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Physico-Mechanical Properties of Ceramics Based on Aluminosilicates Modified by Metallurgical Waste

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The use of metallurgical slag for the synthesis of ceramics is considered as an alternative way to manage this waste. A significant effect on the physic-mechanical characteristics of ceramic materials when metallurgical slags are added is exerted by the heat treatment mode. Aluminosilicates were used as the main raw material metallurgical slags of lead and copper production were used as an additive-regulator of the properties of ceramics. It is shown that the addition of slag leads to an increase in mechanical strength. It was established that the maximum mechanical strength of 73.43 MPa is possessed by a sample obtained from a mixture of zeolite-bentonite-copper slag in the proportions of 50 % – 30 % - 20 %, at a moisture content of 15 % after calcination at 1,000 °C.

1. Introduction

The increase in the amount of industrial waste has become a serious problem for all industrialised countries in the world. Metallurgical plants produce significant amounts of waste, which are one of the most serious environmental problems. If handled improperly, these types of waste can cause permanent damage to the environment. Measures to reduce the formation and disposal of metallurgical waste are relevant. Metallurgical waste can be involved in the production of ceramic materials to solve the problem. The use of technogenic raw materials is one of the effective ways to save natural materials, while at the same time recycling of by-products occurs and a contribution is made to environmental protection.

Traditionally, slags are used to produce slag-Portland cement, as aggregate for concrete (Pizoń et al., 2020), in road construction, mineral wool, slag pumice, slag casting, etc. are produced from slag melts (Shishakina et al., 2019). However, Sadenova et al. (2019) proposed a technology for involving metallurgical slag in the synthesis of ceramic materials for environmental catalysis, based on powder metallurgy methods. According to the technology, the mixture of natural aluminosilicates and metallurgical slag, after preliminary drying and grinding, is wetted to give ductility. After reaching the required moulding moisture, the mixture is moulded by compression or extrusion. Ceramic catalyst supports synthesized on the basis of natural and technogenic materials satisfy the requirements for the supports, and the synthesized zeolite-bentonite-slag contact is capable of catalytic conversion of carbon monoxide $\alpha \approx 70$ %.

Vichaphund et al. (2010) have shown the possibility of reuse of incineration ash in the production of several types of ceramic materials, such as brick, cement, cement-based products, glass and glass-ceramics. Up to 50 %, ash residue was added to the clay mixture. The product had good physical and mechanical properties that met the standard.

In the research work (Teo et al., 2019), the slag of an electric arc furnace was used as a raw material in the production of ceramic tiles. An analysis of the sintering mechanism was carried out, and it was found that the slag of the electric arc furnace functions as a fluxing agent, forming a glassy phase, and contributes to the

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formation of anorthite and wollastonite during firing. The presence of these phases enhanced the compaction of ceramic tiles.
The possibility of involving metallurgical slag containing aluminosilicates was studied in (Utegenova et al., 2019), in which moulding mixtures were prepared from the starting materials in the form of powders, which were then subjected to heat treatment extrusion. Based on the values of mechanical strength, the authors suggested that they can be used for ceramic products.
An analysis of literary sources showed that the properties of ceramic materials and microstructural changes depend on the raw material from which they are made, the method of processing, the composition of the charge and the established heat treatment (Figueirêdo et al., 2019). The selection of the optimal firing regime is essential in the process of production of ceramic materials since it is at this stage that the strength of the finished product increases. Among the phenomena occurring during firing, the most important is the sintering process. In the course of sintering, the formation and growth of contacts between particles of the solid phase and the recrystallization shift of the boundaries between crystals occur (Buchilin et al., 2017). In the studied literature, the need for the heat treatment of various ceramic materials with the addition of metallurgical slag was established. This study analyses the effect of composition and heat treatment on the mechanical strength of ceramic products obtained from natural aluminosilicates and metallurgical slag of lead and copper production to establish patterns of synthesis of new materials.

2. Materials and methods

The main raw materials used were aluminosilicates of East Kazakhstan deposits - zeolite (Z) and bentonite (B), metallurgical slags of lead (SPb) and copper (SCu) plants were used as an additive-regulator of ceramic properties. Compositions of composite systems were prepared by varying the ratio of components zeolite: bentonite: slag. In the ratios of 40 - 60 wt.% zeolite, 20 - 40 wt.% bentonite and 10 - 30 wt.% slag, the compositions are presented in Table 1.

