Disposal of slag of refined ferrochromium by obtaining a sintered and carbonized construction products

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Abstract. The article investigates the material composition of refined ferrochromium slag. It has been confirmed that the main compound in the slag is dicalcium silicate. The disposal problem of self-disintegration slag in the current production of refined ferrochromium can be solved by controlling its basic capacity with obtaining stabilized lump slag that is not influenced to silicate decomposition. This became the basis to researches the production of non-disintegrating burnt construction products from slags using low-melting silica-containing additives that reduce the slag basicity. Briquettes roasting containing from 20 to 30% additives in the temperature range of 1200-1225 °C showed the possibility of obtaining ceramic construction products. Material analysis of the slag also showed that the slag components, such as calcium oxide and magnesium oxide, are compounds prone to the formation of carbonates, which leads to the setting between the slag particles. Which makes it possible to obtain construction products in the process of autoclaving processing of bricks from the slag in the carbon dioxide environment. The influence of fineness, slag moisture, and the dwell time of products in an autoclave in the carbon dioxide environment on the strength of the resulting pellets were evaluated in this paper. It was determined that moderate humidity, in addition to increasing ductility during pellet molding, also increases the strength of products after carbonization. Excessive grinding of slag negatively affected on the quality of the pellets. The increase in compression force during the pellets formation, on the contrary, increased the strength of the products. An increase in the duration of carbonization at constant pressure had a positive effect on the strength increase of pellets.

Keywords: self-disintegration slag, recycling, construction products, sintering, carbonization.

Introduction

The accumulation of man-made wastes in the traditional metallurgical regions leads to increasingly negative consequences, both for the natural environment and for economic indicators of production. Dusting, soil and wastewater pollution with heavy metals, covering vast areas, environmental charges paid by the plants and their annual increase, these are some of the negative aspects of the disposal and storage of production wastes.

The main scopes of accumulated man-made mineral formations of only ferroalloy plants in the Ural mountain region are represented by the slag dumps of the Aktobe plant (14 million of tons of
ferrochromium slag). Serov ferroalloy plant is 6.61 million of tons of ferrochromium slag. Klyuchevsky ferroalloy plant is 5.75 million of tons of slag and the Chelyabinsk Electrometallurgical Plant the slag production of low-carbon ferrochromium is 8.2, carbon and conversion ferrochromium is 3.3, ferrosilicon and ferrochromium silicon is 1.0, ferro-tungsten is 0.53, ferromolybdenum is 0.5 million tons [1, 20-22]. The most problematic of them are self-scattering slags. This type of slag disposal is still a big problem that has not found practical solution in industrial scopes. Among these slags, a separate species can distinguish self-decaying slag from the production of refined ferrochromium (hereinafter - RFC).

At the same time, with the development of engineering and technology, the processing of accumulated wastes becomes more accessible and profitable. Ferroalloy slag is a good raw material for metal concentrate production. In addition, during processing, you can get other materials that can be used as raw materials, for example in the construction industry.

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In the current production, the problem of RFC slag disposal is solved by their stabilization in the alloy smelting process to produce non-crumbling lump slags. Compounds of magnesium, iron, phosphorus, barium, aluminum and boron have a stabilizing effect. To date, the most common stabilizers are boron compounds, which is due to the small amount of additives to obtain stabilized slag [2, 3, 4]. Another method for stabilizing slag is to change the basicity of slag to 1.3-1.4 values or more than 3.2 [5, 6].

In the paper, the chemical composition of the slag of ferrochromium-refined grades was studied (Table 1).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Chemical analysis of refined ferrochromium slag, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂O₃</td>
<td>SiO₂</td>
</tr>
<tr>
<td>6*</td>
<td>26</td>
</tr>
</tbody>
</table>

* - in terms of total chromium to oxide

The metal chromium content is on average about 2%. The composition of the slag from the slag dump according to x-ray phase analysis are given in Table 2.

As the data provide about the slag composition, its use as a raw material for cement production is hindered by the high content of free periclase and the dicalcium silicate availability, which is confirmed by published data [7].

