QUALITY MANAGEMENT OF NEW CERAMIC MATERIALS BY USING STATISTICAL EXPERIMENTAL DATA PROCESSING PROGRAMS

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Abstract: *In this paper, we consider the theoretical foundations of the synthesis of ceramic materials from natural aluminosilicates with the addition of technogenic materials (lead and copper slag) using powder metallurgy methods. The characteristics of the feedstock, properties are presented, the geographical deposits of natural components are shown. The possibility of obtaining pelletized, granular, and block ceramic materials based on natural and technogenic sorbents of Kazakhstan is shown by powder metallurgy methods.*

Keywords: CERAMICS, SYNTHESIS, WASTE, ALUMINOSILICATES, STRENGTH

1. Premises and Means of Solving the Problem

Currently, high-quality ceramic materials for various purposes based on unconventional substandard and / or technogenic raw materials are produced in a limited assortment. The fundamental limitations of the widespread use of natural raw materials and industrial materials for the synthesis of various new materials are attributed by specialists to their heterogeneous chemical and phase composition, the presence of impurities (compounds of iron, manganese, chromium, titanium, gold, silver, etc.) and the absence of an economic processing strategy.

Technogenic waste also has a complex composition, depending on the nature of the production process during which it is generated, and is mainly used in the construction or road industries as fillers in the form of dry mixes or as a binder and others [1,2]. Work on the secondary involvement of technogenic materials over the past 15 years has been carried out worldwide. At present, in some CIS countries, the production of ceramic products from natural clays and metallurgical waste in the form of facing slabs is mainly [3]. The joint use of these types of raw materials for the production of ceramic products based on them is practically not studied.

Kazakhstan has explored more than 100 different deposits of natural materials suitable for the synthesis of ceramic materials. The largest are presented in Figure 1. Their geographical location in the country is shown. These are 6 zeolite deposits - Taizuzgen, Chankanai, Sary-Ozek, Yuzhnoye, Daubabinskoye, Kyzyl-Adyr. Deposits of bentonite clays: Chardarya, Karagiye Depressions, Kushmurunskoe, Verkhne-Ubaganskoe, Andreevskoe, Taganskoe.

Fig.1 *Map of Kazakhstan's zeolite and bentonite deposits*

Many industrial industrial wastes (metallurgical slag) are close in their composition and properties to natural raw materials, so the use of industrial waste can cover up to 40% of the construction needs for raw materials. The use of industrial waste can reduce the cost of manufacturing building materials by 10-30% compared with their production from natural raw materials.

Recently, the unique chemical properties of metallurgical slag [4] have attracted attention to the production of materials for use in the environment for use as adsorbents, catalysts, or a source of active substances in environmental engineering.

2. Solution to the Problem

The development of new ceramic materials is material-intensive; therefore, the use of statistical programs for processing experimental data is an important tool for quality management. The use of software products allows us to reduce the number of practical experiments on the synthesis of ceramics and determine the optimal parameters for the synthesis of ceramics of their natural and technogenic raw materials to obtain materials with desired properties.

In this work, natural aluminosilicates in the form of zeolites and bentonite, industrial materials of metallurgical enterprises of Kazakhstan (slag of lead and copper production) were used as objects of study.

The involvement of natural and man-made raw materials should be preceded by studies of the composition of the material, structure and properties. A physical and chemical study made it possible to obtain information on the material filling of the samples, to trace the sequence of thermal degradations and to determine the composition of volatile components. It was established that the matrix of synthesized materials is formed from clay, and the aggregate from finely dispersed technogenic raw materials. Such a matrix structure has high strength. Based on the data of X-RAY phase and differential thermal analyzes, the stability regions of the studied samples during heat treatment are determined, which made it possible to synthesize materials with desired characteristics.

The production of ceramic products from natural and man-made raw materials is possible subject to preliminary fine grinding [5]. Therefore, the synthesis of ceramic materials was performed on the basis of the classical methods of powder metallurgy, in which molding compounds were prepared from the starting substances in the form of powders, which were then extruded and / or pressed with thermal training at each stage.

A technological scheme has been developed that reflects the logical sequence of work (Figure 2), starting with the preparation of the starting materials and ending with the receipt of new materials from natural and man-made materials.

