Physicochemical Principles of CO₂ Sequestration in Building Materials Based on Nepheline Slime

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Abstract. The results of theoretical and experimental studies to determine the possibility of sequestration of carbon dioxide in building materials based on nepheline slime are presented. The main principles of the technology for the utilization of CO₂ in the building materials and products industry are presented, in particular, on the basis of nepheline slimes produced during the production of alumina from nepheline ores. Using the method of thermal analysis, the efficiency of carbonization of prototypes in a medium of increased concentration of carbon dioxide was proved. Optimization of technological parameters for the production of carbonized samples based on nepheline slime was carried out using the methods of optimal experiment planning. The equations of regression of strength, density, water resistance and water absorption of prototypes are obtained depending on the main technological factors. Optimal technological parameters for the production of a carbonized material with the necessary properties were established. The physicomechanical characteristics of the prototypes hardened in a medium with a high concentration of carbon dioxide are determined. A forecast is made regarding the possibility of applying the results obtained in the production of building materials and carbonization hardening products based on nepheline slime.

1. Introduction

One of the priority directions of development of science and technology is rational nature management, as well as resource and energy saving. This direction can be fully realized in the construction materials industry, through the use of secondary waste and construction products based on them. Such wastes include nepheline slime formed during the production of alumina oxide from nepheline ores. Nepheline slime is one of the most common and insufficiently mastered varieties of recycled materials. At the present stage of development of methods for the integrated use of natural mineral raw materials, only 25% of nepheline slime is used in the production process as secondary raw materials. The remaining part is sent to the multi-tonnage dumps and, accordingly, is the source of environmental hazard in a certain area of the terrain. Insignificant consumption of this kind of secondary raw materials is mainly accounted for by the cement industry, where nepheline slime is one of the components for the production of portland cement. This is due primarily to the low hydraulic activity of slimes. However, if you broaden the horizons of methods of organizing the hardening of this product, you can significantly increase the percentage of its use in the building materials industry. Therefore, it is of interest to study the possibility of carbonate hardening of nepheline slime and products based on it, obtained by pressing.
2. Analysis of publications, materials, and methods
Features of the chemical and mineralogical composition of nepheline slime make its use in the production of building materials promising. Of the minerals, the nepheline slime contains partially hydrated belite 2CaO·SiO₂ in its β modifications (80-85%). As impurities there are dicalcium ferrite, tricalcium hydroaluminate, calcium and sodium aluminosilicates, and calcium carbonate. Loss on ignition is up to 5%. Currently, the main areas of processing nepheline slime include the production of portland cement, glass and ceramic products, materials used in road construction. At the present stage of science development, the most researched direction of processing this secondary raw material is the production of portland cement clinker and cement [1-4].

In Russia, cement from nepheline slime is produced by three plants: the Achinsk Cement Plant, the Pikalyovo Cement of the company Eurocement and the Volkov Cement Plant of the Pikalyovo Soda Company. The nepheline slime is a more stable product compared to other raw components of the raw mix for the production of cement clinker. The use of slime as a raw material component allows increase the clinker yield by 20%, and the efficiency of the furnaces by 25-30% in comparison with the same parameters for a classical raw mix. In this case, the cement industry processes only up to 20% of the total amount of nepheline slime formed. In small quantities, nepheline slime is used to fortify ground bases in road construction [5-7]. It is known that hydrothermal treatment accelerates the hardening of nepheline cement several times, and also affects the strength of the samples, for example, steaming increases the strength of prototypes by 1.5-2 times, and autoclave treatment by 2.5-3 times [3, 8]. However, nepheline slime was not widely used in the production of silicate autoclave products, probably because of the poor knowledge of the use of slime in such technologies.

Currently, foreign scientists are actively researching the mechanism of carbonate hardening systems based on cement [9-13]. It was found that cements with high content of belite more actively absorb carbon dioxide with the formation of stable calcium carbonate than alitic cements. In this case, after the artificial carbonization process in systems based on belitic cements, the total porosity decreases substantially, and a significant number of closed pores appears. Accordingly, the physical and mechanical characteristics of samples based on belite cements were 1.5-2 times higher than those for samples based on alitic cements, as well as samples based on belite cements hardened in natural conditions without preliminary carbonization. It was also found that the artificial carbonization of alitic cements promotes the formation of cohesive porosity in the samples, as a result of which the water absorption of the carbonized material increases and its frost resistance decreases. The degree of carbonation of the samples by 28 days of hardening reached 77-92% with XRD analysis showing an increase in the peak intensity of calcite for carbonized samples in comparison with samples not subjected to carbonization. These studies indicate a high potential of carbonate hardening for systems containing large amounts of belite, which include nepheline slime.

