Influence of clay mineral composition on properties of blended portland cement with complex additives of clays and carbonates

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Abstract. Resources of currently used mineral additives in production of blended Portland cement do not provide their increasing needs. The complex additives which differ in the presence of a synergetic effect in the co-introduction of multiple mineral additives play the great importance in creation of blended cements. One of the promising directions is creation of complex additives based on combination of calcined clays with limestone. But sometimes there are clay impurities in carbonate rocks which adversely effect on properties of received cements and concretes. At the same time calcium carbonate contained in marl clays during calcination allows to get high quality pozzolanic material. The effective complex additive based on the calcined mixture of clay and limestone was the creation. The results of research show the influence of the complex additive on blended cement stone properties. It has been established that strength of cement stone with complex mineral additive depends on the content of kaolinite in initial clay, and on calcination parameters.

Ключевые слова: blended cement, active mineral additives, thermally activated clay, limestone, carbonate, polymineral clay.

1 Introduction
Portland cement (OPC) is the primary hydraulic binder used in construction. However, its production is characterized by high energy and resource consumption and involves significant amounts of polluting emissions. One of the most effective and recognized approaches to solving these problems in the cement industry is the development of low clinker blended Portland cement with mineral additives. Currently, the average content of mineral additives in Portland cement is about 20%. The predicted increase in the global production of Portland cement, coupled with the increased dosage of mineral additives up to 30-40%, leads to an increase in the volume of additives production and application. Available resources of currently used mineral additives do not suffice to cover the expanding demand.

In search of alternatives, recent times have engendered studies of the effectiveness of calcined clay additives [1-7], as evidenced by the first “International Conference on Calcined Clays for Sustainable Concrete” [2] held in 2015 in Lausanne. The high efficiency of metakaolin (the product of calcined kaolinitic clay) is proven [8-12]. However, because of their limited resources and high cost, the search for affordable mineral additives has been expanded to include a study of the effectiveness of calcined polymineral clays of widespread provenance containing little or no kaolinite [2, 5, 7].

Complex additives differing by the synergetic effect presence in the co-introduction of multiple mineral additives play a major role in the creation of blended cements [13-20]. One of the more promising approaches is devoted to the creation of complex additives based on combinations of calcined clays, including kaolinite with limestone [13-15]. The effectiveness of joint introduction is achieved when the component ratio is 2:1 (clay: limestone) [13]. The role of limestone in the formation of monocalcium carbonat is noted [13, 18].

At the same time and in most cases of use, carbonate rocks contain clay impurities with adverse effects on the properties of the resultant cements and concretes. In 1920s, Weiner found that mixture of finely divided calcium carbonate with clay leaded to the decomposition of the first at temperatures
lower than 910 °C (temperature of calcite dissociation). Monocalcium aluminate is formed at a temperature of 500 °C, and dicalcium silicate at 700 °C, in which, at a temperature of 800 °C the entire balance of silicic acid is completely converted in calcium aluminate formed from metakaolinite.

Gorland showed that, in the temperature range 660 to 810 °C almost all calcium carbonate contained in spondyl clay (marl clay) decomposed, and that, at 800 °C, the clay contains was no more calcium carbonate, but free lime was present.

In the work about glinite-cement creation (about 1935 year), it was found that marl clay calcination at a temperature of 700 to 800 °C yielded the best pozzolanic properties and, in some cases, even surpassed those a burnt kaolinitic clay. According to Jung V.N. (1988) calcium carbonate contained in marl clays in “close mix” with clay particles and during calcination makes it possible to get the high quality glinite-cement.

Ramachandran V.S. (1977) found that the process of calcium carbonate decarbonization and clay dehydration in obtaining cement clinker starts at temperatures below 800 °C with CA formation. In the temperature range 800 to 900 °C, dicalcium silicate begins to form. The author emphasized that the processes were observed earlier in the mixture of “clay-CaCO₃” than when pure oxides were used.

Voznesensky V.A. at 1987 showed that carbonate impurities dissociation with red-burnt clay composition occurs at temperatures of 600-830 °C, with a maximum endothermic effect at 760-780 °C.

The aim of this work was to obtain high-performance complex additives for Portland cement based on calcined mixtures of finely divided carbonate rocks and polymineral clay.

2 Materials and methods
All experiments were carried out using OPC CEM I 42.5 N according to EN 197-1 (C₃S-68.0; C₂S-10.0; C₃A-3.7; C₄AF-15). Kaolinitic clay (KC) and polymineral clay (PC) were selected for use. The specific surface area was 500 m²/kg. The mineral and chemical compositions of the materials are presented in Table 1. Differential thermal curves of selected clays are shown in Figures 1 and 2. Limestone (L) has mineral composition, by mass %: calcite – 99, quartz – 1.