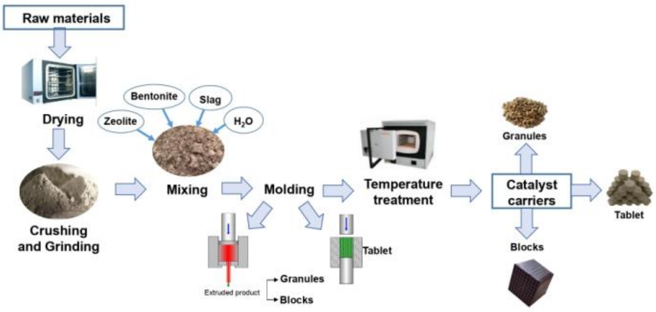

Fig.2 *The technological scheme of the synthesis of ceramic catalyst supports*

In the process of ceramic synthesis, to obtain products with desired properties, it is necessary to select the composition of the molding mixture. Such work involves the implementation of a large volume of experiments with obtaining a significant amount of experimental data requiring systematization. An important tool for managing the quality of synthesized new ceramic materials is the use of statistical programs for processing experimental data, for example, Statistica, Statgraphics, and others [6]. The use of software products allows us to reduce the number of practical experiments on the synthesis of ceramics and determine the optimal parameters for the synthesis of ceramics of their natural and technogenic raw materials to obtain materials with desired properties.

Statistical programs evaluate simultaneously the impact of several factors on the final required function. In our case, the controlled factor was the value of the mechanical strength of the synthesized ceramic samples. Influencing factors are the composition of the mixture, the dispersion of the components of the mixture, humidity, calcination temperature, the magnitude of the load during pressing, the design of technological equipment and others.

3. Results and discussion

In ceramic technology, three methods of forming products are used: from plastic masses, semi-dry pressing, and slip casting. The method of mass preparation also depends on this: for plastic molding, plastic masses with a moisture content of 18-22% are prepared, for semi-dry pressing masses with a moisture content of 6-9% are prepared, and for slip molding, with a humidity of 45-55%.

The masses are selected according to the mineralogical composition, setting the required ratio of clay, quartz, feldspars and other additives. Mass preparation is carried out more often by the weighted dosage of the components according to the approved recipe. It gives a more accurate ratio than volumetric.

The synthesis and heat treatment conditions of the contacts were maintained the same; only the composition varied. The natural zeolites of the Chankanai (Ch), Sary-Ozek (C) and Taizhuzgen (T) deposits, as well as the bentonite of the Tagansky deposit, were selected as natural raw materials. Zeolites and bentonite clays have a similar chemical composition, are represented by aluminosilicates containing oxides of alkali and alkaline earth metals. Bentonite was used as a binder component. When varying the composition of the experimental batch of natural and technogenic raw materials, the following markings were used: when copper slag was added, the "Cu" index was assigned, for example, T_{Cu}, Ch_{Cu} and S_{Cu}, and when the lead slag was added, the "Pb" index (Table 1).

Table 1: *Marking of samples from natural and technogenic materials*

1	Taizhuzgen zeolite + bentonite + lead slag	T_{Pb}
2	Taizhuzgen zeolite + bentonite + copper slag	T_{Cu}
3	Sary Ozek zeolite + bentonite + lead slag	C_{Pb}
4	Sary Ozek zeolite + bentonite + copper slag	C_{Cu}
5	Chankanai zeolite + bentonite + lead slag	Ч$_{Pb}$
6	Chankanai zeolite + bentonite + copper slag	Ч$_{Cu}$

The manufacture of granular materials includes the stages of preparation of the initial mixture, its extrusion in the form of granules and sintering. A plastic mass suitable for this method must have certain structural and mechanical properties, due to which it becomes less viscous, acquires plasticity and can be forced through a matrix. Under the influence of mechanical stresses, the plastic strength decreases, and after the release and release of stress, its thixotropic recovery occurs. The mixture was prepared of various composition and wetin the range up to 20 mass. % (wet = 15 wt.%; 17.5 wt.% and 20 wt.%). The prepared mass, satisfying the plasticity requirements, was pressed through the matrix with the formation of extrudates with a diameter of 2.5, 4, 6 mm, depending on the size of the matrix used. The obtained granules were dried and calcined in a muffle furnace at a temperature from room temperature to 500 °C, 750 °C and 1000 °C.

Statistical processing of experimental data on the influence of the composition of the molding material on the mechanical strength of the synthesized ceramic was performed. The results of the study, obtained by varying the nature of the zeolite, humidity in the composition of the press mass and the calcination temperature of the finished samples, processed using the Statistica program, are graphically presented in Figures 3-5.

