Development of the Technology of Building Ceramics Based on Fusible Clays and Dolomite

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Abstract:

The article examines the possibility of obtaining a high-strength composite material based on low-grade clay and dolomite. Also it was described the new technology of getting composite material from clay and dolomite. In particular, it is noted that the clay-dolomite composite materials after burning gain sufficient strength due to the formation of silicates, aluminum silicates and aluminates of calcium and magnesium. In further steps of hydraulic hardening there were created silicates, aluminates and CaO, interacting with water, forms a hydro silicate and hydro aluminate, which plays a significant role in strengthening and shaping the structure of the clay, dolomite composites.

Keywords: composite material, clay, dolomite, hydro silicates, energy-saving technologies, firing, density, hydrothermal treatment

1. Introduction

Building materials industry is a huge consumer of energy and raw materials. Currently, due to the sharp increase in the price of energy, cost of traditional building materials at the construction industry as well as in other sectors is growing steadily. Regarding that it's obvious to find other materials, does not requiring expensive processing, i.e., transition to resource- and energy-saving technologies.

Thus, the search for and implementation of new technology for low-burnt composite materials presents particular scientific and practical interest [1, 2, 7]. A composite material obtained by molding and firing (as a ceramic material), contains in its structure a sufficiently large amount of binder, which in hydraulic conditions may eventually form the corresponding hydrated silicate. This material has almost the same physical properties as the ceramic one burned at a temperature of 1000-1200°C.

2. Materials and Method

The purpose of research – to study of the influence of the hydraulic treatment on physical and mechanical properties of clay-dolomite composite materials and the formation of structure in the process of hardening of these materials.

In the experiments, samples were prepared on the basis of two investigated fusible clays, which, after firing were the most durable and dolomite Gobustan field (ratio "clay:dolomite" 70:30 ... 30: 70%). After burning, the samples were placed in water for 1 hour and then kept under humid conditions. Samples which are 10 and 30-day-old are subjected to tests in order to study the effect of the hydraulic treatment on physical and mechanical properties. There was identified

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compressive strength and the average true density and frost resistance of the obtained material [3,5, 6].

It was established that the humid hardening, after annealing the portion of exposed samples, increases their strength 1.5-2 times (table 1). Increase of strong characteristics observed in all samples prepared on the basis of different clay deposits. It is found that the highest increase in strength after wet curing was observed in samples containing 50-70% dolomite. Increase of the strength of the samples containing more than 70% of clays, in hydraulic terms is negligible.

3. Results

Comparison of the samples strength values by kinds of hardening permits to suggest that at the samples burnt at 750^0C, solid-phase reactions take place with the formation of minerals that provides increase strength.

It is proved that the density and frost resistance material decreases with increasing clay content i.e. decrease in the values of these indicators directly related to the increase in the content of dolomite in mixtures.

Table 1. Strength indicators clay-dolomite composition materials

Ratio of “clay dolomite”:	Strength of samples on base of Zych clay, MPa			Strength of samples on base of Sumgait clay, MPa			Strength of samples on base of Absheron clay, MPa		
	after burning	HH-10 days	HH-30 days	after burning	HH-10 days	HH-30 days	after burning	HH-10 days	HH-30 days
30:70	18	35	37,5	18,8	36	37,5	17,8	34	37
40:6 0	23	42	46	22	38	44,5	22	41	44
50:50	25	40.5	43	26,5	39	44	25	41,5	45
60:40	27	39	41,5	28,4	40,7	43,5	27,4	39,8	42,5
70:30	28	38	40	30	36,5	39	28	37	39

Note: HH-hydraulic hardening

Based on chemical analysis there were calculated molecular ratio of the basic components (CaO + MgO) / SiO_2 composite materials in the compositions. It was found that with increasing content of dolomite to the value ratio (MgO+ CaO)/SiO_2=2,12 increases the compressive strength obtained clay-dolomitic compositions, burnt at 750°C, exposed to hydration for 30 hours. At the same time tensile strength contains 43 MPa. A further increase of this ratio leads to decrease in strength.

Increased strength with an increase in value of RO/SiO_2 characteristic for all composition materials submitted in the work.

