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RESEARCH PAPER

Studying the compositions and modes of manufacturing refractory products using steel production slag

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ABSTRACT

The article presents the results of studying the possibility of using steelmaking waste as an anthropogenic raw material for manufacturing refractory materials. Steelmaking slag, which is characterized by an increased content of calcium silicates, was used as an additive that increased the heat resistance of refractory materials. The studies show that it is most appropriate to use as the main filler a fraction of fireclay scrap 0.8-0.9 mm (60%); fine-grained fireclay (0.2-0.3 mm, 10%); clay suspension with a moisture content of 7-8% (30%), which ensures the production of high-quality refractory material. In this case, it is advisable to press the samples with the pressure of 22-23 MPa to sinter at 1250 - 1270 ºC within 10-12 hours. The microstructure of the samples was studied, and it was shown that the experimental fireclay sample had a more uniform structure and a smaller number of rounded pores. Thus, based on anthropogenic raw materials, it is possible to obtain refractory fireclay products that can be recommended as alternative materials for lining various types of thermal units of foundry and plants of metallurgical production with a maximum application temperature of 1250-1300 ºC.

Keywords: refractory materials, anthropogenic raw materials, metallurgical slag, compressive strength.

INTRODUCTION

At present, ferrous metallurgy has an unsolved problem of comprehensive and maximum use of available raw materials. This is caused by the depletion of used mineral deposits and the fact that new deposits are usually poorer and located in areas with poorly developed transport and energy infrastructure. In conditions of limited natural resources and high costs of raw material extraction, one of the possible solutions to the problem is the use of man-made waste from metallurgical production [1,2]. The high-performance properties of refractories are provided by the content of calcium silicates and magnesia silicates and their ratio [3].

The metallurgical industry annually generates huge volumes of waste, such as slag, dust, sludge, which are often not processed and are stored in dumps, which creates environmental problems. For example, 32 billion tons of industrial waste have been accumulated in the Republic of Kazakhstan, which is increasing yearly. The waste is mainly man-made mineral formations comprising 70% of the total volume. About 42% of the total waste is disposed of; the rest is stored in dumps in the territories of production facilities. However, these wastes contain useful components that can be reused in production processes. For example, slags formed during metal smelting can be processed into building materials or used to produce new refractory materials. Based on previous studies, it was found that the man-made waste of the Karaganda Ferroalloy Plant and the Karaganda Plant for Processing Secondary Materials are suitable for use in the production of refractory materials. Steelmaking slags in the industries mentioned above contain a high level of calcium silicates and magnesia silicates, which is confirmed by studies as the key factor providing excellent refractory properties. Their composition is also optimally balanced in terms of magnesia and silicon content, which further improves the heat resistance of refractories [5-7].

Most modern studies in developing functional high-quality refractories focus mainly on low-carbon magnesia-carbon refractories [8] and spinel-carbon materials [9]; studying flake graphite content's effect on refractories' properties, etc. However, the results showed that increasing the carbon content can significantly reduce the samples' compressive strength and thermal expansion coefficient. As for spinel-carbon refractories, their disadvantage is the impossibility of controlling spinel formation in carbon-containing materials and ensuring the desired structure and properties, which leads to the inefficiency of using such materials in practice [8-10].

It is worth noting that many attempts have been made to control the material's composition to improve refractory thermal stability [11]. Various methods have been proposed, such as building a nanostructured matrix, structural optimization of pyrolytic carbon from the binder, introducing multiple additives [12, 13] and regulation of secondary ceramic phases. However, some of the above methods are accompanied by an increase in the cost of production and create difficulties for the production process (there is a need to use additional shell equipment, materials, and production areas). For example, the high cost of nanosized additives and poor dispersion in the material hinders their large-scale application. This can be effectively improved by simply adjusting the particle size distribution, ensuring dense packing of materials.

As mentioned above, the use of man-made waste for the production of refractory materials is one of the current areas. The slag composition varies depending on the specific slag production process, but it usually contains large amounts of calcium, magnesium, aluminum, and silicon in various forms. These components provide the refractory material with the needed thermodynamic and mechanical properties, making it suitable to produce refractory materials that can withstand extreme temperatures and chemical influences.

The Republic of Kazakhstan's production facilities analysis shows fireclay bricks are the most common lining material.

Usually, fireclay refractory materials are obtained by firing raw materials obtained using a mixture of kaolin and/or refractory clays and fireclay. In addition to traditional natural raw materials used to produce fireclay products, various types of waste that act as man-made raw materials, are increasingly used. Using such waste in processing allows for reducing the resource and energy intensity of technological processes, conserving natural resources and, as a result, reducing the negative impact on the environment.

Most studies focus on using slags as raw materials to produce building materials, prepare updated multifunctional materials, etc. At the same time, several studies deal with anthropogenic waste, such as electric steelmaking and ferroalloy production [14-15].

