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Manufacture of construction materials based on slag binders. Production of forsterite-spindle non-fired

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Abstract. Utilization of man-made slags of metallurgical production as binders for the development of building materials, as well as the study of the composition and properties of slag binders for the development of technology for their processing and production of refractory bricks based on them.

Keywords: *utilization of industrial waste, slag binders, refractory bricks*.

1. Introduction

Every year, more than 120 billion tons of minerals are extracted and processed worldwide, averaging 20 tons per person on average. In some regions, this figure exceeds 300 tons per person. Meanwhile, the components used constitute up to 40%, while the remaining extracted resources, processed, and transformed into waste material, account for 60% [1].

Slag is a byproduct of high-temperature processes in the smelting of metals, the combustion of solid fuels, as well as certain chemical manufacturing processes [5].

Metallurgical slags are formed through the interaction of fuel, barren rock contained in the ore, and the smelter, and they are classified into slags of ferrous and non-ferrous metallurgy. When evaluating slags as raw materials for construction materials, a crucial characteristic of their chemical composition is the percentage ratio of basic and acidic oxides – the basicity index (Mo). Slags are classified as basic when Mo>1 and as acidic when Mo<1 [6]. By analyzing phase diagrams of the respective oxide systems, the possibility of the existence of up to 40 double and triple compounds in slags has been established. Among these, silicates, aluminosilicates, aluminates, and ferrites hold a prominent position.

With an increase in the content of the glassy phase in slags, their hydraulic activity, and consequently, the strength of solutions and concretes, increases [7]. Among all types of metallurgical slags, blast furnace slags are the most widely used in the production of construction materials. This is due to their leading position in the overall balance of metallurgical slags, as well as the similarity of their composition to that of cement, their ability to acquire hydraulic properties when rapidly cooled, and other factors.

Slag binding materials are products derived from the processing of residues from metallurgical production – slags, which were formerly considered waste and were not utilized in construction. They possess several advantages, such as high strength, resistance to various aggressive factors, improvement of thermal and sound insulation, as well as environmental safety. Additionally, the use of slag-based binding materials in construction allows for cost reduction in production and mitigates the environmental impact.

The use of slag in the secondary processing of metals for steel deoxidation reduces the consumption of scarce ferrosilicon. It is even permissible to use metallurgical slags as abrasive material for cleaning ship bottoms. Converter slags can be utilized in hydraulic engineering for dam embankment instead of soil. Ferrochrome slag is processed and enriched, and magnetic separation is applied to remove metallic inclusions from blast furnace slag.

1.1. Subsection

Slags contain a significant amount of modifier oxides, so they are added to the charge instead of dolomite. For the synthesis of green and brown glass, a mixture is prepared using quartz sand, slag, soda, sulfate, and, if necessary, small amounts of calcium and magnesium oxides, varying the «slag-dolomite» ratio. The chemical composition remains unchanged (for green glass grade ZT, for brown glass grade KT) [12].

Ferrochrome slag contains chromium oxide Cr_2O_3, and blast furnace slag contains iron oxide Fe_2O_3 and other impurities, eliminating the need for additional coloring agents for green and brown glass. Thus, inexpensive slag not only introduces necessary oxides into the glass but also serves as a colorant, which is economically advantageous [13].

Research into the physico-chemical properties of industrial by-products from the ferroalloy plant has revealed the presence of significant amounts of valuable components such as chromium, iron, silicon, and others. Therefore, integrating them into the operations of the existing plant or other sectors of the economy remains a relevant task.

The company's semi-finished products are currently used to produce glass by melting in a silica furnace at a temperature of 1350-1400°C for 3.5 hours. The resulting glass samples are dark green and brown.

