Application of Ceramsite Dust as an Active Pozzolan Additive in the Cement-Based Compositions

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Abstract. Ceramsite (expanded clay) dust is a waste material, obtained in large volumes all over the world as a by-product of ceramsite gravel production. With the development of the construction industry and the ever-growing amount of ceramsite dust disposed in the landfills, the recycling and rational use of this material is becoming a relevant issue. The currently available technologies for the ceramsite waste recycling are very limited, this is why it is necessary to develop a new effective way to involve this waste into the new production. The present research is based on the assumption that ceramsite dust can be applied effectively as an active pozzolanic mineral additive in the cement-based materials. In order to study the composition, structure and properties of the original clay used for the production of ceramsite, as well as the dehydrated clay dust, captured in the dust removing systems of kilns at ceramsite gravel plants, physical and chemical analysis methods were used. Based on the experimental data, the influence of ceramsite dust on the structure and properties of cement compositions was evaluated. Mechanical tests of the samples showed that the introduction of ceramsite dust as an additive in the amount of 3% by the cement weight leads to an increase in compressive strength by 23% in comparison with the reference composition. The paper also presents the results of microstructural analysis, IR spectral analysis and differential thermal analysis of samples modified with the optimal amount of this microadditive. The study of the microstructure of the modified samples shows that the introduction of ceramsite dust into the composition of the cement stone does not only change the morphology of new formations, thus increasing the density of the structure, but also varies the mineralogical composition of the cement matrix with the formation of stronger and more water-resistant minerals in the form of calcium silicate hydrates and calcium aluminosilicate hydrates. This technology allows the recycling of waste from the production of ceramsite stone, thus improving the environmental situation and contributing to the creation of a circular economy.

1. Introduction

In recent decades, the constant tightening of environmental safety regulations and the growing involvement of the society into creating a circular economy has stimulated an increased demand for the development of new modes of the industrial waste disposal. Construction industry, being one of the largest industries worldwide, is creating millions of tons of different types of wastes, that need to be recycled and reused. Elements of demolished buildings are currently being disposed in the landfills, substandard materials are thrown away because their recycling is not economically effective. Even the original production of building materials is followed by significant emissions of waste of various compositions into the atmosphere, soil and water. Some of these emissions, however, are distinguished by increased hydraulic and pozzolanic activity, which makes it possible to reuse them as an active mineral additive for different types of building materials.
These artificial mineral additives include granulated blast-furnace slags, nepheline sludge, fuel ash and slag, clay and others [1, 2]. Obviously, the composition and properties of such additives are quite diverse. However, the one feature that they share is a large amount of active silica of amorphous structure, metakaolinite, alumina and dehydrated aluminosilicates, which can interact with lime in the cement past, creating hardly soluble compounds by the reactions [3]:

\[
\begin{align*}
    n \text{SiO}_2 + m \text{Ca(OH)}_2 + p \text{H}_2\text{O} & \rightarrow m \text{CaO} \cdot n \text{SiO}_2 (p + 1) \text{H}_2\text{O}; \\
    \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{Ca(OH)}_2 + \text{H}_2\text{O} & \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}
\end{align*}
\]

Traditionally, the amount of additive in the clinker composition is directly proportional to its activity: additives of sedimentary origin are introduced into pozzolanic cement in an amount of 20–30%, and additives of volcanic origin, clays, ash and others - in the range of 25–40%. At the same time, the cost of the modified material is lower than the cost of traditional Portland cement due to the fact that the production of clinker is more expensive than the whole course of extraction, crushing, grinding, drying and transportation of mineral additives. Kuzmenkov et al. [3] estimated that the introduction of each percentage of the additive reduces the cost of Portland cement by 0.2–0.8%.

Lower concentrations of mineral additives can also be used to modify the structure of cement-based materials [4]. In this case, the improvement of characteristics of the cement composites is achieved by changing the morphology of hydration products and the formation of a denser structure. It should be noted that the grinding method and the dispersion degree of such additives directly affect the phase composition of the hydration products [5].

Ceramsite (expanded clay) dust is a large-tonnage waste of the building materials industry, potentially suitable for modifying the structure and properties of concrete. It is generated in the course of the expanded clay gravel production and captured in the dust capturing systems of kilns: dust collection chambers, cyclones and filters (Figure 1).

