Composite gypsum binder under introducing thermally activated clay as a pozzolanic component and adding ground limestone

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Abstract. The purpose of this article is to study the effect of ground limestone additives on the basic physical and mechanical properties of the composite gypsum binder. It includes portland cement and pozzolanic additive of thermally activated clay as hydraulic components to reduce the consumption of more expensive calcining components of the binder. Using standard methods of research building materials we have obtained dependencies that characterize the effect of adding ground limestone on the water demand of the composite gypsum binder, its density, strength, water absorption, and water resistance of artificial stone based on it. It was established that the introduction of limestone into the composite gypsum binder composition with specific surfaces 500-800 m²/kg in an amount of up to 5-10 % by weight causes an increase in compressive strength by 15 % compared to control samples. When introducing up to 10-15 % by weight of limestone with a dispersion of 300 and 500-800 m²/kg, respectively, the strength remains at the level of additive-free samples with the preservation of the softening coefficient corresponding to water-resistant binders.

Keywords: composite gypsum binder, gypsum cement pozzolanic composition, active mineral additives, thermally activated clay, ground limestone, mineral filler.

1 Introduction
The production and use of mineral binders with the introduction of pozzolanic additives to increase the properties were known in the era of Ancient Egypt and Rome. Research carried out in the 30-50s of the 20th century by P.P. Budnikov, A.V. Volzhensky, A.V. Ferronskaya and others showed that the most effective way to increase the water resistance and strength of materials based on gypsum binders is to use of gypsum cement pozzolanic compositions [1, 2]. Further research on the production of waterproof materials and products based on gypsum binders was associated with the composite gypsum binders [3].

At the end of the 20th century metakaolin was used as a highly active pozzolanic additive in cement [4], gypsum lime pozzolanic and gypsum cement pozzolanic compositions [5]. However, kaolinite clay deposits are of limited distribution, which reduces accessibility and increases the cost of metakaolin additives. A similar problem exists with other known types of effective pozzolanic additives [6, 7].

In this regard, the current problem is the search for affordable and effective pozzolanic additives for obtaining composite gypsum binders with high water resistance [8, 9]. In recent years, the number of countries around the world has been conducting research aimed at obtaining pozzolanic additives from thermally activated clay raw materials with different kaolinite composition [4, 10].

The introduction of mineral fillers into the composition of binders instead of more expensive calcining components is one of the ways to save energy in the production of binders and reduce their cost [11, 12]. A number of studies on the effect of mineral fillers of various nature on the properties of gypsum binders have shown the effectiveness of applying ground limestone additive [13, 14]. As in [15–17] the effectiveness of adding carbonate fillers to cement compositions increases when they are introduced together with aluminum-containing additives such as slags, thermally activated clays, etc.
Another important way of improving the operational properties of products based on gypsum and gypsum cement pozzolanic compositions is the modification of their structure using chemical additives [18]. Some studies have shown the effectiveness of plasticizing additives [19], water repellents [20, 21], setting retarders [22] and complexes based on them [23] in gypsum cement pozzolanic compositions, that can significantly increase the product strength and producing ability.

The purpose of this paper is to study the effect of the composition and dispersion of ground limestone additives on the basic properties of the composite gypsum binder with thermally activated clay as a pozzolanic component to reduce the consumption of more expensive calcining components of the binder without significantly reducing its properties.

2 Materials and Methods

The preparation of the composite gypsum binder was carried out by mixing the components of the gypsum cement pozzolanic composition, the Melflux 2651 F superplasticizer additive and the limestone as a mineral filler.

Building gypsum, portland cement, thermally activated clay of the Saray-Chekurchinsky deposit were used as components of the gypsum cement pozzolanic composition in the composite gypsum binder.

The initial chemical composition of clay (in % by weight) is SiO₂ – 52.84; TiO₂ – 0.86; Al₂O₃ – 13.42; Fe₂O₃ – 6.18; MnO – 0.10; CaO – 1.33; MgO – 1.66; Na₂O – 1.20; K₂O – 1.82; P₂O₅ – 0.09; SO₃/S – <0.05; ignition loss – 4.62. The initial mineralogical composition of clay (in % by weight): quartz – 28; mica – 10; orthoclase – 7; plagioclase – 8; mixed-layered clay mineral – 40; chloride – 4.

The initial particle size distribution of clay (in % by weight): clay fractions – 49.5; dusty – 37.1; sand – 13.4.