Table 1: The composition of ceramic mixtures

Zeolite, %	Bentonite, %	Slag, %
40	40	20
60	30	10
40	30	30
50	30	20
60	20	20

To ensure the required moulding moisture, the moisture content was changed in the range of 15 ÷ 25 %. The resulting materials were kept in air, and then subjected to heat treatment in a muffle electric furnace at each stage in the temperature range 100 - 1,000 °C. During calcination, evaporation of moisture occurs, and the physical structure of the carrier is formed due to sintering processes. A total of 120 ceramic systems were synthesized.
The strength of the obtained samples was determined on a universal Shimadzu Autograph AG-Xplus machine (OS Shimadzu, 2019), using TRAPEZIUM X software, which allows full control of the test process through a PC. The tensile strength of the obtained samples was determined by compression. The tests were carried out by laying samples in the form of a cylinder (12.6 mm in diameter) between the plates of the testing machine and gradually increasing the load continuously. At the same time, a compression diagram was drawn on a computer monitor. The test speed is 0.5 mm/min. TRAPEZIUM X software in automatic mode after testing each sample displays the characteristics of the samples specified for output when creating the test method. The following characteristics were displayed: maximum applied force and maximum compressive stress.
Scanning electron microscopy analysis (SEM) was used to study the structure and morphology of particles. A JSM-6390LV microscope was used with an INCA Energy dispersive microanalysis system at an accelerating voltage of 5 to 20 kV, equipped with back-scattered and secondary electron detectors and a Superprobe 733 electron probe microanalyser from JEOL (Japan). Analysis of the elemental composition of the samples and photographing in different types of radiation was performed using an INCA Energy dispersive spectrometer from OXFORD INSTRUMENTS (UK) mounted on a Superprobe 733 electron probe microanalyzer at an accelerating voltage of 25 kV and a probe current of 25 nA.
Thermogravimetric analysis was used to study the thermal behaviour of materials during heating. Thermogravimetric analysis was performed on a TGA / DSC 2 METTLER TOLEDO (Switzerland) instrument.
Heating temperature from 25 °C to 1,000 °C or 1,200 °C depending on the sample. The heating rate is 10 °C/min. In a crucible with a capacity of 70 μL from corundum (aluminum oxide), a sample of the powder of the studied material is poured. The number of samples is not regulated. The weight of the sample depends on the

density of the material and ranges from 30 to 50 mg. The device takes two characteristics: the change in mass of the sample upon heating and the change in heat flux. Dry air is used as a purge gas, and the air is used as a protective gas. Air consumption: up to 266 mL/min. Gas consumption: up to 54 mL/min.

3. Results and discussion

Currently, in many industrialized countries, the use of slag from metallurgical enterprises is more than 60 %. The construction industry uses mainly its astringent properties. The ceramic properties of the slag are much less well known. The phase composition, texture, and morphological features of crystalline phases affect the performance properties of ceramic products. Studies of the structure of ceramic materials show that after high-temperature training, the final phases present in the synthesized ceramics are cristobalite, albite, quartz, mullite, spinel. It is necessary to establish the laws of the genesis of ceramic materials containing metallurgical slag depending on the composition and processing conditions.
According to the selection of the press mass to ensure the maximum possible porosity and specific surface area, it was found that the highest content in the mixture to obtain the press mass should be represented by zeolite. In order to develop a specific surface in order to impart plastic properties to the press mass, additives of bentonite clay were introduced into the zeolite powder. The main components of metallurgical slag, as well as natural aluminosilicate raw materials, are oxides of silicon, aluminium and iron, which allows them to be used in the manufacture of ceramics as an additional component of the charge. The developed ceramic presses possess structural homogeneity, which is ensured by efficient mixing of the dispersed medium and the completeness of spontaneous dispersion of particles when interacting with water. Samples of synthesized ceramic materials are presented in Figure 1.