To determine the stabilization capacity by reducing the basicity, calculations were performed to determine the equilibrium phase composition of the six-component Cr₂O₃-SiO₂-Al₂O₃-FeO-CaO-MgO system based on the chemical composition of the natural slags. The calculation was carried out using a software package worked out by HMI named after J. Abishev [8]. The basicity was varied by increasing / decreasing the fraction of silica in the composition with an unchanged amount of the remaining components of the slag. Based on the results of calculating the equilibrium phase composition of the system, the dependence of the change in the content of 2CaO·SiO₂ in the slag on the change in the basicity of the slag is shown in Figure 1. The diagram shows that there are two regions in the system in which dicalcium silicate is substantially absent with a basicity of less than 1.4 and more than 3.2.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Material composition of the slag of refined ferrochromium production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>Percentage, %</td>
</tr>
<tr>
<td>Ca₂(SiO₄)</td>
<td>33.2</td>
</tr>
<tr>
<td>MgFeAlO₄</td>
<td>22.5</td>
</tr>
<tr>
<td>CaMg(SiO₄)₂</td>
<td>20.5</td>
</tr>
<tr>
<td>CaAl₂SiO₆</td>
<td>7.9</td>
</tr>
<tr>
<td>MgO</td>
<td>6.5</td>
</tr>
<tr>
<td>Ca₀SiO₂</td>
<td>5.9</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Figure 1 Change in the 2CaO·SiO₂ content in the slag depending on basicity

To stabilize RFC slag as regards technology is more efficient by reducing the basicity to less than 1.3 values, since slag with a basicity of more than 3.2, where tricalcium silicate is the main phase, have a high melting point. RFC slag with a basicity of less
that 1.3 as concerns physical properties are similar to raw materials for the ceramic products manufacturing.

The practical goal of this part of the work is to develop the composition of ceramic products with a base from stabilized by sintering RFC slag with reduced basicity obtained from raw materials kempsyrsay ore massif. Ceramic products in industry are obtained by firing molded products from various clays. Firing products is usually carried out at a temperature of 900-1000 °C. Fire-resistant and high-melting clays have a large sintering interval (more than 100 °C) and are used to obtain products with a dense sintered shard; burn them at 1150 ... 1400 °C. For firing ceramic materials use special furnaces (ring, tunnel, slot, roller, etc.) [9].

The current RFC slags, having a ~ 1.9 basicity, contains about 75% of 2CaO·SiO$_2$ and corresponds to the maximum of the curve in Figure 1. Therefore, any change in basicity leads to a decrease in the content of 2CaO·SiO$_2$. In this paper, non-deficient silica-containing materials with a relatively low melting point (not higher than 1300 °C) - expanded clay (hereinafter – Clay 1) and clay of kempsyrsay ore massif (hereinafter – Clay 2), as well as ground natural crushed stone (hereinafter – Breakstone) were considered as stabilizing additives. The average chemical composition of these materials is presented in Table 3.

To obtain basicity below a 1.4 value, the least additive component of stabilizing additives is estimated. When using Clay 1, it should be at least 15%, Clay 2 - 17.5%, Breakstone - 22%.

The sintering temperature of the RFC slag itself is above 1500 °C; however, the addition of these components significantly reduces this temperature. Correspondingly, in the state diagrams of SiO$_2$-CaO-MgO and SiO$_2$-CaO-Al$_2$O$_3$, with the inclusion of the above additives in an amount of 15-45%, the melting temperature of the system will lie in the range of 1320 - 1400 °C. In this regard, the studies of the sintering process were carried out in the range of 1000 - 1250 °C.

Below is the table containing the chemical composition of stabilizing additives, mass. %

<table>
<thead>
<tr>
<th>Item</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
<th>Cr$_2$O$_3$</th>
<th>FeO</th>
<th>C</th>
<th>S</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay 1</td>
<td>1.6</td>
<td>60.8</td>
<td>2.5</td>
<td>16.9</td>
<td>1.4</td>
<td>8.1</td>
<td>1.0</td>
<td>0.6</td>
<td>7.0</td>
</tr>
<tr>
<td>Clay 2</td>
<td>6.9</td>
<td>58.5</td>
<td>2.8</td>
<td>12.4</td>
<td>-</td>
<td>6.4</td>
<td>-</td>
<td>0.2</td>
<td>12.8</td>
</tr>
<tr>
<td>Breakstone</td>
<td>9.7</td>
<td>51.4</td>
<td>4.9</td>
<td>14.3</td>
<td>0.2</td>
<td>13.8</td>
<td>-</td>
<td>0.01</td>
<td>5.7</td>
</tr>
</tbody>
</table>

The materials used were pre-dried and ground for the researches. The moistened mixture of the slag and stabilizing additives was subjected to semi-dry pelleting (+15% of water over dry weight) with a compression force of 3 kN / cm$^2$. The pellets had a rectangular shape with a dimension of 50 × 50 × 30 mm. The firing was carried out in an electric muffle furnace; the heating time of the samples was 8-10 hours, exposure at a maximum temperature of 3-5 hours, cooling along with the furnace for 12-14 hours.