Figure 1. Cyclones for expanded clay dust capturing: a) general view, b) principle of operation, c) a waste product - ceramsite dust

In modern conditions, most of this waste is transported to the dump, perniciously affecting the environmental situation. It has been calculated, that even according to the most conservative estimates, each of more than 300 enterprises for the production of expanded clay gravel in Russia produces 7-8 tons of ceramsite dust daily [6,7]. Undoubtedly, the disposal and recycling of this dust is a relevant problem.

Previously, a number of researchers [8, 9] stated that expanded clay dust can be used effectively as a pozzolanic mineral additive in cement, gypsum-lime and gypsum-cement compositions. At the same time,
the specific mineralogical composition, high dispersion and porosity, as well as the nature of the surface of the expanded clay dust grains determine its high water absorption and pozzolanic activity, and therefore it is advisable to use it together with plasticizers [10].

At the same time, it should be noted that the chemical and mineralogical composition and dispersion degree of the expanded clay dust can significantly vary depending on the composition of raw clay materials, technological modes of ceramsite production and the collection method [11].

2. Materials and methods

In this research, expanded clay dust was used as an active mineral additive for the modification of cement-based compositions. The chemical composition of this additive is presented in Table 1.

Table 1. Chemical composition of the ceramsite dust.

| Component | SiO₂ | TiO₂ | A₁₂O₃ | Fe₂O₃ | MnO | CaO | MgO | Na₂O | K₂O | P₂O₅ | SO₃ | LOI* |
|-----------|------|------|--------|-------|-----|-----|-----|------|-----|------|-----|------|
| Content, %| 61.35| 0.84 | 16.23  | 7.94  | 0.14| 3.6 | 2.81| 0.72 | 2.03| 0.2  | 0.56| 5.50 |

* LOI – loss on ignition

In order to determine the possible application fields of this fine-grained material in the building materials industry, a comprehensive study was carried out using the following methods:

- particle size distribution analysis of expanded clay dust on a SALD-7500nano analyzer manufactured by Shimadzu with the 7 nm to 800 μm measurement range;
- X-ray phase analysis of expanded clay dust using a general-purpose diffractometer MiniFlex 600 manufactured by RIGAKU (Japan) with a graphite monochromator and a copper anti-cathode;
- thermal analysis of the original clay and expanded clay dust on a TGA/DSC1 Starsystem derivatograph manufactured by Mettler Toledo in the temperature range from 60° C to 1100 °C with the heating rate of 30 °C/min;
- IR-spectral analysis of the initial clay and expanded clay dust on a Shimadzu IRAffinity-1 spectrometer in the frequency range 400 - 4000 cm⁻¹;
- microstructure analysis on a scanning electron microscope Quattro ESEM Thermo Fisher Scientific with a resolution of up to 0.8 nm.

The study of the properties of expanded clay dust on a laser analyzer (Figure 2b) showed that the average particle size is 4.159 μm. However, according to the microstructural analysis of the dust (Figure 2a), the particle size distribution is in the range of 30 to 150 μm. This can be explained by the fact that during the lazer particle size analysis, the large and heavy ceramsite dust pieces settled as sediment and were not taken into consideration. In this case, the microstructural analysis proved to be more reliable.

The phase composition of expanded clay dust was determined using X-ray phase analysis (Figure 3) on a MiniFlex 600 general-purpose diffractometer. For decoding, ASTM standards were used.
Based on X-ray spectral analysis, silicon oxide SiO$_2$ ($d_\alpha = 3.345$ Å) predominates in the composition of dehydrated clay. There are feldspars (orthoclase: $d_\alpha = 3.19$ Å), reflections corresponding to calcium carbonate CaCO$_3$ ($d_\alpha$, Å = 3.04), calcium oxide CaO ($d_\alpha = 2.41$ Å) and montmorillonite ($d_\alpha =$4.48 Å).

The phase and mineralogical composition of expanded clay dust (wt.%) includes non-dehydrated and dehydrated clay minerals (hydromica, montmorillonite) - 45; quartz - 24; feldspars - 6 and X-ray amorphous phase - 25.

In order to determine the properties of the initial clay and the ceramsite dust, physical and chemical studies were carried out using differential scanning calorimetry and thermogravimetric analysis.