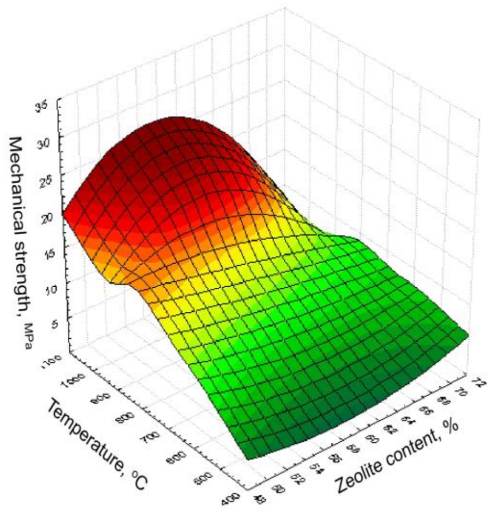

Fig.3 *The dependence of the mechanical strength of the catalyst carrier on the zeolite content and temperature treatment (Wet = 15 %)*

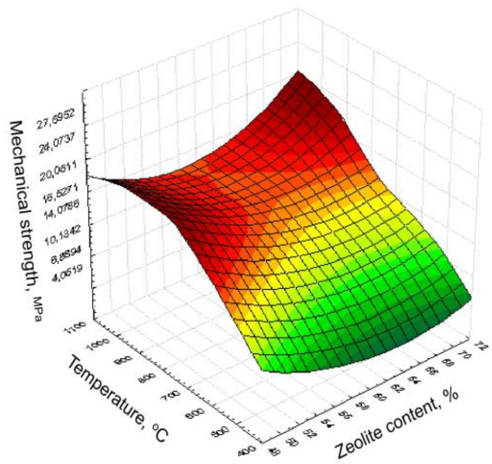

Fig.4 *The dependence of the mechanical strength of the catalyst carrier on the zeolite content and temperature treatment (Wet = 17.5 %)*

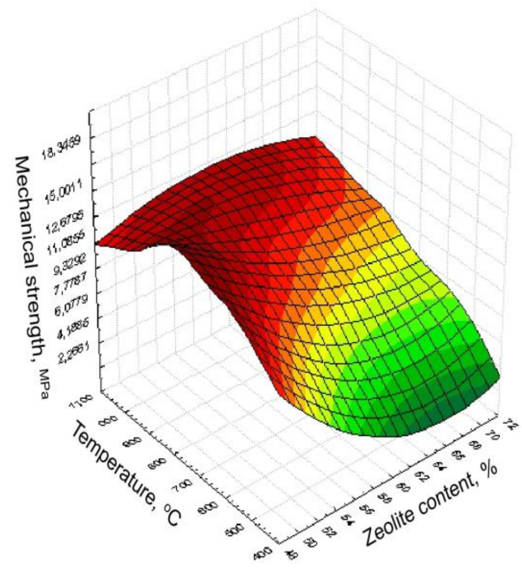

Fig.5 *The dependence of the mechanical strength of the catalyst carrier on the zeolite content and temperature treatment (Wet = 20 %)*

According to the data obtained, the optimum moisture content of the press powders was determined. It was found that an increase in pressing pressure and annealing temperature lead to an increase in the value of mechanical strength. Wet, providing the necessary strength, should be within 17.5%. At low temperatures, shrinkage of poorly calcined particles occurs, due to which the strength properties deteriorate. An increase in the temperature treatment from 500 to 750 °C in the manufacture of a catalyst carrier contributes to an increase in its strength.

Using the Statgraphics graphical editor (Figure 6), we studied the effect of pressing pressure on the mechanical strength of the samples.

As can be seen in Figure 6, with a change in wet from 15% to 17.5%, an increase in the mechanical strength index with an increase in temperature is observed for a composition containing 60% zeolite. With a further increase wet up to 20% in samples containing 60 and 70% zeolite with an increase in sintering temperature, an increase in mechanical strength is observed. While at a zeolite content of about 50%, a decrease in strength occurs. Thus, ceramics containing 60% zeolite with the addition of 40% bentonite clay are recommended as the material for the catalyst carrier. The results are explained by the fact that zeolite particles, having a porous structure and surface, contacting each other in the bulk of the material form a rigid reinforcing structure, and bentonite, possessing astringent properties, increases the strength of the product. A change in this structure leads to a decrease in the strength of the material.