This paper presents the results of studying the compositions and modes of manufacturing refractory products when used in the composition of steelmaking slag. This satisfy the requirements of SS-390-96 "General-purpose fireclay and semi-acid refractory products," which are used as lining for various thermal units of metallurgical and machine-building enterprises.

MATERIAL AND METHODS

The main component of the batch is chamotte of different fractions; clay suspension. Steelmaking slag is proposed to be used as a binder. Slag from the production of 35HGSL steel in an induction furnace was used. The slag formed during the production of 35KhGSL steel contains oxides of calcium (CaO), magnesium (MgO), aluminum (Al2O3), and silicon (SiO_2), which are characterized by a high melting point and resistance to oxidation.

We used fireclay scrap, the dispersion of which is the as follows: large fraction (0.5-1.0 mm) - 60%; small fraction (smaller than 0.5 mm) - 10%, clay suspension - 30%. Over one hundred percent, 2-8% slag was introduced. The fractional composition of the materials was determined on an analytical sifting machine AS 200 control (Retsch, Germany).

All the charge components were pre-ground in an Emax ball mill within 10 minutes. Mixes weighing 10 kg were made in a laboratory mixer. The resulting mixture was molded into tablet-shaped samples with a diameter of 70 mm and a height of 50 mm. The pressing of samples from the batch on the Instron-100 unit was carried out within 12-15 seconds; the base (initial) pressure was 25 MPa. Then, sintering was carried out at 1250 - 1280 ^{0}C within 12 hours in a Nobertherm furnace in the air atmosphere.

After complete cooling, the samples were tested for compressive strength, gas permeability, viscosity and open porosity. Samples were selected using random (cluster) sampling.

Porosity was studied to establish the relationship between gas permeability and porosity. Open porosity was determined using a PoreMaster 60 mercury porosimeter, which allows determining the volume and size distribution of open pores.

The structure was studied using a MAGUS Metal V700 metallographic microscope in the bright field. The surfaces of the test samples were pre-polished. Clay in the pressed mass is present as a binder; therefore, it should be uniformly distributed throughout the entire volume of the mixture. Technologically, it should be present in a finely dispersed state. Viscosity of suspensions based on clay from the Fedorovskoye deposit was considered. In the experiments, viscosity of binder suspensions introduced into the chamotte mass was studied.

The experiments were carried out on an SV-1A viscometer. The solvent and clay concentration effect on viscosity was studied using an SV-1A vibration viscometer based on the tuning fork vibration method, contributing to the accuracy of the measurements. The fireclay brick scrap (**Fig. 1**) was crushed in a roller crusher and ground in a rod mill. The resulting powder was sifted in sieves. The components were weighted on a Shimadzu Corporation scale, model TXB 6224.

Fig.1 Chamotte rubble

RESULTS AND DISCUSSION

The coarse chamotte fraction's effect on the samples' compressive strength was considered (Fig. 2); slag was 8 % (over 100%), and the fine filler of the fraction was 0.2-0.3 mm.

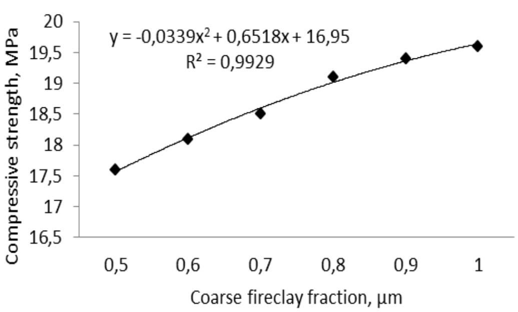


Fig.2 The fraction of the main fireclay filler effect on the sample compressive strength

The fraction of 0.8 - 0.9 mm is most appropriate as the main filler.

The effect of the fine chamotte fraction on the sample compressive strength was also determined (**Fig. 3**). The coarse chamotte filler was 0.8-0.9 mm in size, and the slag was 8 % (over 100%).

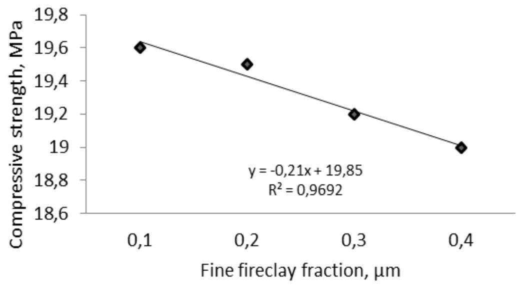


Fig.3 The additional chamotte filler fraction effect on compressive strength of the samples

It is obvious that fine chamotte fills the pores between particles of large chamotte and increases the sample strength. It is most advisable to use chamotte of 0.1 - 0.2 mm as a filler of fine fraction, since it is this fraction that contributes to the densest placing of the mixture in combination with chamotte of fraction 2 - 3 mm (**Fig. 4**). At the same time, the fraction of fine chamotte does not have a significant effect on the samples**.**

Fig.4 – Fine and large chamotte fractions

The effect of slag content on sample strength (**Fig. 5**) was studied. Porosity was determined using a PascalPoreMaster 60 porosimeter.