The complex of physical and chemical methods of analysis allows us to establish that an increase in the strength of burnt clay-dolomite composition materials after wet hardening is due to the formation of binder component which is hydrated under humid conditions. The strength of the samples after the hydraulic hardening considerably increases with the content of dolomite in their composition.

The study of the phase content of hydrated clay-dolomite composition materials using X-ray diffraction and differential thermal analysis showed that the composition of all materials present minerals: calcium hydroxide - $Ca(OH)_2$, foshagit - $[Ca_6Si_6O_{17}\ (OH)_2\cdot 2Ca(OH)_2)]$ hydrous magnesium - $Mg_3[Si_4O_{11}]\cdot nH_2O$ and highly basic calcium hydro aluminate - $4CaO\cdot Al_2O_3\cdot 13H_2O$ [2, 8].

For samples with the highest number (50 and 70%) (Fig. 1) dolomite to 10 days of hydration age revealed a very intense lines belonging to the $Ca(OH)_2$. It is also detected weak line (2,92 Å), relating to calcium hydro silicates. It is found that with increasing time of hydraulic treatment of intensity of the lines relating to Ca $(OH)_2$ is reduced. There is a growing intensity of the lines belonging to the calcium hydro silicates. Detection of calcium hydroxide line indicates that the firing of 750°C resulted in partial decomposition of $CaCO_3$. The forming CaO, interacting with water, forms a $Ca(OH)_2$, which plays a significant role in strengthening and shaping the structure of the clay-dolomite composites.

In diffraction patterns of the samples containing 50-70% dolomite there were detected lines related to magnesium hydro silicates. But at the diffraction patterns of the samples containing 70% clay and 30% dolomite, these lines disappear.

For the microstructure of the clay-dolomite composite materials in the later stages of the hydraulic processing is characterized by a pointed crystals, which were identified by electron microscopic analysis (Fig. 2).

In order to clearly identify tumors that are difficult to detect under normal conditions of hardening of composite materials, the goal was set to enter hydration under more severe conditions. Therefore, there were held hydrothermal treatment of clay, dolomite composite materials at a temperature of 175°C and a pressure of 9 atm. for 24 hours to achieve the maximum degree of cure. Of course, this step is not included in the practical purpose of this study, but is important for understanding the role of kinetic factors of firing at selected temperatures.

Burned (at 750°C and 800°C) clay, dolomite mixture at a ratio of C:D = 30:70; 50:50; 70:30 were subjected to autoclaving.

The results of X-ray analysis of the products of hydrothermal treatment of composite materials all ratios show that the ratio of C:D = 70:30 and 50:50 calcium carbonate completely consumed in the formation of calcium hydro silicates. Complete absence of carbonate and magnesium oxide in the product is indirect evidence of the formation, along with calcium hydro silicates and Mg-containing isomorphically substituted silicate.

Calcium silicate type of CSH, and CSH (II) in the diffraction patterns are characterized by broad diffuse peak d=3,03Å. The difficulty of their determination primarily associated with the presence of small amounts of calcium carbonate. This phase is almost always present in the products and gives a very strong diffraction line (d = 3,03Å), which interferes with the determination of some hydro silicates. In such cases, for more reliable identification we are using derivatografic analysis. On the DTA curves of hydrothermal treatment products there were observed exothermic effects in the temperature range 845-895°C with a maximum at 870°C. Crystallization of wollastonite ($CaSiO_3$) was installed by X-ray diffraction analysis of the products. As a result of the thermal decomposition of calcium silicate there was formed anhydrous wollastonite as evidenced by a sharp diffraction lines (3,88; 3,30; 3,08; 2,96; 1,70 Å) of thermal products [4, 5].

