

Mineral Formation of Autoclaved Binders Using Amorphized Raw Materials

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Abstract—The article presents the peculiarities of the mineral formation in the “lime - mineral modifier from amorphized raw material” system depending on the composition of an additive. It is shown that the chemical activity of modifying components in terms of CaO binding and the formation of crystalline neoplasms are significantly different. The similarity of the crystalline ligament of autoclave systems has been established regardless of the raw material composition of a modifier, which is conditioned by the specificity of the mineral components of raw materials and their ability to interact. At the same time for the formation of the maximum amount of the newly formed substance of the hydrosilicate composition, a different amount of the additive is necessary, which is connected with its initial activity.

Keywords— *hydrothermal synthesis; phases; minerals; quartz; hydrated calcium silicate; amorphized raw material.*

I. INTRODUCTION

Autoclaved aerated concrete is most widely used in construction as a structural thermal insulation material. To enhance the competitiveness of manufactured products under production conditions, the coefficient of the structural quality of a material, which consists in increasing the strength properties while reducing its density [1–3], is to be increased.

As it is known, in the traditional technology of silicate autoclaved materials, quartz is the main silica component of the binder in the CaO – SiO₂ – H₂O system as a rock-forming mineral of the traditionally used sands [4–9]. At the same time, its solubility increases during high-pressure steam treatment. Therefore, to reduce the energy intensity of hydrothermal processing in terms of reducing the time or temperature of autoclaving, or to improve the performance of products while maintaining processing parameters, one of the effective ways to control the structure formation processes is to change the composition of a binder, for example, when using highly active dispersed components. The effectiveness of this approach in the use of holocrystalline raw materials was proved by the author in her earlier research works [10, 11].

The use of amorphized rocks instead of crystalline can provide the energy consumption reduction for the production due to their greater activity and “readiness” of raw materials for transformations during treatment of obtained building materials [12, 13].

Technical and operational properties of cellular products directly depend on the macro- and micro-porosity of a

composite, formed during pre-autoclaved structure formation, as well as on the composition and properties of its constituent components. That ensures the formation of the required composition of new formations and structure during hydrothermal processing.

Taking into account the fact that materials of a disordered structure (amorphized raw materials) initially have greater activity, in this research the author studied the effect of mineral modifiers, based on amorphized raw materials, on the phase formation processes occurring under hydrothermal conditions, as well as the final properties of the finished cellular products.

II. METHODS AND MATERIALS

Lump quicklime and modifying additives based on amorphized raw materials were used as the raw materials.

The perlite of the Mukhor-Tala deposit (Buriatia) and the silica clay of the Alekseevsk deposit (Mordovia) were used as raw materials for the production of modifiers.

The modifiers were obtained applying the suspension method: at the first stage, the dry raw material was ground in a ball mill until the grinding limit. This limit was determined visually by the aggregation of particles. Then, the grinding of the raw material in the aqueous medium was performed to obtain a sedimentation-stable suspension with a solids concentration of at least 0.7, humidity up to 20% and high dispersion, determined by passing through a sieve with a mesh size of 0.063 mkm with a residue not exceeding 1%.

The phase composition of the materials was determined by means of ARL 9900 X-ray WorkStation. In the course of the test a method of quantitative full-profile X-ray phase analysis was used with X-ray tube radiation with a Co-anode (diffraction angle interval is $2\theta = 8-80^\circ$, scan step is 0.02°, filtering of β -radiation). The essence of this method, also called the Rietveld method, is in the maximum approximation of the form of the experimental diffraction spectrum to the calculated one. The diagrams were constructed and interpreted on the basis of the PDF-2 diffraction data base using the CrystallographicaSearchMatch program, as well as using the full-profile DDM program of 1.95 s. The preparation of samples for the study was carried out by grinding in an agate mortar with the addition of alcohol.

Due to the complexity of the investigated system and the high complexity of the identification of individual, often X-ray

amorphized phases of mineral formation under conditions of hydrothermal synthesis, the model systems of the composition “lime - modifier from amorphized raw materials” were studied at a ratio of 1/3; 1 / 1.5; 1/1; 1.5 / 1 and 3/1. The silica component in the form of sand as a filler and cement was excluded from the system for the “purity” of the identification of phases newly formed as a result of the interaction of the lime and amorphized components.

It is necessary to note that the ratios of the main interacting components adopted in the research were higher than the real ones used in the production of silicate autoclaved materials (as a rule, the lime / sand ratio is within 1/5). Such elevated concentrations of the constituents of the composition were selected to ensure the interaction of the components and the crystallization of the identified new formations.