The TGA and DSC spectra of clay and ceramsite dust show endothermic processes at 164 ºC, 201 ºC, and 145 ºC, associated with the dehydration of clay minerals. Further heating, followed by the characteristic gradual decrease in the mass of the sample, reflected in the TGA curve, is associated with the removal of adsorption and constitutional water from the clay structure. At the same time, the weight drop of ceramsite dust is insignificant up to a temperature of 700 ºC. Compared to it, the removal of constitutional water from montmorillonite in the composition of the original clay (Figure 4a) at a temperature of 700-820 ºC is quite noticeable.
Besides, the DSC curve of clay (Figure 3) shows an endothermic effect at a temperature of 581 °C. Similar peaks are noted on the DSC curve of ceramsite dust, but they occur at temperatures of 509 °C and 579 °C. Both effects are associated with the process of recrystallization of quartz in the composition of clay with the transition of β-quartz to α-quartz. These effects can also appear due to the removal of illite constitutional water.

Characteristic for the DSC curve of ceramsite dust is the endothermic effect at 784.7 °C, which indicates the dehydration of minerals in the dust, which, compared to original clay (807 °C), occurs quite early. This can be explained by the fact that the initial heat treatment of montmorillonite initiated a change in the lattice of the minerals, due to which the removal of the constitutional water upon repeated heating during DTA runs at lower temperatures.

The endothermic effect at a temperature of 879 °C for the original clay and 879.6 °C for ceramsite dust is associated with the destruction of the crystal lattice and amorphization of clay minerals.

To confirm the results obtained by the differential scanning calorimetry, the analysis of the initial clay and expanded clay dust was carried out using Infrared spectroscopy in the frequency range 400-4000 cm⁻¹ (Figure 5).

The IR spectrum of the original clay (Figure 5b) contains absorption lines corresponding to OH-stretching and bending vibrations of free and bound water (3630.03 cm⁻¹, 3412.08 cm⁻¹, 1629.85 cm⁻¹),
silicate groups SiO$_4^{4-}$ (1028.06 cm$^{-1}$, 1002.98 cm$^{-1}$, 796.60 cm$^{-1}$, 474, 49 cm$^{-1}$) and carbonates CO$_3^{2-}$ (1425.40 cm$^{-1}$, 873, 75 cm$^{-1}$).

The shift of absorption lines in the frequency range 1028.06 - 1002.98 cm$^{-1}$ of dehydrated clay towards higher frequencies (1031.92 cm$^{-1}$) can be due to amorphization of clay minerals and their ability to interact with calcium hydroxide more actively.

The infrared absorption spectra of minerals of the montmorillonite group are characterized by a double absorption peak at 3620 and 3400 cm$^{-1}$, an intense peak at around 1032 cm$^{-1}$ and weak peaks at 920 and 842 cm$^{-1}$. The spectra of bentonite, a clay mineral, the main component of which is montmorillonite, and montmorillonite itself are practically the same. The quality of bentonite depends on the amount of montmorillonite in its content and the ionic form of montmorillonite. The difference is noted in the presence of intermediate absorption lines in the region of 1679...1600 cm$^{-1}$, as well as in a weak splitting of the peak at 1032 cm$^{-1}$, while the weak peak at 1105 cm$^{-1}$ is absent.

Thus, based on the research results, ceramsite dust can be considered as an additive, which consists of a thermally activated clay, containing clay minerals with an intact crystalline structure (relict non-dehydrated) and dehydrated clay minerals with a crystal structure of various degrees of defectiveness, as well as X-ray amorphous phase, including the products of thermal treatment of clay minerals, characterized by complete absence of crystallinity. These conclusions correlate with the results obtained by Khalilullin et al. [12, 13].

To assess the effect of dehydrated clay dust on the structure and properties of cement compositions, it was introduced in an amount from 1% to 10% of the cement mass into the composition of fine-grained cement concrete with a cement: fine aggregate ratio of 1:3. The standard beam specimens with the dimensions of 40x40x160 mm were prepared. Bending and compressive strength tests of concrete samples were carried out on a PGM-100 MG4-A hydraulic press with a maximum load of 100 kN and a loading rate of 0.5 MPa/s.

SEM and EDX studies were performed using Thermo Fisher Scientific Quattro S microscope in the Center of Shared Facilities “Surface and new materials” of UdmFRC UB RAS (Izhevsk, Russia) supported by Russian Ministry of Science and Higher Education (project № RFMEFI62119X0035).

