазоне температур 600–1750 °C, подтвердившее возможность выделения трёх целевых продуктов: оксида цинка, железоуглеродистого сплава и силикатного шлака. Экспериментально показано, что при восстановительном обжиге с использованием энергетического угля вместо дефицитного кокса достигается высокая степень восстановления железа с образованием корольков размером 20–50 мкм. При последующем плавлении восстановленных брикетов возможно получение чугуна или ферросилиция, пригодных для производства литейной продукции. Полученный металл содержит медь и серу, что ограничивает его применение в качественной металлургии, однако позволяет использовать для изготовления мелющих чугунных шаров с твёрдостью до 59 HRC, соответствующей IV классу ГОСТ. Шлаковая фаза перерабатывается в пропанты и строительные заполнители. Предложена технологическая схема микрозавода, обеспечивающего комплексную переработку шлаков с минимальными капитальными и операционными затратами. Разработка поддержана Уральским научно-образовательным центром и соответствует приоритетам ресурсосбережения, экологической безопасности и импортозамещения в металлургической промышленности.

Ключевые слова: медеплавильные шлаки, пирометаллургическая переработка, улавливание оксида цинка, восстановление железа, чугунные изделия, керамические изделия, микрозаводы, безотходные технологии