It is impossible to assess the prospects for using natural aluminosilicates and metallurgical slags for the manufacture of gas purification catalyst carriers without a preliminary study of the structural and mechanical properties. Therefore, according to the results of experimental studies, the optimal charge compositions based on a zeolite-bentonite mixture with the addition of technogenic raw materials to obtain ceramic materials with a matrix structure (wt.%) With a ratio of components of 60:20:20, respectively, were determined.

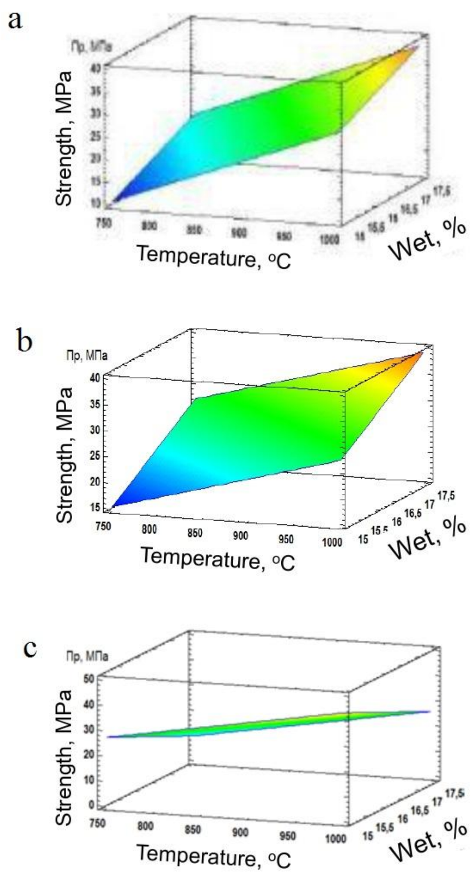

Fig.6 *The effect of temperature treatment and wet on the mechanical strength of the catalyst carrier depending on the zeolite content:*
а – Zeolite:Bentonote = 50:50; б – Zeolite:Bentonote = 60 : 40;
в – Zeolite:Bentonote = 70 : 30

Figures 7-9 show the research data on the strength of ceramic catalyst carrier depending on the composition of the charge and the calcination temperature. To determine the mechanical strength, a batch of samples was prepared from zeolite: bentonite: slag mixture in a ratio of 60:20:20 (Z: B: S (Cu) and Z: B: S (Pb)).

Among the series of samples with the addition of copper slag with various zeolites, the composition based on Taizuzgen zeolite has the highest strength. It should be noted that at a heating temperature of 500 °C the strength of the sample with the Taizhuzgen zeolite is the same with Sary-Ozek and Chankanai (15-17 MPa). At an annealing temperature of 750 °C, the indicator for all three samples increased. An increase in temperature to 1,000 °C led to a twofold increase in the strength value for the sample with Taizuzgen zeolite (T_{Cu}) and amounted to 54 MPa, while for Ch_{Cu} and S_{Cu}, the strengths were 25.4 and 28, respectively. The smallest strength after heat treatment was observed for a sample of the Chankanai deposit synthesized with zeolite.

The introduction of a lead plant slag instead of a copper plant slag into the composition of the charge significantly affected the properties of the synthesized materials. In this case, the maximum value of mechanical strength at 1000 °C is also observed for samples based on the Sary-Ozek zeolite (S_{Pb} = 55.4 MPa), and for T_{Pb} and Ch_{Pb} 32.4 and 49.7, respectively.

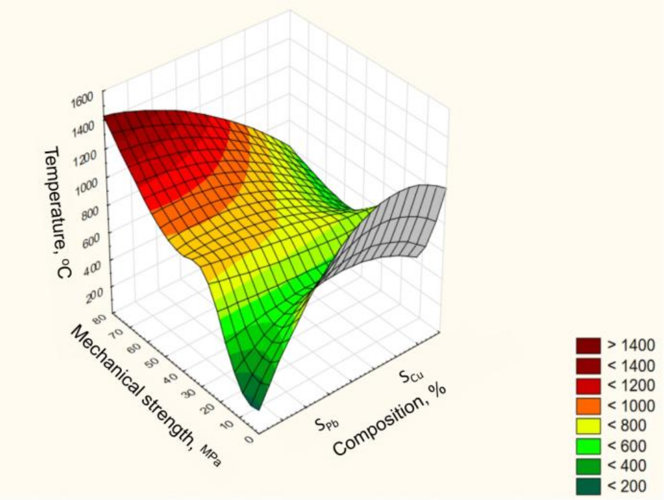

Fig.7 *The dependence of the mechanical strength of the catalyst carrier on the composition and sintering temperature (composition of the Sary-Ozek Zeolite + Bentonite + Slag)*