Other studies have established [14-17] that the process of active carbonation of calcium hydroxide, as well as hydrated cement silicates, occurs at a water content of a mixture of not more than 15% by weight. Within 2 hours of carbonization, the samples absorb 19.8% by weight of CO₂, and the compressive strength was 28.6 MPa. Data on changes in porosity dynamics of the samples are also consistent with studies [9-13]. Quantitatively, the total porosity decreases by 34-76%, depending on the carbonation time. In this case, the number of macropores decreases mainly, while the amount of micro and mesopores increases due to the formation of nanoscale calcium carbonate crystals.

The authors of this work carried out a number of studies on the process of artificial carbonization of lime-based systems [18-20]. It is established that Ca(OH)₂ enters into an active chemical interaction with carbon dioxide only at the optimum water content of the system. Under these conditions, the Ca(OH)₂ transition to CaCO₃ takes no more than 3 hours, and the obtained artificial carbonate stone is characterized by high physical and mechanical properties and can be used for the production of various building materials and products, including facing materials.

The analysis of the literature sources made it possible to conclude that research by scientists around the world aimed at studying the artificial carbonization of systems based on cements and lime has positive results. At the same time, waste from the production of alumina in the form of nepheline
slime is a valuable secondary raw material for the development of methods for the sequestration of CO₂ into building products based on nepheline slime.

3. Purpose and statement of the research task
In connection with the foregoing, the purpose of this work is to determine the possibility of obtaining high-quality construction products based on nepheline slimes of carbonate hardening, by establishing regularities in the interaction of carbon dioxide with minerals of nepheline slime, the formation of physico-mechanical properties of the material after its artificial carbonization and the stability of the properties obtained over time.

4. The main section with the results and their analysis
For research, nepheline slime formed as a result of the activities of the company «BazelCement-Pikalyovo» was used. Chemical analysis of the raw material was determined by X-ray fluorescence analysis using an Epsilon 3XLE ED spectrometer (PANalytical). The results of the analysis are presented in Table 1.

| Title       | CaO   | MgO   | SiO₂ | Al₂O₃ | Fe₂O₃ | Na₂O  | K₂O   | SO₃ |
|-------------|-------|-------|------|-------|-------|-------|-------|-----|
| Nepheline slime | 61.77 | 0.82  | 27.83| 2.34  | 2.51  | 1.15  | 0.88  | 0.07|

Thermal analysis of the nepheline slime was carried out using a high-temperature synchronous TGA/DTA/DSC STA 8000 system of the Perkin Elmer in a temperature range of 30-1000°C at a heating rate of 10°C/min in a nitrogen medium.

According to the data of the thermal analysis (see Figure 1), two pronounced endothermic effects at temperatures of 672 and 771°C are present in the presented derivatogram, as well as a slight thermal effect at a temperature of 828°C. The two lower temperatures correspond to the presumably complete dehydration of calcium hydrosilicates. The endothermic effect at 828°C corresponds to the dissociation of calcium carbonate, which is present in the mixture in an amount of 0.2-0.8% by weight. The total weight loss was 4.6%.

To determine the possibility of carbonate hardening of nepheline slime from it, prototype cylinders were made from it by pressing. The diameter and height of the samples were 30 mm. The water content of the molding mixture ranged from 0 to 25% by weight, the specific pressing pressure was 30 MPa. The obtained samples were subjected to artificial carbonization in a specially designed chamber. The thermal analysis of the carbonized samples is shown in Figure 2.
As can be seen from Figure 2, the nature of the DTA curve undergoes significant changes. The derivatogram contains three distinct endothermic effects at temperatures of 159, 702 and 851°C. The first effect corresponds to the removal of adsorption water. The endo-effect at 702°C corresponds to the dehydration of calcium hydroxide, but it is also possible to decompose amorphous calcium carbonate, confirmed by studies [21]. The loss of mass at 851°C corresponds to the dissociation of calcium carbonate, which is present in the mixture in an amount of 10.5% by weight. The total weight loss was 15.04%.