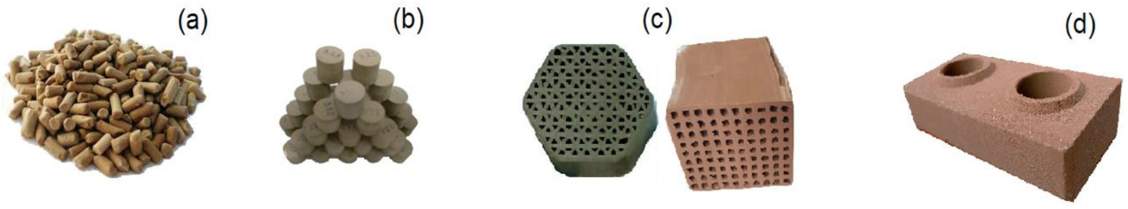

Figure 1: Prototypes of slag-containing ceramic materials in the form of (a) granules, (b) tablets, (c) blocks, (d) lego brick

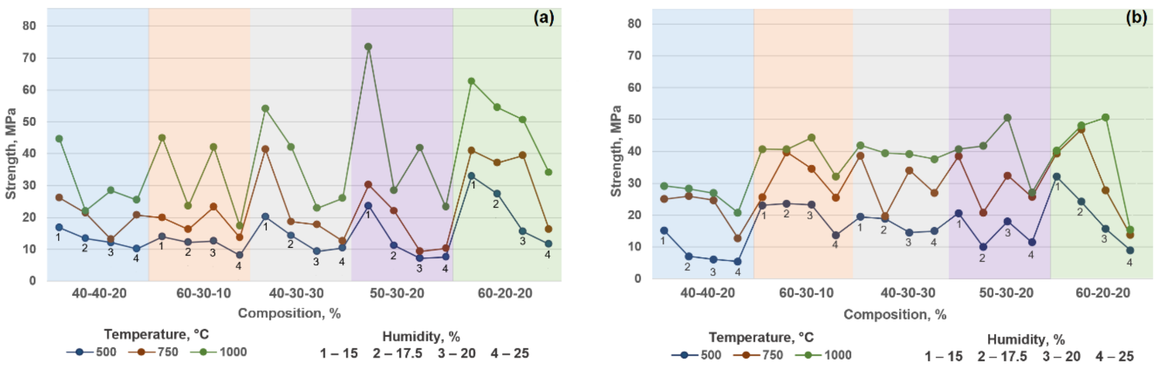

Figure 2: Strength of slag-containing ceramics (a) copper production, (b) lead production

Based on the data obtained, it is seen that the maximum mechanical strength of 73.43 MPa is observed in the sample obtained by mixing zeolite-bentonite-copper slag in the proportions of 50 % - 30 % - 20 %, at a moisture content of 15 % and an annealing temperature of 1,000 °C. The next strength value of 62.74 MPa is also a sample with copper slag at a moisture content of 15 % and an annealing temperature of 1,000 °C, but in proportions of 60 % - 20 % - 20 %. For samples with the addition of lead slag, the highest value is also at a composition of 60 % - 20 % -20 % and amounts to 50.64 MPa (calcination temperature 1,000 °C). The lowest

values are 5.49 MPa for systems with lead slag with a moisture content of 25 % and a treatment temperature of 500 °C.
It was found that the higher the calcination temperature, the higher the values of mechanical strength. From this, it follows that due to sintering processes, a crystalline structure is formed that provides the required mechanical strength of the synthesized ceramic samples from a mixture of zeolite-bentonite-slag.
Studies have been conducted to determine the optimal concentration of slag additives in the composition of the ceramic mass. The addition of slag from 10 % to 30 % of the total mass of the charge leads to an increase in mechanical strength; however, the greatest value of mechanical strength is observed with the introduction of 20 wt.% slag into the charge.
The effect of humidity on the strength characteristics of samples was also studied. The moisture content was 15, 17.5, 20 and 25 wt.%. It was found that with increasing humidity, the value of mechanical strength decreases in the series: Humidity: % 15 < 17.5 < 20 < 25. Strength: MPa 62.74 > 54.4 > 50.7 > 34.1. The highest values of mechanical strength are observed in samples with a moisture content of 15 % and a processing temperature of 1,000 °C. The smallest values are observed in samples with a humidity of 25 % and a treatment temperature of 500 °C. At the next stage, thermal changes in the structural parameters of the experimental batch at the lowest and highest values of mechanical strength were studied. Images of slag-containing ceramics based on zeolite and bentonite are presented in Figure 3.