In addition it is worth noting that in this research work, the qualitative composition of the products of the interaction of the main components was studied only for crystalline new formations. Their share in the total volume of the formed phases, depending on the ratio of the components of the lime - mineral modifier (MM) system, is in the range of 55–85% when using silica clay MM. The initial concentration of the amorphized component in it is ~ 60%, and 20–70% in the case of perlite MM. The initial concentration of the amorphized component in it is ~ 90%. It is supposed that the content of the amorphized component in the model autoclaved samples is adequate to the dilution degree of MM with lime.

Nevertheless, the concentration of crystalline C – S – H new formations has a rather high informational value, since their real concentrations, taking into account the content of the amorphized phase, as a rule, do not exceed the first ten percent.

III. RESULTS

Model composition “lime – silica clay MM”

According to the results of X-ray phase analysis (Fig. 1), the mineral composition of silica clay modifier is identical to that of the initial silica raw material — silica clay. In addition, except for crystalline quartz, nanostructured mineral forms of silica - low-temperature cristobalite and tridymite, which are components of CT-opals (from the English abbreviation Cristobalite-Tridymite), present the base of this mineral formation of sedimentary origin.

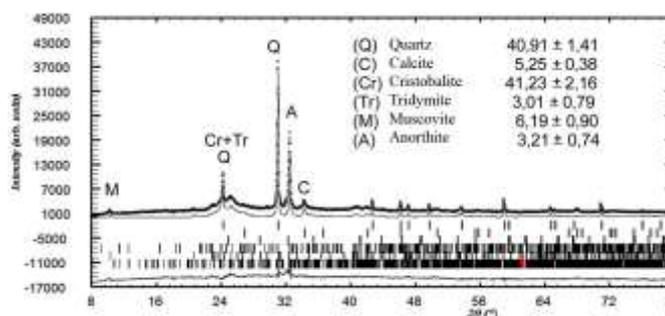


Figure. 1. X-ray diagram of the silica clay modifier at the age of 6 months

A quantitative analysis of the mineral composition of the formed phases allows concluding that the phase composition is strictly dependent on the initial ratio of the components (Table 1).

TABLE I. MINERAL COMPOSITION OF THE CRYSTAL PHASES IN MODEL BINDING COMPOSITIONS OF “LIME – SILICA CLAY MM” AFTER AUTOCLAVING

Mineral	Ratio of components lime/MM				
	1/3	1/1,5	1/1	1,5/1	3/1
Quartz	68,6	32,9	24,4	2,6	1,5
Portlandite	0	9,30	20,8	47,9	48,5
Calcite	17,4	29,3	24,7	6,6	0
11Å- tobermorite	2,4	13,2	1,98	0	0
α-C ₂ SH	0	3,5	20,3	40,4	39,8
Muscovite	11,6	11,8	7,7	2,5	2,78

X-ray diagnostics based on the PDF-2 diffraction database showed the presence of such hydrated calcium silicates as 11Å-tobermorite - Ca₄(Si₆O₁₅)(OH) 2.5 (H₂O) and α-C₂SH (α-Ca₂(SiO₄) • (H₂O)) (Fig. 2).

In addition, all X-ray diagrams show no signs of the existence of nanosized crystalline forms of silica in the form of a CT opal in model compositions (Fig. 2, 1–5). The last fact may indicate that the CT-opal was completely dissolved in the alkaline medium of the lime solution and entered into a reaction with it to form a hydrosilicate gel, from which the 11Å-tobermorite and α-C₂SH partially crystallized.

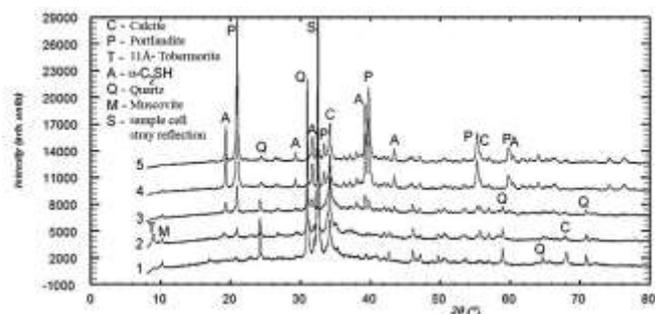


Figure. 2. X-ray diagram of model binding compositions “lime – silica clay mm” after autoclaving:
1 – 1/3; 2 – 1/1.5; 3 – 1/1; 4 – 1.5/1; 5 – 3/1;
C – Calcite; P – Portlandite; T – 11Å- Tobermorite; A – α-C₂SH;
Q – Quartz; M – Muscovite; S – sample cell stray reflection

The increase of the silica component content in the system leads to a shortage of interacting components. The formation of a small amount of crystalline low-basic hydrated calcium silicates is noted. The increase in the share of the lime component (1 / 1.5) contributes to the optimal ratio of the reacting phases, which leads to the formation of a larger amount of tobermorite. Further displacement of the ratio of the main interacting components leads to the deficiency of active reactive silica, which in its turn leads to the formation of unstable highly basic new formations of the type α-C₂SH.