Table 1. Mineral composition of clays.

| Mineral composition, by mass (%) | Kaolinitic clay (KC) | Polymineral clay (PC) |
|---------------------------------|---------------------|----------------------|
| Kaolinite                        | 82.3                | 4.06                 |
| Quartz                           | 17.7                | 35.8                 |
| Albite                           | -                   | 14.79                |
| Microcline                       | -                   | 17.4                 |
| Montmorillonite                  | -                   | 17.9                 |
| Chloride                         | -                   | 4.1                  |
| Mica                             | -                   | 6.0                  |
The calcination of mixture was conducted in the laboratory chamber furnace SNOL 7.2/1300 with a vacuum fiber chamber. The heating rate for kaolinitic clay mixture was adopted equal to 10 °C/min, and that for polymineral clay was 3 °C/min according to previous studies [21].

The experiments were carried out on sample cubes of cement stone with an edge length of 2 cm. The physico-mechanical properties of cement stone of normal density were evaluated via variation of compressive strength, water absorption and average density.

Calcined mixtures were introduced into the OPC in amounts of 20 % of its mass according to GOST 31108-2003 and EN 197-1:2000.

The thermal analysis of mixtures and blended cement stone were carried out using a combined method of thermogravimetry (TG) and differential scanning calorimetry (DSC) using a
thermoanalyzer (Netzsch STA 449C) under continuous heating (40 to 1000 °C) of samples with a mass of about 35 to 40 mg at a rate of 10 °C/min in a flow (50 ml/min) of air in alundum crucibles. The temperatures of the thermal effects were determined within an accuracy of ±1 to 3 °C, warmth – ±5 %, weight ±0.01 mg.

Determination of mineralogical composition of thermoactivated mixtures, relevant changes, and hydration products identification were carried out by means of X-ray phase analysis on an automatic X-ray diffraction D2 phaser (Bruker Company). For CuKα radiation, monochromatization (λ (Cu-Ka) = 1.54184 Å) curved Johansson-type germanium monochromator, the mode of operation of a 40 kV, 40 mA X-ray tube was adopted. The experiments were performed at room temperature in the geometry of Bragg-Brentano flat samples. Analysis and plotting of diffraction patterns were carried out using the Bruker Diffrac Eva program.

The optimization of compositions and calcination parameters of complex additives was determined by B3 plan experimentation on a hypercube with three factors.

3 Results

To investigate the possibility of creating complex additives based on calcined mixtures and their influence on properties of blended cement, the following mixtures were employed:

- mixture of kaolinitic clay and limestone (KC+L);
- mixture of polymineral clay and limestone (PC+L).

The specific surface area of mixtures was 500 m²/kg.

Research on the thermal reactions occurring in the artificial mixtures of clay and limestone was carried out using differential thermal analysis.

According to Figure 3, during calcination, the endothermic effect corresponding to the loss of weakly bound water in KC, as observed at 154 °C, is smoothed (Figure 1).

![Figure 3. Simultaneous TG-DTA- DSC data the mixture of limestone and kaolinitic clay.](image)

The endothermic effect characterized the polymorphic aragonite transformation into calcite CaCO₃ is observed at 494 °C. Almost invisible, the endothermic effect in the temperature range 580 to 600 °C is
associated with kaolinite dehydration, while for the kaolinitic clay, this effect is clearly expressed (Figure 1). The deep endothermic effect involving a large loss of mass (27.89 %) is typical for calcite dissociation, and is observed much earlier in a mixture with clay than in clean calcite according to the literature [22-24]. However, the exothermic effect disappears, hence characterized the kaolinite transformation into mullite [22-23], which is observed at 990 °C for kaolinitic clay (Figure 1). Thus, the lack of distinct peaks accompanying the endothermic effect of kaolinite dehydration, and the exothermic effect of mullite crystallization indicates kaolinite binding in the presence of calcite in different connections.

Thus, the carbonate decomposition in the presence of clay occurs at temperatures below 810 °C. This confirms results which are presented in some works [22-23]. The common clay and carbonate calcination at temperature range up to 800 °C makes it possible to obtain qualitatively new thermoactivated material with not only pozzolanic but also hidden hydraulic properties.