According to the results of previous studies [24] thermal activation of clay was carried out in a muffle laboratory furnace at a temperature of 400 °C for 4 hours at a heating rate of 1.7 °C per minute. The thermally activated clay was ground in a laboratory planetary mill until it reached a dispersion characterized by specific surfaces 300, 500, and 800 m²/kg.

In this work, the composition of the composite gypsum binder was supplemented with the Melflux 2651 F superplasticizer additive in the solid aggregate state and in the amount of 0.8 % by weight of the binder produced by BASF Construction Polymers [24].

The paper investigates the introduction of limestone additive as mineral filler into the composition of the composite gypsum binder which is extracted by LLC “Dobryatinsky Quarry Management” (Vladimir Region, Russian Federation). The mineralogical composition of limestone (in % by weight) is CaCO₃ – 92.9; MgCO₃ – 4.1; clay and fine dust fractions – 3. Limestone previously was ground in a planetary mill to specific surfaces 300, 500 and 800 m²/kg.

Determination of the required amount of a thermally activated clay additive in the gypsum cement pozzolanic composition was carried out based on the method proposed in Moscow Engineering and Construction Institute named after V.V. Kuibyshev [25]. The required amount of the mineral additive in the gypsum cement pozzolanic composition is selected by the concentration of calcium oxide contained in special samples, which are water suspensions of semi-aquatic gypsum, portland cement and an active mineral additive. Two sample batches of six compositions in each batch were prepared for testing; they vary in composition of active mineral additive. Each sample prepared and stored in separate conical flasks contains 4 grams of semi-aquatic gypsum, 2.5 grams of portland cement, 100 ml of distilled water and a different amount of active mineral additive. The composition of the active mineral additive in various samples of each batch was 0.25; 0.75; 1.25; 2.5; 3.75 grams. The first sample batch was tested in 5 days after preparing, the second batch in 7 days after preparing. To determine the concentration of calcium oxide after 5 and 7 days, we took 50 ml of an aqueous solution from each flask by filtration through filter paper. The filtered aqueous solution is titrated over phenolphthalein with a 0.1N hydrochloric acid solution.

The concentration of calcium oxide in g/l is determined by the formula:
\[ \text{CaO} = 768-A*T/\text{VL}, \]  
(1)
where $A$ is the amount of hydrochloric acid spent on titration in ml;
$T$ is hydrochloric acid titer ($\text{HCl}$ content in g/ml);
$B$ is the amount of solution taken from the flask in ml.

The required amount of the active mineral additive is selected, provided that the concentration of calcium oxide on the fifth day does not exceed 1.1 g/l and on the seventh day it is less than 0.85 g/l.

Samples of the composite gypsum binder for testing to determine strength, average density, water absorption by weight, softening coefficient were kept in a normal hardening chamber for 28 days, after which they were dried at 55°C until a constant weight was reached. The softening coefficient was determined as the ratio of the compressive strength of water-saturated samples of artificial stone based on a composite gypsum binder to the tensile strength of samples of artificial stone based on a composite gypsum binder, dried to constant weight.

### 3 Results and Discussions

The results of the research performed to determine the required amount of thermally activated clay additives of the Saray-Chekurchinsky deposit ground to specific surfaces 200, 300, 500 and 800 m$^2$/kg to obtain a gypsum cement pozzolanic composition have shown (Figure 1) that while grinding fineness increases, the required content of pozzolanic additive decreases from 30 to 10 % by weight of the gypsum cement pozzolanic composition or from 100 to 30 % by weight of portland cement.

![Figure 1](image1.png)

Figure 1. Kinetics of CaO absorption by adding thermally activated clay: concentration of CaO in solution for samples: 1, 2, 3, 4 – 5 days old; 5, 6, 7, 8 – 7 days old. The specific surface of thermally activated clay in m$^2$/kg is 1, 5 – 200; 2, 6 – 300; 3, 7 – 500; 4, 8 – 800.

Figure 2 shows the results of studies that determine the required amount of known high-performance pozzolanic additive metakaolin to obtain a gypsum cement pozzolanic composition.
Figure 2. Kinetics of CaO absorption by adding metakaolin: Concentration of CaO in solution for samples: 1 – 5 days old; 2 – 7 days old.

The presented data demonstrate that the required metakaolin content is 30 % by weight of portland cement, which is comparable with the results obtained for the previously considered additive of thermally activated clay, ground after calcination to a specific surface 800 m²/kg and demonstrate its rather high efficiency as a pozzolanic component.