According to the obtained data, it is possible to assess the concentration limits of the existence of determined hydrated calcium silicates in the system “lime – silica clay MM” (Fig. 3).

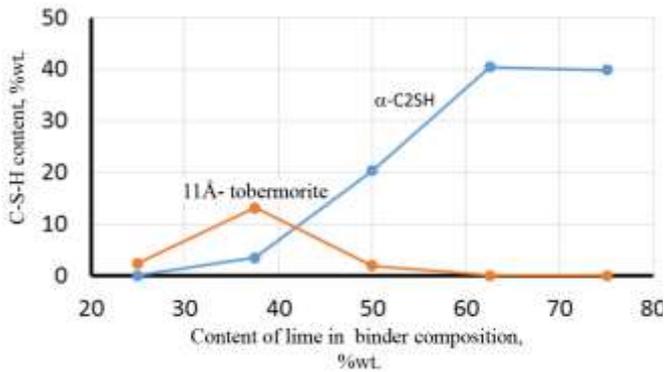


Fig. 3. Concentration dependencies of homogeneity areas C – S – H phases in “lime-MM binder” composition

It is necessary to note that the experimentally defined boundaries of existence for 11Å-tobermorite ~ 37 wt. % CaO and α-C₂SH ~ 60 wt. % CaO are more appropriate according to the modern data of K. Garbev [14] (Fig. 4, a) than the classical scheme of F. F. Taylor [15] (Fig. 4, b).

The absence on radiograms of hardened binding compositions of broad reflection profiles characteristic of the CT opal, which are present on radiographs of silica clay and a modifier based on it, is of great importance. The concentration of quartz in the hardened samples of model binding compositions differs significantly from the theoretical values, which can be obtained from the values of quartz concentrations in the raw material (silica clay), diluted to model concentrations. For example, if the concentration of quartz in silica clay is 38 %, then in model compositions (assuming no interaction with components of the binding system) it should be equal to:

$$C_{MM} \times C_{Quartz \text{ in silica}},$$

where C_{MM} – the concentration of the mineral modifier in the model binding composition.

Taking into account that the main reaction-active component of silica clay in the synthesis of a mineral modifier based on it is a nanostructured form of silica in the form of CT-opal (low-temperature cristabolite and tridymite), it is logical to assume that silica of these mineral formations will firstly participate in the formation of a C-S-H gel from which hydrated calcium silicates will crystallize out.

Figure 4 shows the dependences of the calculated and experimentally determined concentrations of quartz in model binding compositions, depending on the concentration of MM in them.

The significant difference in concentration dependencies can be interpreted as the result of the dissolution of quartz in the highly basic area of model compositions (the left part of the diagram).

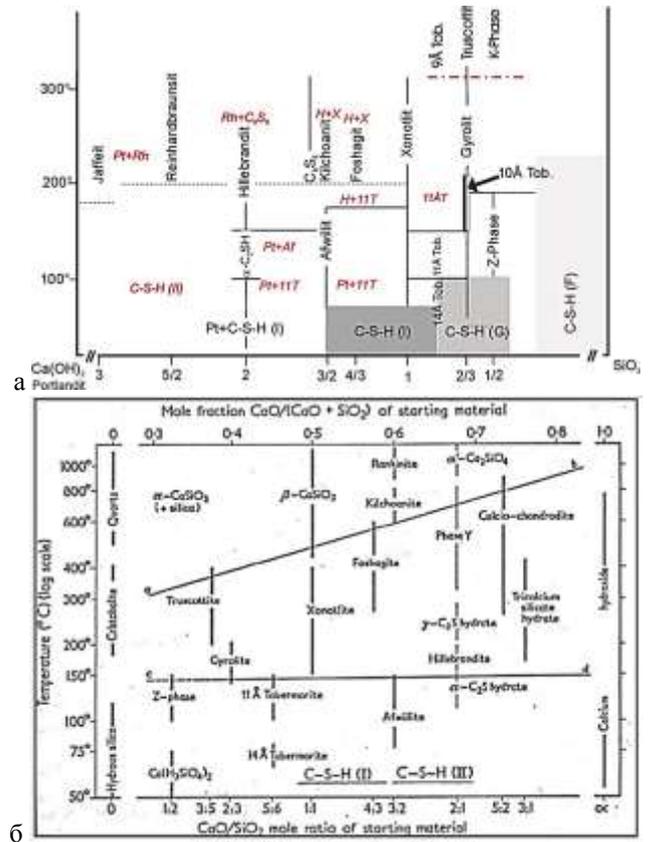


Fig. 4. Temperature-concentration regions of existence of hydrated calcium silicates according to K. Garbev (a) and H. F. W. Taylor (b)

The excess of experimentally determined concentrations of quartz over its theoretical values (the right-hand part of the diagram) is probably the result of auto-epitaxial crystallization of colloidal silica on crystalline quartz individuals.