Enhancing the competitiveness of metal products can be achieved by reducing the consumption of raw materials in their production. Therefore, the processing and utilization of slags and waste from metallurgical production is a relevant and necessary element of zero-waste technology, contributing to resource conservation and reducing pollution in water and air basins. The comprehensive and in-depth development of zero-waste production is a long-term and meticulous task that will engage generations of scientists, engineers, technicians, ecologists, economists, workers of various profiles, and many other specialists.

The production of ferroalloys is accompanied by the generation of significant amounts of dump slag. The slag-to-metal ratio (the ratio of slag mass to metal mass) depends on the type of alloy and is as follows:

- Ferrosilicon smelting – 0.05-0.1 (slag-free process);
- Silicomanganese – 1.1-1.3;
- High-carbon ferromanganese (flux process) – 1.2-1.6;
- Metallic manganese – 3-3.6;
- High-carbon and extra-high-carbon ferrochrome – 0.9-1.1;
- Refined ferrochrome – 2.5-3.2;
- Silicocalcium – 0.2-0.4;
- Ferromolybdenum – 1-1.1;
- Ferrotungsten – 0.5-0.7. [15].

Ferroalloy slags contain droplets of the finished alloy and unreduced oxides of the major alloying elements. Additionally, they possess strength, abrasiveness, and refractory properties. The total output of ferroalloy slags is more than 1.5 million tons per year, with approximately 45% of these slags currently being processed. The methods for processing ferroalloy slags are diverse, including metallurgical refinement, air and magnetic separation, mechanical crushing, water granulation, and others. The choice of method depends on the specific characteristics of the slag. Slags from high-carbon ferrochrome are characterized by high strength and are used instead of crushed stone in foundation construction. In contrast, slags from refined ferrochrome are self-disintegrating and contain up to 5% alloy droplets and 15% chromium in oxide form. Alloy droplets are separated from this slag through air or magnetic separation. To reduce the content of chromium oxides in the slag, it needs to be reduced during metallurgical processing. The final slag is widely used as lime fertilizer in agriculture, for manufacturing liquid self-hardening mixtures in foundry production, and as part of mineral powder for asphalt concrete in construction.

The solution to the stated problems was carried out in accordance with the generally accepted methodology for conducting scientific research, including the compilation and analysis of previous studies, analytical and laboratory research, the development of technology, and methodological support.

- The scientific novelty of the work lies in:
- The use of slag-based binders instead of traditional components in refractory materials
- The utilization of industrial waste for creating environmentally friendly and sustainable materials;
- The replacement of traditional binding materials with more environmentally friendly alternatives, as traditional materials are a major source of greenhouse gas emissions.

Successful fulfillment of ambitious tasks in the field of the most important industries: ferrous and non-ferrous metallurgy, energy, chemical industry, building materials industry, etc. – is largely determined by meeting the industry's need for high-quality refractory materials [16].

2. Materials and methods

The intensification of technological processes, the elevation of temperature regimes, and the use of oxygen-enriched air demand that workers in the refractory industry create and implement new types of refractories. Further refinement and expansion of refractory production, supported by a rich raw material base, are necessary, along with a significant expansion of their application in various industrial sectors. Representative examples of this group are forsterite refractories.

The issue of forsterite refractories in metallurgical plants has been extensively studied. Some plants consistently produce forsterite refractories, and there are plans to expand their production by 4-5 times with the commissioning of new workshops. However, the application areas of forsterite refractories remain relatively narrow. Currently, these refractories have firmly established themselves primarily as linings for regenerators in Martin furnaces [17].

The use of forsterite refractories in other industries is primarily of a research nature, with their high resistance being the main focus. Therefore, it is time to consider a broader application of forsterite refractories in various industrial sectors. It seems expedient and timely to summarize some results of the service of refractories in industry, along with recent research data, and outline ways for further improvement in line with industrial requirements.