The optimization of compositions and the calcination parameters of complex additives were determined by B3 plan experimentation on hypercube with three factors. The experimental factors were arranged on three levels. The mathematical processing of experimental data was done accomplished by special program written on the VBA setting.

To improve the reliability of the statistical findings, the models’ adequacy was checked against two criteria: the Fisher criterion and the average relative error criterion. The tabulated value of the Fisher criterion for all models is $F_{\text{tab}} > 19.2$. For all models, $F_{\text{calc}} < F_{\text{tab}}$, made them adequate for the Fisher criterion. Constructed models were adequate for the average relative error criterion, because, for them, the relation is $A_{\text{av}} < 10 \%$, which could be used for solving the optimization aspects, where the value of limestone in the mixture (X1), the calcination temperature (X2), the calcination time (X3) were determined, after which the maximum strength of the cement paste was reached at 7 days, R7, and after steam curing RCS. After solving optimization aspects by Newton’s method in combination with the method of penalty functions, the calcination parameters and the content of limestone in a mixture were determined for all types of clay. Obtained results are presented in Table 2.

According to the Table 2, the optimal content of limestone additives in calcined mixtures is 40 % and 15 %, respectively, for mixtures with kaolinitic and polymineral clays. The optimum content of limestone in mixture with kaolinitic clay corresponds to the relationship between metakaolin and calcium carbonate as 2 : 1 corresponding to the mass proportions of chemical reaction of 1 mole of alumina in calcined clays with 1 mole of calcium carbonate in the presence of calcium ion excess in aqueous solution to form 1 mol of calcium hydromonocarboaluminate.

### Table 2. Optimal parameters for calcination and composition of calcined mixtures.

| №  | Compositio n | The content of limestone in the mixture, % by weight | Calcined temperature, °C | Curing time, hours | Cement stone properties |
|----|--------------|----------------------------------------------------|--------------------------|------------------|-------------------------|
|    |              |                                                     |                          |                  | R$_{\text{CS}}$, MPa | ρ, kg/m$^3$ | w, %       |
| 1  | OPC          | -                                                   | -                        | -                | 60.0                    | 2095      | 5.66       |
| 2  | KC+L         | 40                                                  | 812                      | 3.2              | 56.4                    | 2231      | 4.69       |
| 3  | PC+L         | 15                                                  | 800                      | 3.1              | 60.8                    | 2152      | 4.90       |

In the case with polynineral clay, the calcined temperature reduction associates with an elevated content of alkali oxides causes acceleration the reaction between active alumina and calcium oxide formed at thermal dissociation. The optimum temperature of calcination of mixture with polymineral clay is lower due to the high content of alkali oxides in clay.

Identification the calcined mixture products was effected by XRD. The resulting diffraction patterns are presented in Figures 4 and 5.
In the calcined mixture of kaolinitic clay KC and limestone L (Figure 4), the estimated content of main components amounted: calcite (40 %), kaolinite (49 %) and quartz (11 %). The estimated content of components after calcination became: calcite (80 %), quartz (20 %), kaolinite (undetermined).

The actual content of calcite is 37.1 % (diffraction peaks with interplanar spacings \(d = (3.036; 2.494; 2.284; 1.875) \text{ Å}\)), and of quartz is 59.25 % (diffraction peaks with interplanar spacings \(d = (4.462; 3.347; 2.459; 2.130) \text{ Å}\)), which is indicative of limestone transition into amorphous phases. The theoretical content of the amorphous phase must be between the amounts contained in KC (30.5 %) and in L (21.8 %), while the actual amount of content is 45.3 %. Therefore, the amorphous phase contains not only amorphized kaolinite, but also new formations from interaction of kaolinite and carbonate decomposition products [20]. On the XRD pattern, the CaO is not identified, but there are peaks with interplanar spacings \(d = (2.844; 2.566; 1.982) \text{ Å}\), corresponding to \(\beta\)-\(C_2S\).

In the mixture of polymineral clay PC and limestone L (Figure 5), the estimated content of main components amounted: calcite (15 %) and quartz (30 %). The estimated content of components after calcination became: calcite (38.7 %) and quartz (19.4 %).

The XRD pattern in Figure 5, shows that the absorption line of calcite is absent, and the content of quartz is 45.47 %, as confirmed by the diffraction peaks with interplanar distances \(d = (4.262; 3.345; 2.459; 2.284; 2.238) \text{ Å}\). The amorphous phase increases up to 47.2 %, while the calculated composition

Limits of an amorphous phase are 21.8-24.7 %. The kaolinite content of the initial clay is negligibly low, so the amorphous phase contains noncrystallization amorphous new growths. The
diffraction peaks with interplanar distances $d = (3.030; 2.901; 2.628) \text{ Å}$ correspond with the formed $\beta$-$\text{C}_2\text{S}$.