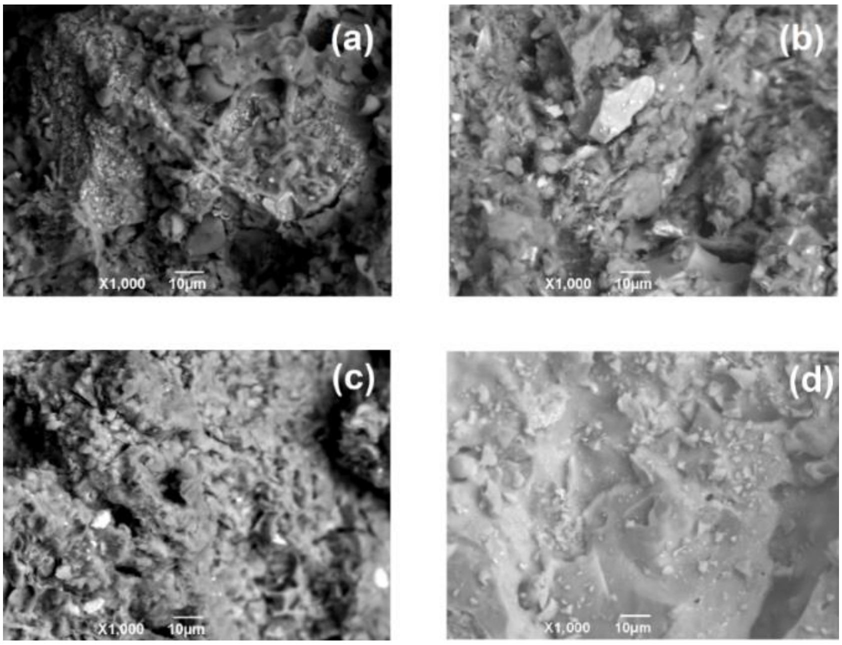

Figure 3: SEM images of slag-containing ceramics, with an increase of x 1,000: at 500 °C (a) copper production, (b) lead production, at 1,000 °C (c) copper production, (d) lead production

Figure 3a shows a cellular microstructure, the main morphological feature of which is the presence of isometric open cells; in Figure 3b, irregular-shaped slag grains that do not have direct contact with each other are visible. Figures 3c and 3d show the microstructure of the matrix with closed, round, or oval pores; in addition, there are irregular, mainly elongated, macropores in the boundary layer. Note that ceramic systems form a different structure during heat treatment up to 1,000 °C due to the formation of crystalline phases (mullite and cristobalite). The structure becomes more uniform and dense, molten crystals are visible, which contributes to an increase in reactivity during sintering of ceramics. Such a matrix structure has high mechanical strength.
Also, laboratory studies using the thermogravimetric method in the temperature range 100 °C – 1,170 °C were carried out. Thermogram samples are presented in Figures 4 and 5.

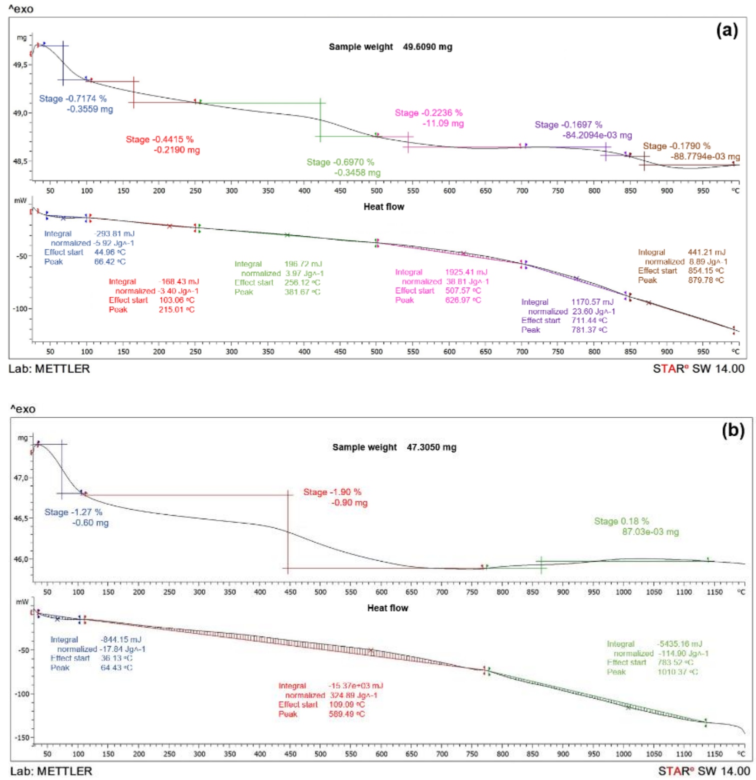

Figure 4: Spectra of slag-containing ceramics at 500 °C (a) copper production, (b) lead production