Refractory products made from natural magnesial-silicate raw materials are called forsterite refractories, named after the mineral formed during the firing of magnesial-silicate rocks with additions of caustic or sintered magnesite. The group of magnesial-silicate, or forsterite, raw materials includes the following rocks: olivinites, dunites, serpentinites, talc, and talc-magnesites. Depending on the raw material used, different types of forsterite refractories are distinguished, such as olivinite, dunite, serpentinite, and others. The considerable diversity of magnesial-silicate rocks, their mutual transitions, and significant fluctuations in the content of key rock-forming minerals—olivine and serpentine—do not allow for a strict scientific classification of these rocks. Therefore, in practice, a certain conditional division of these rocks based on the content of the mineral olivine $(Mg,Fe)_2SiO_4$ is used, which represents an isomorphic mixture of forsterite Mg_2SiO_4 and fayalite Fe_2SiO_4.

Olivinites. The predominant mineral in these rocks is olivine – $(Mg, Fe)SiO_4$, which represents an iron-rich variety of forsterite, or more precisely, a solid solution of iron oxide orthosilicate – fayalite (Fe_2SiO_4) in forsterite Mg_2SiO_4. In addition to olivine, the rocks contain 2-15% impurities, with enstatite ($MgSiO_4$), magnetite (Fe_3O_4), talc, serpentinite, and occasionally pyroxenes and chromite as the most commonly occurring impurities. The chemical composition of olivine usually varies within the following ranges: 50-45% MgO, 8-12% FeO, occasionally up to 20%, with traces of nickel, cobalt, manganese. It has a rhombic crystal system, a yellowish-green color, often colorless, refractive indices Ng = 1.68; Nm = 1.66. It has a hardness of 6.5-7, true density of (3.3-3.5)*103 kg/m^3 (increasing with higher FeO content), and refractoriness ranging from 1750 to 1830°C.

Serpentinites. The prevalence of serpentine in the rock leads to its transition to another type of forsterite raw material – serpentinites, in which the olivine content does not exceed 20%. A distinctive feature of these rocks is high loss on ignition (12-14%) due to the constitutional water of serpentine; refractoriness is 1500-1570°C, true density of the rock is 2.649 g/cm^3, apparent density 2.46-2.64, water absorption 0.6-2.8%, and porosity 1.6-6.8%.

Talc and Talc Stone. Talc belongs to the group of magnesium hydrosilicates and is one of the widely used types of ceramic raw materials. The formula for talc is $MgO*4SiO_2*H2O$, corresponding to the theoretical chemical composition of 31.7% MgO, 63.5% SiO_2, and 4.8% H_2O. It has a monoclinic crystal system, a pale-green color, a hardness of around 1, true density of 2.7-2.8 g/cm^3, refractive indices Ng = 1.575-1.590, Np = 1.538-1.545. The melting temperature of pure talc is 1500-1550°C. A dense variety of talc is called steatite, and such varieties are mainly used in ceramics. In nature, talc is often formed as a product of hydrothermal alteration of magnesium-rich ultrabasic rocks according to the approximate scheme:

$4\ (MgFe)2SiO_4 + H_2O + 3CO_2 >$

$Mg_3(Si_4O_{10})(OH)_2 + MgCO_3 + Fe_2O_3$.

Talc rock may also contain magnesite, altering their properties, particularly enhancing refractoriness. Such rocks are called talc-magnesites. When heated to 900 °C, talc undergoes dehydration and subsequently decomposes into magnesium metasilicate and silica. Similarly, to the aforementioned talc and talc-magnesites, they can be used to produce forsterite refractories with the addition of calcined magnesite, in quantities determined by the degree of impurity in the rock [14].