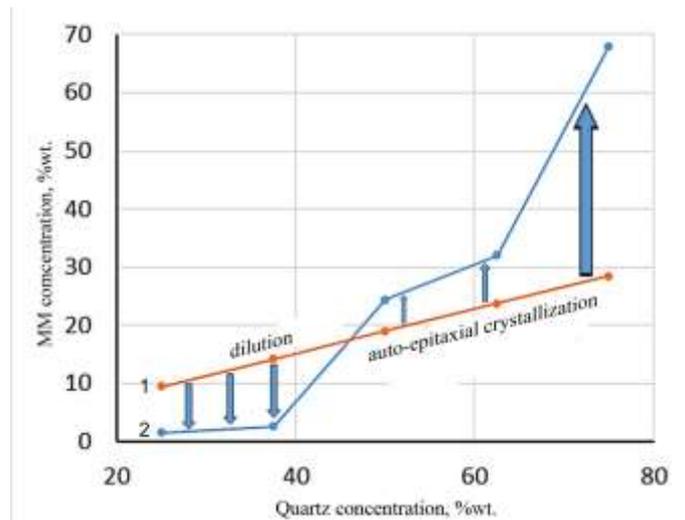


Fig. 5. Dependence of quartz concentration in model compositions on modifier concentration: 1 - calculated, 2 - experimental
Model compositions “lime - perlite MM”

The mineral modifier based on the rock of volcanosedimentary origin - perlite, differs significantly from MM on the basis of silica clay by its mineral and phase composition. According to X-ray diffraction data, perlite is composed mainly of X-ray amorphized material. The difficulty of unambiguous determination of mineral composition of perlite lies in the nanoscale state of its mineral components. In particular, on the radiogram of perlite, besides the intense profile of the amorphized phase (the so-called "halo"), separate selective reflections of crystalline mineral components are recorded. At the same time, unlike silica clay, crystalline perlite formations are represented to a greater degree by quartz, whereas opal reflections are predominantly observed in silica clay. It is explained by the genesis of the rocks: the formation of silica in the form of opal is impossible under the conditions of the formation of effusive rocks.

A quantitative analysis of the content of the amorphized component of perlite was not carried out, but from the ratio of the integral intensities of the diffraction profiles of the amorphized and crystalline components, the content of the amorphized component in perlite was at least 95 %.

The mineral composition of MM on the basis of perlite differed from the initial material by the presence in its composition of the product of shallow bodies grinding - corundum (Fig. 6).

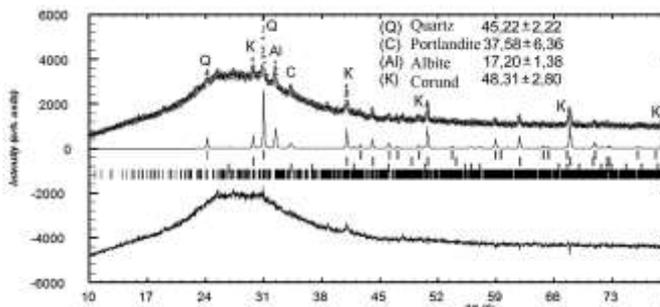


Fig. 6. X-ray diagram of the perlite clay modifier at the age of 6 months. The mineral composition of the model "lime - perlite MM" binder compositions after autoclaving, determined by the method of quantitative full-profile X-ray phase analysis, is similar to the data for the silica clay modifier (Fig. 7, Table 2).