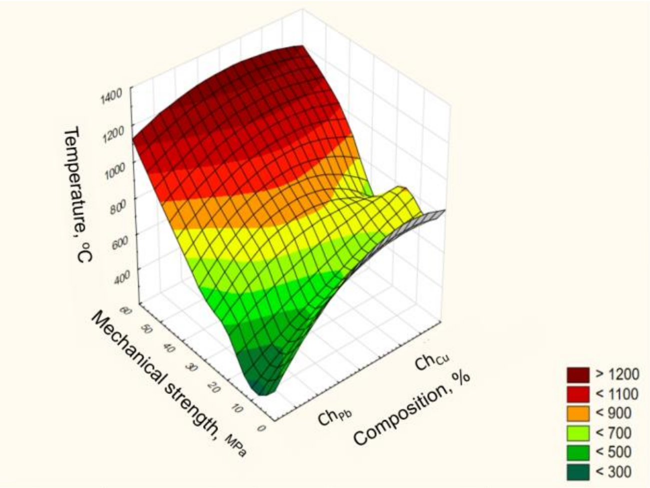

Fig.8 *The dependence of the mechanical strength of the catalyst carrier on the composition and sintering temperature (composition of the Chankanai Zeolite + Bentonite + Slag)*

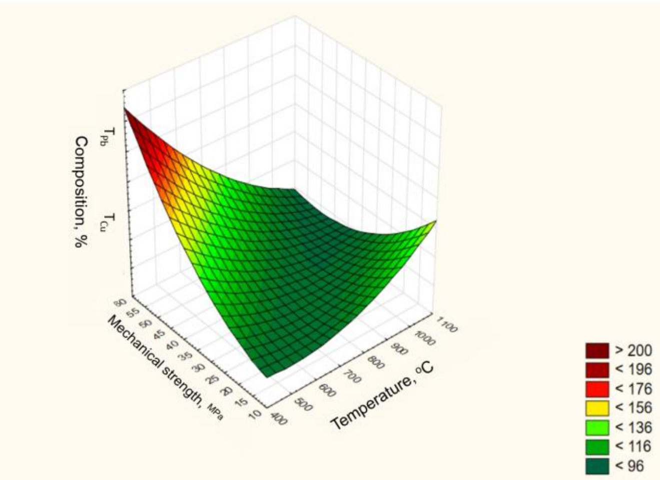

Fig.9 *The dependence of the mechanical strength of the catalyst carrier on the composition and sintering temperature (composition of the Taizhuzgen Zeolite + Bentonite + Slag)*

It is shown that the mechanical strength of the samples synthesized under the same conditions by varying the nature of the zeolite and slag is quite high. It should be noted that high-temperature training of samples up to 1000 °C contributes to an increase in strength. According to the data obtained, it was determined that the optimum value of mechanical strength is observed for the sample obtained by mixing bentonite slag with the zeolite of the Taizhuzgen deposit and is more than 30 MPa, which corresponds to the requirements for catalyst supports.

4. Conclusion

The synthesis of ceramic materials was performed on the basis of the classical methods of powder metallurgy, in which molding compounds were prepared from the starting substances in the form of powders, which were then extruded and / or pressed with thermal training at each stage. Previously, the components of the mixture were subjected to fine grinding to a fraction of 0.01 mm to obtain a homogeneous mixture. The initial charge components — natural zeolite and bentonite - were mixed with technogenic products represented by slag or dust in proportions of 60:20:20, respectively.

An important characteristic of the charge is the moisture capacity of the starting components and the resulting mixture. The moisture content was varied in the range of 15 ÷ 20% to ensure the required molding moisture and satisfactory ductility. After mixing, the prepared mixture was sent to molding by compression in the form of tablets or by extrusion in the form of granules. The resulting materials were kept in air, and then subjected to heat treatment in a muffle electric furnace in the temperature range 500–1000 °C.

The compositions and properties of the feedstock and ceramic materials synthesized based on them were studied. The results obtained are a prerequisite for creating a technology for the synthesis of new ceramic materials from a mixture of natural and technogenic raw materials.

A batch of synthesized samples was tested in catalytic oxidation reactions of methane and / or carbon monoxide. It was found that all synthesized contacts provide catalytic activity in the reactions of oxidative catalysis of carbon-containing toxic components and can become basic models for which, by improving the preparation method, it is possible to develop a technology for the synthesis of ceramic materials for use in environmental catalysis.

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