Previous experiments made in the laboratory regarding stabilizing RFC slag by adding silica-containing materials by fusing them showed that their addition in the minimum amount required did not ensure stabilization of the samples in the entire volume. A 20% increase in the amount of stabilizing additive allowed the slag to be completely stabilized. Given this feature of the process, the share of the stabilizer in the mixture was set to at least 20%.

No sintering was observed in the temperature range of 1000–1150 °C; pellets scattered with minimal physical impact. Strength values did not exceed 8 kgf / cm$^2$.

Pellets sintering occurred at a temperature of 1200 and 1225 °C. Studies were carried out with the addition of stabilizers in the slag in the amount of 20, 25 and 30%. The results of testing sintered pellets for compressive strength are provided in Figure 2.

As Figure 2 provides, sintering with the content of stabilizer additives in 20% sintering did not occur. An increase in the additive content up to 25% at a temperature of 1200 °C leads to sintering of pellets. While strength indicators are obtained that are in the range of 30-35 kgf / cm$^2$ for all types of stabilizers, an increase in firing temperature to 1225 °C increases this value for expanded Clay 1 by 85% (65 kgf / cm$^2$), for Clay 2 100% (60 kgf / cm$^2$), and for Breakstone it remains unchanged (30 kgf / cm$^2$). Pellets containing 30% additives showed an increase in strength compared to 25% at 1200 °C for Clay 1, Clay 2 and Breakstone at 1200 °C by 130% (80 kgf / cm$^2$), 150% (75 kgf / cm$^2$) and 67% (50 kgf / cm$^2$) respectively. The same content of additives at 1225 °C showed an increase in strength by 330% (150 kgf / cm$^2$), 230% (100 kgf / cm$^2$) and 100% (60 kgf / cm$^2$), respectively.
A significant increase in strength occurs with a content of 30% stabilizing additives and firing at a temperature of 1225 °C. A further increase in the firing temperature (≥1250 °C) leads to the appearance of cracks on the surface and deformation of the pellets. Figure 3 demonstrates samples of sintered pellets.

In [10], studies were carried out to determine the ceramic properties of various metallurgical slags with the addition of a clay component. Ceramic products with a compressive strength of 200 to 400 kgf/cm² were obtained. The sintering temperature was in the range of 1150 - 1350 °C. In [11], it was proposed to obtain porous pellets from a mixture of slag, diatomite, and sodium silicate solution, sintered aggregates for concrete sintered at 1050 °C.

Another way to utilize RFC slag can be the method of obtaining high-strength building products by autoclave carbonization. Given the high content of calcium and magnesium oxides in the slag, it has a high tendency to form carbonates [12]. Similar work on the use of slag from steelmaking, having a similar chemical and mineral composition, indicates the possibility of carbonization of self-dissolving slag with obtaining agglomerated products of high strength [13, 14, 15].

It is clear that metal carbonates are formed by exothermic reactions of the where MeO is a divalent metal oxide.

\[ \text{MeO} + \text{CO}_2 = \text{MeCO}_3 \]  

(1) type

With increasing pressure of carbon dioxide in the \( \text{MeO-CO}_2-\text{MeCO}_3 \) system, the affinity of MeO to \( \text{CO}_2 \) increases, and the carbonization reaction proceeds with the release of heat. Carbonization occurs most intensively with a moisture content of 5-8%. It is noted that with complete drying of the material, as well as with its excessive moistening, the process stops or extremely slows down [16, 17].

Based on the above reasoning, we conducted studies on the carbonization of stale slag of refined ferrochromium. For the experiments were used: steel mold with a mesh size of \( 50 \times 50 \) mm; test press,
hydraulic IP-50; high pressure autoclaves with a volume of 0.7 and 2.0 liters. Food carbon dioxide from cylinders was used as CO$_2$.