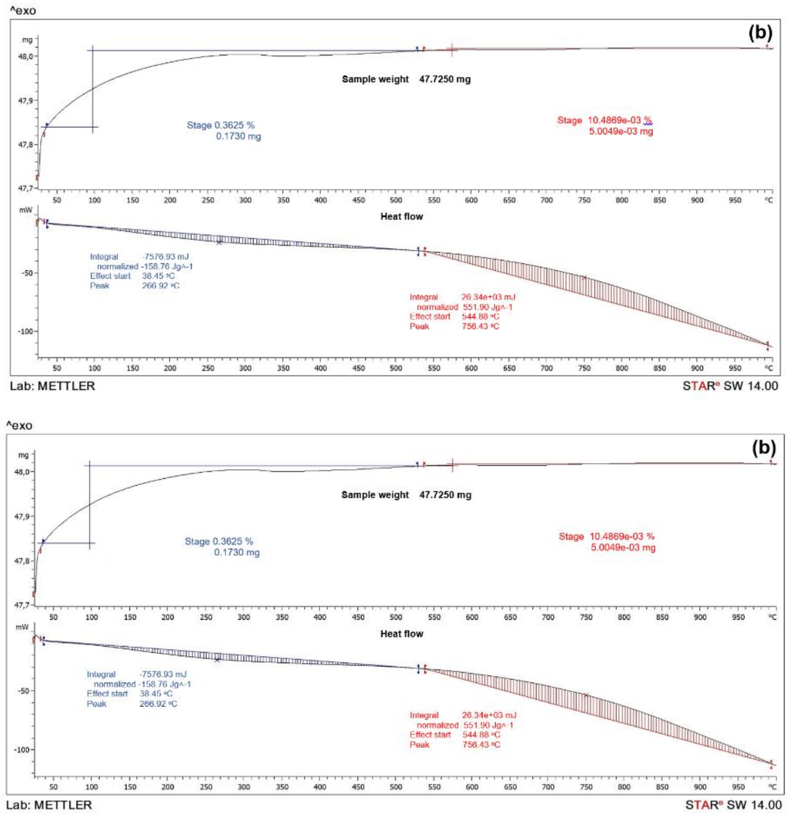

Figure 5: Spectra of slag-containing ceramics at 1,000 °C (a) copper production, (b) lead production

The calcination temperature affects the final stability of the samples. At an annealing temperature of 500 °C, samples 4 a and 4 b in the temperature range 26-100 °C showed an insignificant mass loss, and the mass fluctuations of the remaining samples were insignificant. The most thermostable can be recognized as sample 5 b, in which the mass loss in the temperature range 25 - 520 °C was 0.36 %, and there was no further loss of mass. In sample 5 c, in the temperature range 25 – 450 °C, the change in mass was 0.61 %, 450 - 1,000 °C – 0.1 %, and then at 1,162 °C the heat flux jumps, accompanied by a change in mass (0.29 %) and the formation of a certain amount of liquid phase. Analysis of the curves shows that in the temperature range 25 - 1,000 °C, the mass loss is not significant. On all samples, it is tenths of a per cent. It can be argued that in this temperature range, the samples are stable. An analysis of the heat fluxes of the samples also shows that they do not undergo strong changes. Only when sample 4 b is heated to 1,170 °C does the heat flux sharply decrease, which indicates the formation of a certain amount of the liquid phase and subsequent sintering of the powder. According to the data obtained, it was determined that the calcination temperature leads to an increase in the value of mechanical strength. At low temperatures, shrinkage of poorly calcined particles occurs, due to which the strength properties deteriorate. An increase in sintering temperature from 500 to 1,000 °C while contributing to an increase in the strength of synthesized ceramics.

4. Conclusion

The data obtained show an excellent possibility of using metallurgical slag for the synthesis of ceramics. Through analysis of the compositions, it was found that the addition of slag 10 – 30 % of the total mass of the mixture leads to an increase in mechanical strength. It was also found that an improvement in mechanical strength was observed with increasing firing temperature due to the formation of crystalline phases (mullite and cristobalite). The maximum value of mechanical strength is observed for the sample obtained by mixing zeolite-bentonite-copper slag in the proportions of 50 % - 30 % - 20 % at a moisture content of 15 %, an annealing temperature of 1,000 °C and is 73.43 MPa. The revealed regularities make it possible to predict the properties of the studied composite systems and create a platform for the synthesis of ceramic materials with the addition of metallurgical slags.

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