Analyzing the thermal analysis of nepheline slime before and after carbonization, it can be concluded that the process of binding of CO₂ by minerals of the slime is intensive, with the formation of stable calcite crystals. This conclusion is also confirmed by a significant change in the physico-mechanical characteristics of the prototypes. So the compressive strength after carbonization for 3 hours increases to 40-45 MPa, in comparison with 12.7 MPa without carbonization. The average sample density also increases and water absorption decreases. However, the preparation of samples by pressing from pure nepheline slime has the disadvantage of a low initial raw strength of the material. Its value does not exceed 0.1-0.25 MPa. This value is not sufficient for technological movement of freshly formed products. To increase this index, dispersed limestone wastes were added to the nepheline slime, formed during the stone-cutting and crushing of natural limestone.

To determine the optimal technological parameters for the production of a carbonized material based on the nepheline slime with the addition of disperse limestone with the necessary physico-mechanical properties, methods for the optimal design of the experiment were used. Optimization was carried out on the basis of the orthogonal central composition plan. The initial optimized factors affecting the physico-mechanical properties of the carbonized material under study were the initial water content of the raw mixture and the amount of dispersed limestone. The conditions for planning the experiment are presented in Table 2.

| Name of factor                        | Unit of measurement | Code | Variation levels |
|---------------------------------------|---------------------|------|-----------------|
| Water content of the mixture          | %                   | X1   | -1   0  1       |
| Amount of limestone                   | %                   | X2   | -1   0  1       |

As optimization parameters after carbonization, we took: Y1 – the density after carbonization and drying, kg/m³; Y2 – compressive strength after carbonization and drying, MPa; Y3 – water absorption by mass, %. The planning matrix and the experimental data are presented in Table 3.
The experimental data of Table 3 was processed using StatSoft STATISTICA software. As a result, regression equations were obtained that describe the dependence of the change in strength, density, and water absorption by weight of the carbonized material on the initial water content of the raw mixture and the amount of dispersed limestone. The equations have the following form:

\[
Y_1 = 1.988 + 0.713X_1 - 0.0087X_2 + 0.0026X_1^2 - 0.0587X_2^2 - 0.165X_1X_2
\]  (1)

\[
Y_2 = 28.28 + 7.8X_1 - 0.03X_2 - 5.06X_1^2 - 3.89X_2^2 - 5.49X_1X_2
\]  (2)

\[
Y_3 = 15.507 - 0.34X_1 + 0.52X_2 - 1.53X_1^2 - 0.028X_2^2 + 0.44X_1X_2
\]  (3)

According to the equations (1-3), an increase in the water content of the raw mix (X1) contributes to the strength and density of the samples, as well as to a decrease in water absorption. Accordingly, increasing the amount of dispersed limestone reduces density and strength and increases water absorption. Addition of limestone has the greatest value on the strength of carbonized limestone. It should be noted that the maximum strength value obtained during the mathematical experiment was 31.8 MPa, which is significantly lower than the strength of pure carbonized sludge (40-45 MPa). However, the strength of the samples immediately after pressing (raw) increased and varied within 0.8-1.8 MPa, depending on the amount of limestone, which corresponds to regulatory requirements.

5. Conclusions

Analyzing the physicomechanical characteristics of the carbonized samples of Table 3, it can be concluded that the obtained data are sufficient for a more detailed study of the artificial carbonization of systems based on the nepheline slime. The values obtained during the experiment meet the regulatory requirements for wall products, including facing. At this stage of studying these systems, it can be argued that the potential of the nepheline slime at the current stage of its processing is not fully utilized. The conducted studies prove the possibility of CO₂ sequestration in building materials and products based on nepheline slime, obtained by pressing. This technology will make it possible to more comprehensively use the waste products of alumina oxide production and additionally capture and use in the process as a raw material component released into the atmosphere carbon dioxide. This approach will allow us talk about biopositivity and resource saving in the building materials industry. This work was partially supported by the V.I. Vernadsky Crimean Federal University Development Program for 2015 – 2024

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