At the next stage, in order to reduce the content of expensive calcining components in the composition of the composite gypsum binder and its cost, we studied the effect of introduction of ground limestone as mineral filler on the properties of the binder.

Figure 3-6 show the findings of the effect of introducing the dispersion ground limestone in an amount of up to 20 % on the basic physical and mechanical properties of a composite gypsum binder.

According to research data, the water demand of composite gypsum binder increases from 27 to 28 % with the addition of more than 15 % by weight of limestone additive ground to specific surfaces 300 and 500 m²/kg and over 5 % of limestone ground to a specific surface 800 m²/kg.

When introducing limestone with a specific surface 300 m²/kg up to 10 % by weight of the compressive strength of an artificial stone based on a composite gypsum binder remains at the level of control samples without the introduction of limestone (Figure 3). A further increase in this dispersion limestone content leads to a monotonic decrease in the strength indicators of artificial stone. When introducing limestone additives into an amount up to 10 % by weight with a specific surface 500 m²/kg as well as up to 5 % by weight with a specific surface 800 m²/kg, the strength of the artificial stone is increased by 15 % compared to control samples. When the binder contains limestone additive ground to specific surfaces 500 and 800 m²/kg and in an amount of up to 15 % by weight, the strength of the artificial stone remains at the level of control samples with its further decrease with increasing limestone content.
Figure 3. The effect of ground limestone content on the compressive strength of an artificial stone based on the composite gypsum binder. The specific surface of limestone, m²/kg: 1 – 300; 2 – 500; 3 – 800.

Figure 4. The effect of ground limestone content on density of artificial stone based on the composite gypsum binder. The specific surface of limestone, m²/kg: 1 – 300; 2 – 500; 3 – 800.
Figure 5. The effect of ground limestone content on water absorption by weight of artificial stone based on the composite gypsum binder. The specific surface of limestone, m$^2$/kg: 1 – 300; 2 – 500; 3 – 800.

Figure 6. The effect of ground limestone content on the water resistance of artificial stone based on the composite gypsum binder. The specific surface of limestone, m$^2$/kg: 1 – 300; 2 – 500; 3 – 800.

The observed nature of the change in the strength indicators of artificial stone based on the composite gypsum binder with the introduction of certain amounts of limestone with a various specific surface can be explained by the effect described by V.I. Solomatov and L.I. Dvorkin [26]. It was shown that a certain volume of fillers with optimal particle sizes combined with binder particles were involved in the formation of cluster structures, contributing to the structure ordering, reducing damage and increasing the strength indicators of composite building materials. In this case, as dispersion and the crystal chemical proximity to the binder increased, the efficiency of filler particles as substrates for directed crystal formation increased while forming the structure of artificial stone [27].
The influence of ground limestone on the structure formation processes of artificial stone based on the composite gypsum binder in accordance with the above mechanisms providing an increase in strength indicators can be proved by density increase of samples when limestone additives introduced in the amount of 10% by weight with a specific surface of 500 m²/kg and 5% by weight with a specific surface 800 m²/kg from 2052 kg/m³ for the control additive free sample respectively to 2163 and 2157 kg/m³ (Figure 4) with a slight decrease in water absorption (Figure 5).

According to the data shown in Figure 6, an increase in ground limestone content of the considered dispersion in the composite gypsum binder causes a gradual decrease in the softening coefficient of the artificial stone based on it. Moreover, when the limestone content with specific surfaces 500 and 800 m²/kg up to 20% by weight, the softening coefficient of the samples remains at the level of 0.8, proving that the composite gypsum binder is waterproof.

4 Conclusion
The introducing limestone ground into specific surfaces 500-800 m²/kg and in the amount of 5-10% by weight while maintaining the water demand of the binder into the gypsum binder composition based on a gypsum cement pozzolanic composition with thermally activated clay as a pozzolanic component leads to an increase in compressive strength by 15% by compared with control samples without the introduction of limestone.

When introducing limestone with a specific surface area of 300 m²/kg up to 10% by weight or up to 15% by weight with a specific surface area of 500-800 m²/kg, the strength stays at the level of additive-free samples while maintaining the softening coefficient at the level of water-resistant binders.

A further increase in the ground limestone content in the composition of the composite gypsum binder leads to a gradual increase in the water demand of the binder, a decrease in strength, density, and softening coefficient.

Thus, the introduction of limestone additives in optimal quantities and dispersion ensures that strength indicators and water resistance of the composite gypsum binder are obtained at the level of additive-free samples while reducing the consumption of more expensive calcining mineral components of the binder.

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