Free calcium oxide absence on the XRD pattern makes it possible to claim that it was completely bonded by products of clay mineral decomposition, for example, by kaolinite. Partial formation of silicon and aluminum oxides was also not identified on the XRD pattern. That gives the reason to assume the possible formation of amorphous calcium silicates and aluminates. Two-calcium silicate formed at the same time contains approximately equal quantities in all thermoactivated mixtures, so that the polynuclear clay testifies to the possibility of receiving actual complex agents based not only on kaolinitic, but also polynuclear clay.

Since the content of kaolinite in the original clay was negligibly small, the amorphous phase contains amorphous formations. Diffraction peaks with interplanar distances $d = (3.030; 2.901; 2.628) \text{ Å}$ correspond with the resulting $\beta$-$\text{C}_2\text{S}$.

Free calcium oxide is missing in Figure 5. This suggests that it was completely bonded by decomposition products of clay minerals such as kaolinite. Partial formation of silicon and aluminum oxides, which were also not identified in Figure 5, is also possible. This, in turn, suggests the formation of weak-base amorphous calcium silicates and aluminates. The fact that the resultant dicalcium silicate contains approximately equal amounts in all thermoactivated mixtures indicates the possibility of obtaining an effective additive based not only on kaolinitic, but also polynuclear clays.

Increased content of alkalies in clay tends to accelerate the decomposition of clay minerals with formation of active amorphous silicon and aluminum oxides [22] that can react with lime of the carbonate and products of its decomposition.

As revealed above, cement stone properties changing in dependence on the employed kind of complex additives are bound with changes in the hydration product composition. The research on hydration product composition was conducted on cement stone samples at 28 days of age with the following compositions:
1. The control sample of OPC;
2. The blended cement with 20 % of complex additive based on the calcined mixture of kaolinitic clay and limestone (KC+ L).

In Figure 6, simultaneous TG-DTA-DSC data the control sample OPC cement stone are submitted.

![XRD pattern the control sample from the OPC cement stone.](image)

The structure is characterized by larger peaks of unreacted clinker minerals – alite ($d = (2.748; 2.609; 2.316; 2.188) \text{ Å}$) and belite ($d = (4.655; 2.787; 2.777; 2.293; 2.195; 2.050; 2.028) \text{ Å}$). The diffraction peaks with interplanar distances $d = (7.312; 4.260; 3.178; 2.672) \text{ Å}$ correspond to calcium hydroaluminosilicates. The presence of a small content of calcite ($d = (3.037; 2.494) \text{ Å}$) and the formed ettringite ($d = (9.826; 5.934) \text{ Å}$) is observed. The presence of calcium
Hydromonosulfoaluminate is characterized by the diffraction peaks with interplanar distances $d = (9.002; 3.432; 2.973)$ Å. Diffraction peaks with interplanar distances $d = (8.225; 3.871; 2.881; 2.208)$ Å are characterized by hydrocalcium silicates C-S-H (I). The considerable quantity of portlandite corresponds to diffraction peaks with interplanar distances $d = (4.918; 3.110; 2.630)$ Å.

In Figure 7, the simultaneous TG-DTA data the control sample OPC cement stone is presented. The observed endothermic effect with the maximum at 70 °C can be bound with loss of free water from a cement stone [23]. Nearby, there is another effect (100 to 125 °C) that is not absolutely accurately expressed on DSC and that binds with loss of adsorption water [23]. The small endothermic peak in the temperature range 125 to 150 °C is caused by ettringite dehydration. The endothermic effect with a maximum at 461 °C and a 1.86 % loss of weight characterizes the calcium hydroxide decomposition [22]. The loss of weight in the temperature range 480-630 °C is 2.87 %. The endothermic effect with a maximum at 680 °C is followed by a 4.82 % loss of weight and characterizes the decomposition of lime carbonate formed during hardening [22].

Figure 7. Simultaneous TG-DTA-DSC data the control sample from the OPC cement stone.

Compound kaolinitic clay and limestone calcination (Figure 8) leads to a considerable decrease in the formed portlandite content ($d = (4.909; 3.852; 2.631)$ Å) – more than twice as much in comparison with sample 1.