Dunites. The primary minerals in these magnesian-silicate volcanic rocks are olivine and serpentinite. Their content in dunites is not constant, which leads to significant variations in the main properties of the rocks depending on the degree of serpentinization. A higher content of olivine in dunites gradually transitions them to olivinites, while deep serpentinization makes their properties similar to serpentinites. Olivine decomposition processes in nature occur relatively easily, so in the same deposit, a substantial difference in the properties of these rocks can be observed at the surface and at greater depths. As serpentinization progresses, the loss on ignition increases, true density decreases, and all other properties change. Such phenomena are especially characteristic of dunite deposits. Significant fluctuations in olivine content in dunites necessitated the use of the aforementioned conditional classification of these rocks in practice. Refractories contain magnesium oxide (MgO) in their composition, but it is part of the mineral forsterite (2MgO*SiO2), which serves as the refractory basis for them Raw materials for the production of forsterite refractories include olivines, serpentines, dunites, talc, and other magnesian-silicate rocks. Besides forsterite, these rocks (minerals) contain various impurities (CaO, Al2O3, Cr2O3, FeO, Fe2O3, etc.). Therefore, when preparing the charge mix, periclase powder is introduced in necessary amounts. In general, the higher the MgO content in the charge mix, the higher the quality of the products. Depending on the quality of the raw material, the amount of periclase introduced into the charge mix varies from 10-15 to 40-50%. The refractory manufacturing process involves firing and crushing the mineral raw material, mixing it with the required amount of MgO to bind all SiO2 into forsterite.

During the firing of the raw material, the decomposition of olivine, serpentine, and talc occurs, along with the iron oxidation:

$3MgO \cdot 2SiO_2 \rightarrow 2MgO \cdot SiO_2 + MgO \cdot SiO_2$,
$3MgO \cdot 4SiO_2 \rightarrow 2MgO \cdot SiO_2 + 2MgO \cdot SiO_2 + SiO_2$,
$FeO \rightarrow Fe_2O_3$.

As a result of firing, forsterite 2MgO·SiO22MgO·SiO2 is obtained with a melting temperature of 1890°C, enstatite MgO·SiO2MgO·SiO2 with a melting temperature of 1550°C, silica, and iron oxide. The goal of the technology for producing forsterite refractories is to convert these compounds into forsterite and magnesioferrite through interaction with magnesium oxide, which is introduced into the reaction mixture. With an excess of MgO, the following reactions take place:

$MgO \cdot SiO_2 + MgO \rightarrow 2MgO \cdot SiO_2$,
$SiO_2 + \rightarrow 2MgO \rightarrow 2MgO \cdot SiO_2$,
$Fe_2O_3 + MgO \rightarrow MgO \cdot Fe_2O_3$.

The mass is moistened with a water solution of sodium water glass to a moisture content of 3.5-4.5%. The products are pressed under pressure up to 100 MPa.

Depending on the type of magnesite used, non-fired or fired products are manufactured. If caustic magnesite is used, the molding mass is prepared with a water solution of magnesium chloride. The resulting magnesia cement provides sufficient strength to the raw material, and after storage for 10 days, it can be used as a non-fired refractory. If magnesite in the form of periclase is used, the raw material is subjected to sintering at a temperature of 1600-1700°C. Such products have sufficiently high refractoriness – 1850-1900°C, withstand 1-2 water quenching cycles, and resist the action of iron-rich slags.

Forsterite refractories are used for laying the upper rows of nozzles, walls of regenerators, shakhts, heating wells, and other thermal units. A variety of forsterite refractories are periclase-forsterite and forsterite-chromite products, which, in addition to the main component (forsterite), contain periclase and chromite. The introduction of chromite ore into the charge in the amount of 15-20% contributes to an increase in thermal resistance up to 5 water quenching cycles.

In addition, forsterite-based ceramics are produced. Unlike forsterite refractories, the latter has a denser structure and is mainly used as a high-frequency dielectric. Like steatite ceramics, forsterite ceramics have low dielectric losses and high specific electrical resistance but are characterized by a higher thermal expansion. The advantage of forsterite ceramics is that it is not subject to aging due to the absence of polymorphic transformations. It is used for bonding with metals. Forsterite ceramics are made from talc and magnesium oxide or magnesite by the method of hot pressure casting.