3. Results and discussion

The mechanical tests showed an increase in compressive strength of specimens, modified with ceramsite dust (Table 2). The introduction of an additive of dehydrated clay in the amount of 3% by weight of the cement leads to a 23% increase in compressive strength compared to the control sample. The flexural strength increases insignificantly.

| Composition                  | Compression strength (MPa) at the age of 7 and 28 |
|------------------------------|--------------------------------------------------|
|                              | 7 days   | 28 days |
| Reference sample             | 14,12    | 19,33   |
| With ceramsite dust 10 wt.%  | 15,99    | 22,2    |
| With ceramsite dust 5 wt.%   | 15,8     | 22,03   |
| With ceramsite dust 3 wt.%   | 17,31    | 23,39   |
| With ceramsite dust 1 wt.%   | 14,58    | 19,51   |

Analysis of the microstructure of the samples (Figure 6) showed that the addition of finely dispersed additive in the form of dehydrated clay significantly changes the morphology of hydration products in the cement matrix. The microstructure of reference sample without dehydrated clay, is characterized by a "classical" porous structure having fibrous and needle-like formations (Figure 6a). However, when the cement matrix is modified with the ceramsite dust, the mechanism of structure formation changes, leading to a denser package of hydration products (Figure 6b). Figure 5a demonstrates that loose fibrous formations, present in the reference sample, are replaced by dense lamellar structures with octahedral crystals formed on their surface (Figures 6b and 7b). Based on the morphology of these crystals, they can be attributed to...
calcium aluminosilicate hydrates (hydrogarnets). Hydrogarnets compact the structure and increase the strength of the cement matrix.

![Figure 6. Microstructure of the cement matrix at 10,000-fold magnification: a) reference composition, b) composition modified by the ceramsite dust](image)

To clarify the results of the scanning electron microscope study, an X-ray microanalysis of the reference sample (Figure 7a) and the sample modified with the addition of the ceramsite dust (Figure 7b) was carried out.
It was found that calcium silicate hydrates (Si, O, Ca) were formed on the surface of a fine aggregate (quartz sand particles) in combination with clay minerals, characterized by intense lines of aluminum (Figure 7a). At the same time, microanalysis of the surface of lamellar hydration products in Figure 6b showed the formation of calcium silicate hydrates (Ca, Si, O) with a predominance of lamellar crystals of calcium hydroxide (Ca, O), which are partially carbonized. This is confirmed by the presence of carbon (C) in the spectrum. In this case, the intensity of aluminum atoms decreased by 2 times.

The IR spectra (Figure 8) clearly show that the amount of free water in the modified sample (1647.21 cm\(^{-1}\)) decreases compared to the reference sample (1662.64 cm\(^{-1}\)), which indicates its binding by calcium silicate hydrates. The formation of a doublet in the frequency range of 3641.60 cm\(^{-1}\) and 3338.78 cm\(^{-1}\) can be explained by the different degrees of bonding of OH\(^-\) groups in calcium silicate hydrates. Zinyuk et al. [14] note a similar appearance of a doublet in gypsum dihydrate and its absence in a semi-aqueous gypsum.
Thus, the presence of a doublet in the IR spectrum additionally confirms the formation of calcium silicate hydrates of various basicities.

A change in the nature of the peak was also noted with an increase in its area and a change in the ratio between the tops. The intensity of the absorption line in the frequency range of 991.41 cm\(^{-1}\) is changed for the modified sample, which indicates the formation of lower-basic calcium silicate hydrates. A change in the environment and the length of the O-Si-O bonds is evidenced by the shift of the peaks from 1089.78 cm\(^{-1}\) and 1008.77 cm\(^{-1}\) to the lower frequencies of 1082.07 cm\(^{-1}\) and 991.41 cm\(^{-1}\). Thus, when cement composites are modified with expanded clay dust, a larger amount of calcium silicate hydrates is formed, which contributes to the compaction of the structure and an increase in the strength of the modified cement composites.

4. Conclusions

Thus, expanded clay dust can be used as an active pozzolanic mineral additive in cement-based compositions. It was experimentally proven that the introduction of ceramsite dust in the amount of 3% by the cement weight increases the compressive strength of the samples by 23% compared to the reference sample.

Modification of cement stone with ceramsite dust results in a change in the morphology of hydration products, which increases the density of the structure. Besides, it alters the mineralogical composition of the cement matrix with the formation of stronger and more water-resistant minerals, presented by calcium silicate and aluminosilicate hydrates. When the cement matrix is modified with the ceramsite dust, the mechanism of structure formation changes towards denser packing of hydration products, which increases the physical and mechanical properties of the cement matrix.

Other advantages of this technology include the utilization of the ceramsite production waste, contributing to the improvement of the ecological situation in the areas of expanded clay gravel production, and creation of a circular economy due to the involvement of the waste into the production of cement composite materials.

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