Figure 8. XRD pattern the blended cement stone with 20 % of complex additive based on the calcined mixture of kaolinitic clay and limestone.
The considerable part, slightly smaller in comparison with sample 1, consists of unreacted clinker phases of alite \((d = (2.745; 2.697; 2.341) \, \text{Å})\) and belite \((d = (2.790; 2.452) \, \text{Å})\). The considerable content of calcite \((d = (3.031; 2.493; 2.284; 2.106) \, \text{Å})\) testifies to the insufficiently high temperature of calcination and its incomplete decomposition during calcination of the mix. Traces of formed ettringite \((d= (9.719; 5.588) \, \text{Å})\) were found. The diffraction peak with the interplanar distance \(d= (7.264; 3.783) \, \text{Å}\) corresponds to calcium hydroaluminosilicates.

Peaks characterizing the existence of calcium hydromonocarboaluminate are represented with an interplanar distance \(d= (4.249; 3.182) \, \text{Å}\). The diffraction peaks with interplanar distances \(d= (8.091; 2.885) \, \text{Å}\) correspond to the formation of hydrocalcium silicates \(\text{C-S-H (I)}\). The presence of calcium hydromonosulfoaluminate is observed \((d= (9.003; 2.970) \, \text{Å})\), as well as for sample 1.

The simultaneous TG-DTA data the blended cement with 20 % complex additive based on the calcined mixture of kaolinitic clay and limestone are presented in Figure 9. Endothermic effects with a maximum at 79 °C are observed there, similar to what is also observed at control sample 1 and which bounds with loss of free water, and to the effects at 100 to 125 °C that are caused with partial dehydration of hydrosilicates such as C-S-H (I). The endothermic effect with a maximum at 152 °C is specific for ettringite dehydration, the hydrosilicates \(\text{C}_2\text{SH}_2\) and \(\text{C}_2\text{S}_3\text{H}_2\) or the hydroalumosilicates [23]. Portlandite decomposition is followed by an endothermic effect with a maximum at 461 °C. The endothermic effect in the temperature range 669 to 708 °C characterizes the hydrocalcium silicates such as C-S-H (I) decomposition [20]. The endothermic effect at 708 °C characterizes the decomposition of lime carbonate formed during hardening. The decomposition of unreacted limestone proceeds with an endothermic effect at 733 °C. The slight endothermic effect at 850 °C is characteristic for C-S-H (I) [22].

![Figure 9. Simultaneous TG-DTA-DSC data the blended cement stone with 20 % of complex additive based on calcined mixture of kaolinitic clay and limestone.](image)

4 Discussion

The content of portlandite in the sample with the complex additive declines by a factor of nearly 2 in comparison with the OPC sample, the fact that suggests good pozzolanic properties the calcined mixtures. According to sources [23-24] surface reactions are formed between calcium carbonate and portlandite, leading to hardening of the stone structure. In the sample 2, the formation of hydrosilicates C-S-H (I) is observed. The undecomposed limestone acts like a substrate for the formation of hydrated clinker mineral compounds.
The XRD pattern points out that the hydromonosulfoaluminate contained in the control sample, is absent in a sample with the complex additive. In place of it, however, calcium hydromonocarboaluminate is observed in sample 2. The loss of weight in the field of low-temperature endothermic effects increases with the introduction of complex additive in comparison with the control sample. It confirms the formation of accreting amounts of calcium hydrosilicates and hydroaluminosilicates of various compositions, and of hydrocarboaluminate in samples with high limestone content.

5 Conclusions
The calcination of mixtures based on kaolinitic or polymineral clay and limestone with a calcite content 99 % at a temperature of 720-800 °C leads to the formation of C$_2$S, and increases the quantity of amorphous phase. At the same time, no free CaO is identified on the XRD pattern of calcined mixtures, hence demonstrating its binding by products of clay mineral decomposition - kaolinite for example - in new growths like C$_2$S or CA, and new growths in amorphous phase. The formation of accreting amounts of calcium silicates and aluminates in the calcined mixtures makes it possible to receive the complex additives for blended cement, replacing up to 20 % of OPC with no loss of durability.

The optimum parameters of calcined mixtures based on kaolinitic or polymineral clay and limestone arrived at by the method of mathematical experiment planning depend on the chemical and mineralogical composition, the physical and technological properties of the raw materials, and on the degree of component dispersion.

The introduction of complex additives based on calcined mixtures of clays and limestone leads to the formation of an accreting amount of calcium hydrosilicates and hydroaluminosilicates of various compositions, and of hydrocarboaluminate in samples with high carbonate content, hence decreasing the quantity of ettringite and portlandite.

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