3. Results and discussion

Slags contain a large amount of modifier oxides, so they were added to the charge instead of dolomite. The charge for synthesized green and brown glasses was prepared using quartz sand, slag, soda, sulfate, and, if necessary, small amounts of calcium and magnesium oxides, varying the «slag-dolomite» ratio. The chemical composition remained unchanged (for green glass grade ZT, for brown glass grade KT) [4]. In accordance with GOST 8616-1904-AO-04-2014 «Unfired forsterite-spinel refractory products for lining ferroalloy ladles», an experiment was conducted to obtain refractory bricks from baghouse dust of the smelting shop and tailings of the rutile-zirconium product – clay from the «Shokash» deposit. The goal of the work is to determine the optimal ratio of clay and baghouse dust content in refractory bricks with the required mechanical and technological properties.

For the study, 13 types of mixtures were prepared with different clay and baghouse dust content. The components were mixed using a foundry mixer with the addition of water.

Three briquettes were made from each mixture, pressed on an IP-50 press. In the laboratory conditions, a batch of experimental products with dimensions of 100x100x30 mm was manufactured using ground slag of high-carbon ferrochrome and baghouse dust with different concentrations. The pressing force was 350 kN.

Changes in manufacturing parameters, such as baghouse dust concentration (50 and 40%), pressing force (300 and 350 kN), as well as sample preparation before autoclave treatment (without aging, aging in natural conditions for three days, drying at 300°C), yielded positive results, and all tested samples showed good strength after autoclave aging.Further experiments were directed towards testing refractory products made from baghouse dust and ground slag of high-carbon ferrochrome under industrial conditions with drying.The investigated by-products of high-carbon ferrochrome production can be used as raw materials for refractories. Based on the chemical and phase composition of the materials studied, it is possible to produce refractories.

4. Conclusions

The investigated by-products of high-carbon ferrochrome production can be used as raw materials for manufacturing refractories. Based on the chemical and phase composition of the materials studied, it is possible to produce refractories of forsterite-spinel composition. The technological properties of the investigated materials allow for the production of dense and strong refractories. A technology for the production of refractory bricks from baghouse dust of gas cleaning and slag of high-carbon ferrochrome has been developed. This technology has the following advantages:

- Simplicity of the manufacturing process;
- Utilization of baghouse dust from gas cleaning;
- Elimination of the use of expensive liquid glass;
- Possibility of brick production without high-temperature drying;
- Partial elimination of grinding components for brick production;
- Possibility of partial replacement of chamotte brick.

Industrial tests of experimental bricks were conducted on ladles and the tapping box of a melting furnace. The tests demonstrated the real possibility of completely replacing refractory bricks in this production and partially replacing chamotte bricks used for lining the tapping box of melting furnaces.

References

[1] Valiev, N.G., Propp, V.D. & Vandyshev, A.M. (2020). The Department of Mining at UGSGU - 100 Years. *Proceedings of Higher Education Institutions. Mining Journal, (8), 130-143.* https://doi.org/10.21440/0536-1028-2020-8-130-143

[2] Bigeev, V.A., Chernyaev, A.A. & Panteleev, A.V. (2014). Study of a Two-Stage Method for Processing Dust and Slag Using Mathematical Models. *Bulletin of Nosov Magnitogorsk State Technical University, (3), 48-52*

[3] Ben-Awuah, E., Richter, O., Elkington, T. & Pourrahimian, Y. (2020). Strategic Mining Options Optimization: Open Pit Mining, Underground Mining, or Both. *International Journal of Mining Science and Technology, 26(6), 1065–1071.* http://dx.doi.org/10.1016/j.ijmst.2016.09.015

[4] Perepelitsyn, V.A., Kormina, I.V., Karpets, L.A. & Zubov, A.S. (2004). Thermal Stability of Fused Corundum. *New Refractories, (1), 39-42*