In the conducted experiments, the influence of fineness, moisture of the used slag and the duration of exposure of the products in an autoclave in a carbon dioxide medium to the strength of the resulting pellets was evaluated. Pellets were made similar in shape to sintered pellets. The size of the ground slag from which the pellets were molded: −1 + 0 mm; −0.16 + 0 mm; −0.071 + 0 mm. Humidity: 15%, 8% and 5% over dry weight. Moistening of the material is also required to improve the process of forming briquettes. The pressing force during molding was 1.5 and 3 kN/cm$^2$. The pressure in the autoclave in all cases was 10 atmospheres. The exposure time is 12 hours. The quality of the pellets was evaluated by assessing the compressive strength according to GOST 8462-85 on the IP-1000 test press. The results are provided in Table 4.

The data provided make it clear that the moisture content increased to 15% significantly reduced the strength of carbonized products - on average by 37.5% compared with the same samples, but obtained at 5% humidity. Therefore, the remaining experiments were performed at a moisture content of 5% and 8%. In accordance with the known laws of briquetting, the strength of briquettes consisting only of small particles is not high at any humidity and pressing pressure [18]. An increase in the maximum particle size of the used slag significantly increased the strength of the resulting briquettes. The maximum values of compressive strength were obtained with a grain size of −1 +0 mm, a holding time of 12 hours, and a pressing force during molding of 3 kN/cm$^2$. For these samples, sieving was carried out in fractions to determine the particle size distribution. The sieving results are shown in Table 5.

The experiments were carried out according to the best option (material fineness−1 +0 mm, pressing force 3 kN/cm$^2$) with exposure to carbon dioxide for 6, 12, 18 and 24 hours at a pressure of 10 atmospheres to determine the kinetics of the carbonization process. The average values of the obtained strength test results are shown in Figure 4.

As can be seen from this figure, there is an almost linear dependence of the compressive strength of pellets made from stale RFC slag on the time of autoclaving in carbon dioxide. The appearance of pellets after 12 hours of carbonization is shown in Figure 5.

The results make it clear that although the process of carbonization of slag accelerates with increasing fineness of its grinding as stated in [19], nevertheless, the strength of pellets decreases with increasing fineness of grinding. Apparently, this is explained by the fact that in studies [19], the slag was carbonized without preliminary agglomeration. However, in our case, a more optimal particle size distribution (an equal amount of small, medium, and large particles by weight) has a stronger effect on the strength of pellets after carbonization.

It is also noted that in order to achieve maximum strength when working with the same slag, in addition to the particle size distribution, it is necessary to take into account the moisture content of the initial mixture. So, for a mixture with a fineness of −0.16 + 0 mm, the effective humidity is lower than in the case of −1 +0 mm, which is apparently due to the different gas permeability of mixtures of different particle size distribution during autoclaving.

### Table 4 The pellets strength after carbonization

<table>
<thead>
<tr>
<th>Items</th>
<th>Fractional composition of used slag, mm</th>
<th>Relative humidity, %</th>
<th>Strength, kgf/cm$^2$*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>−0.071 +0</td>
<td>5</td>
<td>122.2/112.0</td>
</tr>
<tr>
<td></td>
<td>−0.16 +0</td>
<td>15</td>
<td>84.6/85.3</td>
</tr>
<tr>
<td></td>
<td>−1 +0</td>
<td>5</td>
<td>418.0/349.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>321.4/306.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>309.9/346.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>311.2/357.1</td>
</tr>
</tbody>
</table>

* In the numerator - at a pressing pressure of 1.5 kN/cm$^2$; in the denominator - at 3 kN/cm$^2$.

### Table 5 Granulometric composition of RFC ground slag

<table>
<thead>
<tr>
<th>Fraction, mm</th>
<th>Mass fraction part,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;1.0</td>
<td>0.09</td>
</tr>
<tr>
<td>&gt;0.63</td>
<td>0.22</td>
</tr>
<tr>
<td>&gt;0.4</td>
<td>5.31</td>
</tr>
<tr>
<td>&gt;0.2</td>
<td>26.18</td>
</tr>
<tr>
<td>&gt;0.1</td>
<td>44.64</td>
</tr>
<tr>
<td>&gt;0.063</td>
<td>56.81</td>
</tr>
<tr>
<td>&lt;0.063</td>
<td>42.43</td>
</tr>
<tr>
<td>Sieving losses</td>
<td>0.76</td>
</tr>
</tbody>
</table>
**Findings**