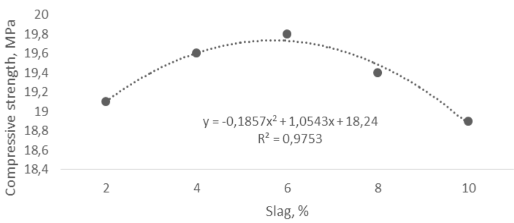


Fig.5 The steelmaking slag content effect on compressive strength of the samples

Laboratory studies have shown that the most optimal use of slag is 6%. A lower content weakens the sample due to decreasing adhesive properties. An increased content probably leads to the formation of brittle phases in the refractory structure, which decreases strength characteristics.

In another series of studies, the clay humidity for the binder effect on the viscosity of the solution was determined (**Fig. 6**). Viscosity of the binder was determined on an SV-1A viscometer.

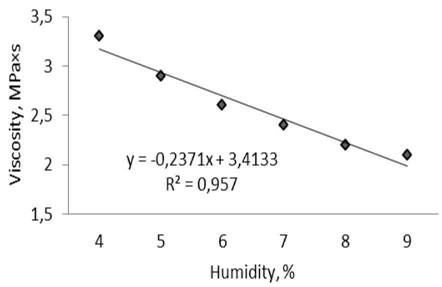


Fig.6 The clay humidity effect on the binder viscosity

The binder viscosity can be adjusted by varying the composition, the form of the solid component and, if needed, the temperature of the suspension. Low viscosity results in poor adhesion of the filler to the binder, and a significant viscosity value makes it difficult to ensure uniform distribution of the binder throughout the volume of the chamotte mass.
The most technologically advanced clay has a 7-8% humidity since lower humidity leads to increased dust formation, and higher humidity reduces the binder's adhesive properties.
The gas permeability and porosity study results are shown in **Fig. 7-8**. It is known that there is a difference between total porosity, which includes all the pores of the body, and open porosity. Depending on the nature of the material porosity, the service life of refractory products in metallurgical units changes significantly.

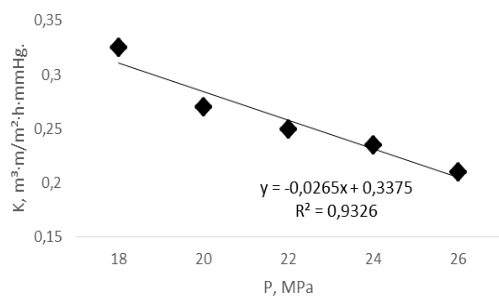
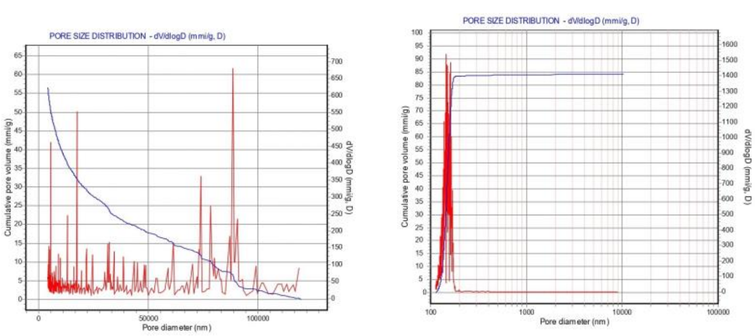


Fig.7 Gas permeability dependence on the pressure value of the molded product



a *б*

Fig.8 Distribution of pores in the chamotte obtained:
a) without the use of slag; b) with the use of 6 % slag in the mixture

As shown in **Fig. 9**, the pattern of pore distribution changes when slag is introduced into the mixture. The presence of slag increases the total pore volume but also shifts the distribution of pore sizes towards smaller diameters.
Studies have demonstrated that using 6% slag derived from steel production promotes the formation of pores with a diameter of less than 200 nanometers. This development is beneficial, as smaller pore sizes reduce slag penetration that forms during smelting and enhance the refractory material's resistance to slag.
The next stage was studying the effect of firing temperature on the heat resistance of bricks. The fire time is 6 hours. In this case, heat resistance was assessed by the change in sample weight due to its destruction. The heat resistance of finished but unfired refractory samples was determined by holding them on the liquid steel surface in a ladle. The metal temperature was 1440-1460 ^{0}C, and the holding time was 10 minutes. After that, the bricks were pulled out of the metal, the slag and metal were removed and then weighed.
The results of the studies are given in **Table 1**.