[5] Nikifirov, B.A., Bigeev, V.A., Sibagatullin, S.K., Panishev, N.V., Usherov, A.I. & Panteleev, A.V. (2005). Metalization of Blast Furnace Slags with Zinc Removal. *Bulletin of Nosov Magnitogorsk State Technical University, (2), 23-25*

[6] Lapkina, Yu.V., Nikulina, L.B. (1976). Properties and Methods of Processing Slags from Carbon Ferrochrome. *Steel, (6), 522-524*

[7] Chebukov, M.F., Pyachev, V.A. & Meike, V.E. (1973). Study of the Possibility of Using Ferrochrome Slag as Raw Material for Portland Cement Production. *Proceedings of the Ural Institute of Ferrous Metallurgy, (17), 136-143*

[8] Gorokh, A.V., Rustakov, L.N. (1973). Petrographic Analysis of Metallurgical Processes. *Moscow: Metallurgiya*

[9] Lapkina, Yu.V., Demin, B.L. & Nikulina, L.B. (1975). Technology for Processing Slags from Carbon Ferrochrome. In: Slags of Black Metallurgy. *Sverdlovsk*

[10] Sreiter, P. (1976). Use of Ferrochrome Slag for the Production of Forsterite Stones. *Silicate Techniques, (3), 85-86*

[11] Fomichev, N.A., Abyzov, A.N. & Abyzova, T.N. (1967). Heat-Resistant Concretes Based on Slags from Ferroalloy Production. In: Building Materials and Concretes. Issue 2. *Chelyabinsk: Southern Ural Publishing House*

[12] Perepelitsyn, V.A., Kormina, I.V., Karpets, L.A. & Zubov, A.S. (2004). Thermal Stability of Fused Corundum. *New Refractories, (1), 39-42*

[13] Khoroshavin, L.B. (2004). Forsterite 2MgOSiO2. *Moscow: Teplotechnika*

[14] Perepelitsyn, V.A., Savchenko, Yu.I., Bezhayev, V.M. & Tabatchikova, S.N. (1986). Petrochemical Calculations in the Technology of Forsterite-Spinel Refractories from Carbon Ferrochrome Slags. *Refractories, (10), 15-18*

[15] Grishenkov, E.E., Kasheeva, I.D. (2002). Refractories for Industrial Units and Furnaces. Reference Book. Vol. 2. Refractory Service. *Moscow: Intermet Engineering*

[16] Savchenko, Yu.I., Stepanova, I.A., Tabatchikova, S.N. & Kuznetsov, G.I. (1987). Development and testing of forsterite-spindle refractories based on high-carbon ferrochrome slags in thermal aggregates. Collection of scientific research. Complex and rational use of magnesium raw materials and refractories. *M. Metallurgy*

Қожды байланыстырғыштар негізінде құрылыс материалдарын әзірлеу. Форстерит-шпинельді өртенбейтін кірпіш өндіріс

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Аңдатпа. Металлургиялық өндірістегі техногендік қождарды құрылыс материалдарын әзірлеу үшін тұтқыр ретінде кәдеге жарату, сондай-ақ оларды қайта өңдеу технологиясын әзірлеу және олардың негізінде отқа төзімді кірпіш алу үшін қожды байланыстырғыштардың құрамы мен қасиеттерін зерттеу.

Негізгі сөздер: *техногендік қалдықтарды кәдеге жарату, қож тұтқыр, отқа төзімді кірпіш*.

Разработка строительных материалов на основе шлаковых вяжущих. Производство форстерито-шпинельного безобжигового кирпича

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Аннотация. Утилизация техногенных шлаков металлургического производства в качестве вяжущих для разработки строительных материалов, а также изучение состава и свойств шлаковых вяжущих для разработки технологии их переработки и получения огнеупорных кирпичей на их основе.

Ключевые слова: *утилизация техногенных отходов, шлаковые вяжущие, огнеупорный кирпич*.

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