Studies conducted have shown the possibility of obtaining building ceramic products from RFC slag with stabilizing additives. The preservation of the structural integrity of the pellets and their high compressive strength are confirmed by theory studies on the stabilization of self-decaying slag by reducing the basicity during sintering. The use of claydite clay and clay of Kempirsay ore massif as stabilizers in an amount of at least 30% at a firing temperature of 1225 °C makes it possible to obtain brick grades M150 and M100 (according to State Standard 530-2012), respectively.

The use of ground natural crushed stone as a stabilizer did not allow to raise the strength of products above the values corresponding to the grade of brick M50.

Autoclave carbonization of RFC stale slag in a carbon dioxide environment makes it possible to obtain molded articles with high strength, which can be adjusted due to the autoclave holding time. Molded carbonized products from stale slag of refined ferrochromium are superior in strength to concrete and silicate construction products.

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брикеттерді температурасы 1200-1225°С аралығында күйдіру процессі керамикалық құрылыс бұйымдарын алуға мүмкіндік береді. Қождың заттық құрамын зерттеуі кальций және магний тотықтары карбонаттар құруға бейім екендігін көрсетті, соның арқасында қождың түйіршіктері бір-бірімен қосылып қатауына соқырады. Карбонизация процессі қождан жасалған кірпіштерді көміртегі қос тотығы ортасында автоклавтық өңдеу арқылы өндіруге мүмкіндік береді. Жасалған зерттеу жұмысында шығарылған брикеттің беріктігіне қождың ірілігі, дымқылдығы және автоклавта ұақытының әсері бағаланы. Ынсапты дымқылдық қорамалау кезіндегі созылымдып тек көбейтпей сонымен бірге карбонизациядан кейінгі беріктілікті арттыратынын көрсетті. Қождың шамадан тыс ұнтақтануы брикеттердің сапасына кері әсер етті. Қормалау кезіндегі қысу күшінің үдей түсуі бұйымдардың беріктілігіне жақсы әсер етті. Көмірқышқыл газ атмосферасында қысым тұрақты болған жағдайда карбонизация ұзақтығын арттыру брикеттердің беріктігіне оң әсер етті.

Түйін сөздер: қож, кәдеге жарату, құрылыс бұйымдары, қақтау, карбонизация.

Утилизация шлака рафинированного феррохрома с получением спечёных и карбонизированных строительных изделий

Сариеv О.Р., Мусабеков Ж.Б., Досекенов М.С.

Аннотация. В статье исследован вещественный состав шлаков рафинированного феррохрома. Подтверждено, что основным соединением в шлаке является двухкальциевый силикат. Проблему утилизации саморассыпающегося шлака в текущем производстве рафинированного феррохрома, возможно, решать регулированием его основности с получением стабилизированного не подвергающегося силикатному распаду кускового шлака. Это послужило основой для проведения исследований по получению не распадающихся обожжённых строительных изделий из шлаков с применением легкоплавких кремнезёмсодержащих добавок снижающих основность шлака. Обжиг брикетов, содержащих от 20 до 30 % добавок в температурном интервале 1200-1225°С, показал возможность получения керамических строительных изделий. Вещественный анализ шлака также показал, что компоненты шлака, такие как оксид кальция и оксид магния являются соединениями склонными к образованию карбонатов, что приводит к схватыванию частиц шлака между собой. Также даёт возможность получать строительные изделия в процессе автоклавной обработки кирпичей из шлака в среде углекислого газа. В приведённой работе было оценено влияние крупности, влажности шлака и длительности выдержки изделий в автоклаве в среде углекислого газа на прочность получаемых брикетов. Установлено, что умеренная влажность помимо повышения пластичности при формировке брикетов, также увеличивает прочность изделий после карбонизации. Чрезмерное измельчение шлака негативно сказалось на качестве брикетов. Нарастание усилия сжатия при формировании брикетов наоборот подняло прочность изделий. Увеличение длительности карбонизации при неизменном давлении сказалось положительно на росте прочности брикетов.

Ключевые слова: Саморассыпающиеся шлаки, утилизация, строительные изделия, спекание, карбонизация.

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