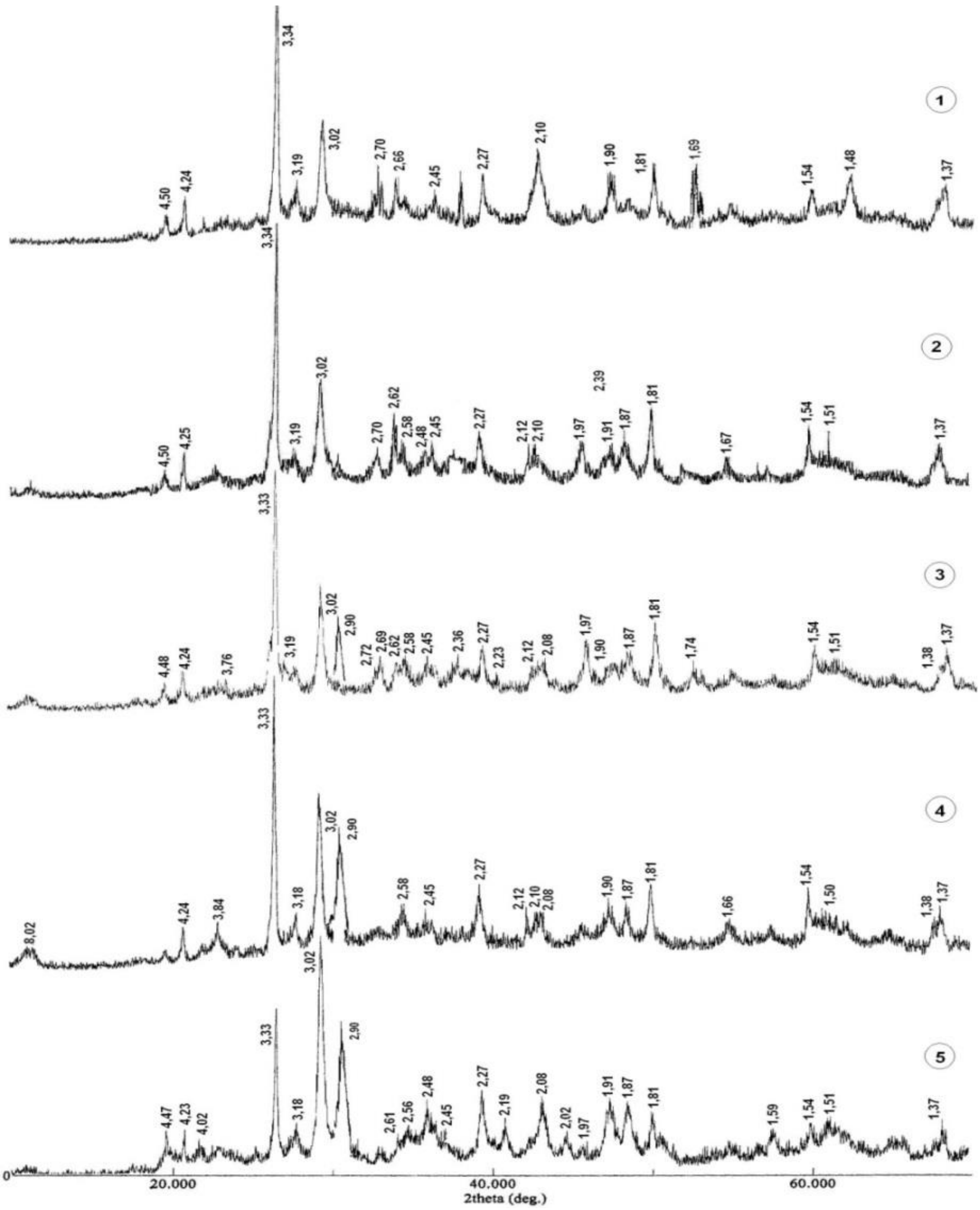
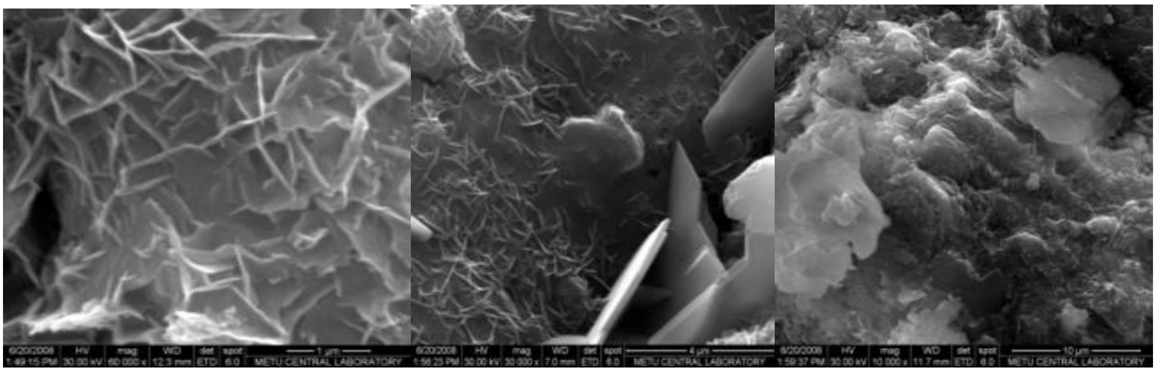