Table 1 The temperature and firing time of samples affect their thermal

№	Technology Parameter		Change in sample weight, %
	Firing temperature, ^{0}C	Duration, h	
1	1000	12	12,5
2		24	15,1
3	1100	12	8,7
4		24	9,4
5	1200	12	9,7
6		24	9,9
7	1300	12	10,6
8		24	12,1
9	1400	12	11,8
10		24	14,2

The annealing temperature of 1100-1200°C is acceptable to ensure sufficient thermal stability due to the tighter fit of the chamotte particles. Increasing the temperature above 1350^{0}C leads to the sample's weakening due to the burning out of the binders.
Compressive strength was studied depending on the pressure and sintering temperature (**Fig.9, 10**). In the first case, different pressures were used, and the samples were sintered at 1270 0C within 12 hours. In the second case, chamotte press pressure of 22 MPa (base) was used.

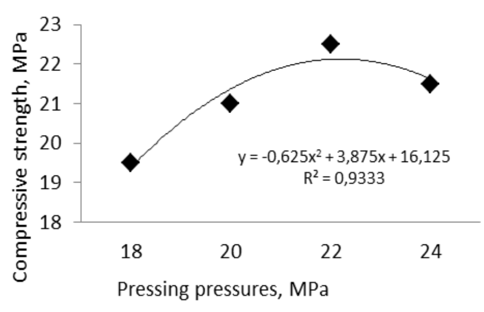


Fig.9 The press pressure effect on compressive strength

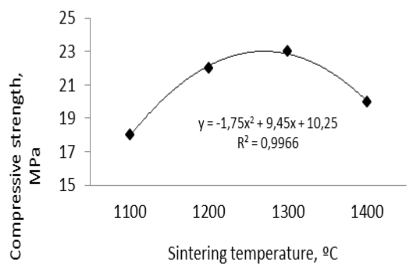
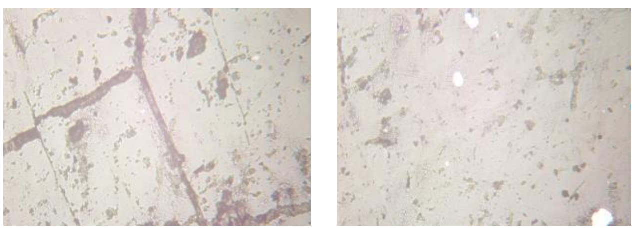


Fig.10 The sintering temperature effect on compressive strength

Press pressure over 23 MPa and sintering temperature over 1350 ^{0}C has a negative effect on bricks' mechanical properties. In the first case, the reason is the crushing of dry particles at the base of the fireclay mass; in the second case, it is the shrinkage of clay and possibly burnout of the binder.



a) b)

Fig. 11 – Structure of the traditional (a) and experimental (b) fireclay with 6% slag content. Reflected light, x200

Transverse microsections were made using an optical microscope using the studied fire clay and the comparison sample. The structure of the experimental sample is dense, has no mechanical damage, and contains few structural pores compared to sample (a) of fireclay without adding slag. In sample (a), the structure is loosening; it contains fairly large pores of an elongated, rounded shape of a closed and open nature.
Thus, the effect of pressing and firing modes on the porous structure of refractory products was studied, and the relationships between the pressing and firing parameters and the parameters of the porous structure were obtained. The microstructure of the samples was also investigated. The experimental fireclay sample has a more uniform structure and fewer rounded pores. Therefore, this work shows the prospect of obtaining refractory using man-made waste, but it is necessary to continue the work on its study.
Thus, this work shows the prospect of obtaining refractory using anthropogenic waste, and it is necessary to continue studying it. The studies confirmed the feasibility of using steelmaking slag with a 6% content and crushed fireclay scrap in a refractory mixture to produce fireclay bricks. This composition ensures the formation of relatively evenly distributed small pores, preventing slag from flowing into them during operation.

CONCLUSION

The studies carried out show that it is most appropriate to use as the main filler the fraction of chamotte rubble of 0.8-0.9 mm, 60%; 10% fine-grained fireclay (0.2-0.3 mm); 30% clay suspension with the humidity of 7-8%, which ensures the production of high-quality refractory material. In this case, it is advisable to press the samples with pressure of 22-23 MPa and sinter at 1250 - 1270 ^{0}C within 10-12 hours. The study of the microstructure showed that the experimental fireclay sample had a more uniform structure and contained fewer rounded pores.
Thus, it is possible to obtain refractory fireclay products based on anthropogenic raw materials that can be recommended as alternative materials for lining various types of thermal units of foundry and plants of metallurgical production with the maximum application temperature of 1250-1300 ºC.

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