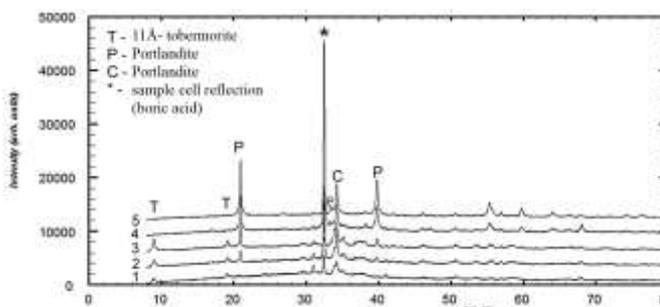


Fig. 7. Radiograms of autoclaved model compositions "lime - perlite MM" 1 - 1/3; 2 - 1 / 1.5; 3 - 1/1; 4 - 1.5 / 1; 5 - 3/1

The basic mass of the crystalline formations is represented by low-basic hydrated calcium silicates, in particular, tobermorite. However, the concentration of the crystalline newly formed substance is higher in comparison to the model

systems from silica clay. The maximum concentration of tobermorite in the case of a perlite modifier is observed with an equal ratio of interacting components (the ratio of lime / perlite MM = 1/1), whereas in the case of silica clay additive, a larger amount of silica component is required (the ratio of lime / silica clay MM = 1/1, 5). At the same time, with the indicated ratios of the components of the system, the amount of crystallized tobermorite when using perlite exceeds almost the same value with the introduction of silica clay almost twice. It is necessary to note the absence of aluminate compounds, fixed, for example, in the usage of crystalline aluminosilicate rocks (granite).

To explain this fact, a petrochemical conversion of the chemical composition of rocks to the standard mineral composition was made according to the CIPW method. For calculations, the PetrExplorer program was used [16].

The chemical composition of perlite was determined by the method of X-ray fluorescence spectral analysis (Table 3).

TABLE II. MINERAL COMPOSITION OF THE CRYSTAL PHASES OF MODEL BINDING COMPOSITIONS OF "LIME - PERLITE MM" AFTER AUTOCLAVING

Mineral	Ratio of components lime/MM				
	1/3	1/1,5	1/1	1,5/1	3/1
Quartz	1,5	0,99	0,78	0	0
Portlandite	0,23	2,24	4,62	13,06	15,3
Calcite	83,9	80,3	67,8	81,9	82,3
11Å-tobermorite	11,8	16,5	23,05	2,04	0,84
Corundum	2,50	0	0	0	0
Magnesite	0	0	2,6	2,9	1,5

According to the data of petrochemical recalculation (Table 4), it can be concluded that the plagioclase in perlite of the Mukhortalinski deposit is probably represented by albite (sodium) types.

TABLE III. PERLITE CHEMICAL COMPOSITION

Oxides	Content, %
SiO ₂	69,5
Al ₂ O ₃	18,3
TiO ₂	0,12
Fe ₂ O ₃	0,87
MgO	0,73
CaO	1,07
Na ₂ O	4,4
K ₂ O	4,6

TABLE IV. RESULTS OF PETROCHEMICAL RECALCULATION OF PERLITE COMPOSITION USING CIPW METHOD

Mineral	Content, %
Quartz	22,66
Plagioclase	42,79
Orthoclase	27,36
Hypersthene	1,84
Corundum	4,1
Rutile	0,12
Hematite	0,87

As a result, it is possible to conclude that the absence of aluminate phases on X-ray images is explained, on the one hand, by the potassium sodium feldspar of perlite, which is characterized by low solubility due to the high degree of polymerization of the silica-containing silicate pattern. On the other hand, this happens because of the high content of the X-ray amorphized phase in a newly formed substance, which can not be identified by X-ray methods.

IV. CONCLUSION

Thus, on the basis of the obtained data, the mechanism of phase formation in the model systems "lime - mineral modifier" was proposed, taking into account the chemical and mineral peculiarities of amorphized raw materials and the technology for the production of a modifier. The use of silica clay (silicate raw materials) in high concentrations leads to the dissolution of active silica and its interaction with lime during the formation of a hydrosilicate gel and its further crystallization into low-basic hydrosilicates of the tobermorite group. In this case, the excess of dissolved silica contributes to its epitaxial crystallization on solid particles of different composition. The reduction in the proportion of silica clay in the system leads to a shift in the balance concentrations of the main components necessary for the formation of low-base hydrated calcium silicates and the formation of unstable α -C₂SH formations.

The use of perlite (aluminosilicate raw materials) ensures the stable formation of low-base hydrated calcium silicates, which is caused by the presence of X-ray amorphized quartz in the perlite composition. The absence of aluminate (aluminum-containing) crystalline new formations is reasoned by the slightly soluble potassium sodium feldspars with a high degree of polymerization of the silicate pattern in the perlite composition.

At the same time, to form the maximum amount of low-base hydrated calcium silicates — the guarantors of the strength of autoclaved hardening products — the optimal ratio of interacting components of the lime-mineral modifier system is 1/1 in the case of perlite and 1 / 1.5 in the case of silica clay.

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