Fig.1. Diffraction patterns of clay-dolomite composition materials (C:D = 50: 50), baked at 750°C: 1 - samples after annealing; 2 - after firing be hydraulically treated for 7 days. 3 - "-" 30 days. 4 - "-" 4 months; 5 - "-" 2 years

A similar result was obtained by thermal conversion of xonotlite ($Ca_6Si_6O_{18} \cdot H_2O$). X-Ray analysis revealed that the product of the hydrothermal treatment of clay-dolomite composition materials is xonotlite - hydrated calcium silicate. This hydrated phase is identified with help of the most intense lines (3,07; 2,04; 1,95Å) of xonotlite.



1 2 3

Fig.2. The microstructure of the clay-dolomite compositions (based on the Absheron clays) with a ratio of clay dolomite: 30:70 (1); 50:50 (2); 70:30 (3), baked at 750 ° C and hydrated for 30 days.

There was studied the interaction of clay-dolomite composite materials with aggressive environment. Tests of the obtained composite materials on chemo resistance conducted in two aggressive environments: acid (H_2SO_4) and alkaline (NaOH). Optimal concentrations were selected: H_2SO_4 - 2.5%, NaOH - 5%. It is found that the samples prepared as ceramic materials more resistant to the effects of H_2SO_4, than the samples prepared as a binder. Materials prepared by both methods were more stable in the environment of NaOH. The strength of hydrated clayo-dolomite composite materials were not reduced after interaction with alkali, but on the contrary, were significantly increased. It is believed that therefore was formed the small amounts of Na, Ca hydrates of aluminum silicates that bind within specific particle components and strengthens the samples.

There was studied the durability of clay-dolomite composite materials. For this reason prepared samples were tested for their strength after storage under humid conditions for 30 d., 2, 4 and 6 years. It is found that the strength values of obtained materials not only do not degrade over time, but even increase after their incubation for 6 years in humid conditions.

Formed structure is constantly changing with period. In order to study the changes in the phase composition after a long time there were held X-ray analysis of the samples. On radiographs of clay-dolomite compositions significant changes were not observed at the age of 2 and 4 years in the phase compositions.

4. Discussion

The works of famous Azerbaijani scientist K.S.Mammadov [4] establish that in systems containing small amounts of CaO or $Ca(OH)_2$ in the presence of SiO_2 can be formed foshagit - hydrous calcium crystal chemical formula [$Ca_6Si_6O_{17}$ $(OH)_2 \cdot 2Ca(OH)_2$)]. He has proved that during hydration $Ca(OH)_2$ can form a mixed structure with all minerals of wollastonite group. According to his theory $Ca(OH)_2$ in the presence of smaller cations (Mg, Al) form with radicals $[SiO4]^{4-}$, compounds possessing astringent properties. These calcium silicates have a layered structure and are stable only in the presence of water molecules.

According to K.S.Mammadov, H_2O molecule in the calcium hydro silicate comprises as a structural unit, the removal of which the structure is accompanied by fairly high energy expenditure and a change of the structure. Validity of this conclusion shows X-ray analysis of hydrated clay, dolomite composite materials.

CONCLUSION

According to the results of experiments we can confidently say that the received clay-dolomite composition materials retain their mechanical strength for a plenty long time. They are also resistant to corrosion, have high frost resistance, strength and water resistance. Clay, dolomite composites combine within the properties of ceramic materials and binders, it is possible to predict the service life of up to 100-150 years.

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