

Issues of structure formation of multi-component construction materials

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Abstract. Growing volumes of construction result in the rising demand for high-quality wall materials and products, growing relevance of availability of resource and raw-material base of natural and industrial products for the construction industry. Structural, physical and mechanical qualities of these products can be improved through systematical selection of compositions based on natural and raw materials, including nano-scale products. The goal of this paper is to provide rationale for structure formation mechanisms of multicomponent materials (silica-lime, silicate, cement materials), with the possibility of using nano-scale products in their production. The primary mechanism of directed structure formation at the interface boundaries of binders are nano- and ultra-disperse particles with high absorption and adhesion properties, which are primarily intended to strengthen the contact area (one of the key structural units of multicomponent binders). The knowledge of genesis, chemical, mineralogical, and phase compositions, as well as specific features of formation of nano-technological raw materials, enables optimization of construction product properties. Using the small-angle neutron scattering method, we identified granulometric and surface properties of a series of nano-technological products (binary and sludge) and materials where such products are used, which enabled us to design optimal mixture compositions and parameters of pressing operations.

1 Introduction

Multicomponent binders are produced by combining various pure binders (sometimes mixed with certain additives), which ultimately enables the production of composite materials with specific properties or with sets of properties characteristic of each component.

Production of multicomponent binders and materials on their basis (silica-lime, silicate, cement materials) is a very promising area allowing the effective use of natural and industrial calcium carbonates, aluminosilicates (zeolite-containing and burnt rocks, ashes of thermal power plants, slag and sludge wastes, pozzolans, limestone, dolomite and chalk processing wastes, and etc.) characterized by nano- and micro-sized original particles.

Manufacture of products with elements of nanotechnology in the construction industry is currently under-developed. In particular, this is due to the need for preliminary preparation of raw components and search for alternative sources of raw materials. The quality of construction materials and products can be improved through the use of

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multicomponent compositions that cannot be produced without complex chemical additives and fillers. Fillers are intended to reduce the use of binders, improve a number of technological and technical properties of end products, as well as for preparation of additives of various applications. Demand for high-quality fillers can be supplied through recovery of industrial raw materials (wastewater sludge, sieve residues of rock crushing products, dust catching, etc.).

2 Materials and Methods

Several technological areas of hydration and autoclave methods for structure formation of multicomponent binder-based construction materials have been developed by a number of authors in their studies [1 - 5]. However, the issues of structure formation of multicomponent binder-based construction materials, including, in particular, silica-lime (silicate) binders of contact-condensation (non-autoclaved) hardening are still relevant [6 - 8]. Thus, rationale for structure formation mechanisms of multicomponent materials with the possibility of using nano-scale products in their production remains the issue of considerable scientific and practical interest.

According to V.D. Glukhovskiy, R.F. Runova, processes of contact-condensation hardening are based on the condensation theory, i.e. due to their energetic instability and high chemical reactivity, separate disperse materials are characterized by condensation ability that reduces as these materials lose free energy [6 – 8]. This process occurs when the structure of a material is in amorphous or submicrocrystalline state. Sufficient proximity of macroparticles is an essential prerequisite for contact hardening. This is achieved by hyperpressing, and irreversible contacts between disperse particles are distinguished by their water-resistance after pressing.

Contact-condensation hardening is characteristic of a large group of silicate and aluminosilicate materials of natural and artificial origin, as well as their hydration and dehydration products, etc. In the process of contact-condensation hardening, the pressure of pressing can range from 20 to 100 MPa and above.

Irreversible bond develops between the particles of the semi-finished product under pressure, which is accompanied by mechanical syneresis of liquids which can occur only in the most stressed area of the system [6 - 15]. Porosity change when pressing the system results in phase displacement, and the unstable phase is to pass through the stressed area, i.e. the interparticle area, to ensure syneresis of liquids [6 - 8]. The binder moves from source to drain under the influence of pressure gradient. In this technology, the binder is evenly distributed by volume at the process stage that precedes pressing operations (preparation of the multicomponent binder, mixing the components). The system of interest is characterized by the complicated topological network of capillaries, their diameter and length, as well as filling of cavities with phases. Furthermore, self-arrangement phenomena with threshold transitions occur in the system [6 - 8]. The pressing process of multicomponent systems is accompanied by structural and phase transitions: small portions of new hydrated calcium silicates appear, the binder breaks into free liquid and solid phase, solid unstable phase condenses, etc. [6, 7]. Some of these transitions play a secondary role in contact-condensation hardening, while structural transitions in the binder are of primary importance. As load is applied, the binder is distributed through the system of pores interconnected by capillaries. Redistribution of the binder causes the occurrence of gas blocks in capillaries, thus defining the spectrum of intergranular areas by the strength of their distribution [6, 7]. Interaction of local cluster structures of the binder leads to appearance of larger clusters and, ultimately, to appearance of an infinite cluster by the binder and its reaching the area boundary. Ensuring the strength of the semi-finished product is viewed as interconnection of two cluster structures of different physical levels:

the binder as clusters of flow distribution through the system of capillaries and force bonds between the contacting areas of structural elements [6, 7]. Growth of either of them leads to gradual degradation of the other, and when the concentration of force bonds reaches the percolation threshold, the main structure of a water-resistant semi-finished product is formed [6, 7].

In the process of pressing, a partially saturated capillary porous system undergoes structural changes at the macro- and micro-level. The system of sources and drains is formed, which plays a major role in distribution of the binder; furthermore, the boundary is impermeable for the liquid-solid phase and partially permeable for the gas phase [6, 7]. Formation of the water-resistant main structure of semi-finished product (at the macro-level) is viewed as statistical occurrence of phase contacts in the structure in the most stressed areas of membrane phases. When the percolation threshold is reached, an infinite percolation force cluster is formed, and this results in a step variation of strength properties of the end product [6, 7]. At the micro-level, the movement of heterogeneous multiphase medium results in formation of tangential stress and velocity gradients in the convergent channel. This triggers rearrangement of solid phase particles with a growth of density. The transition is accompanied by the outlet of uncoupled liquid phase, its destructuring and transition in the drain areas. Smaller peripheral unfilled capillaries and cavities with compressible gas section, partially filled with liquid, will serve as drains. Heat released during pressing facilitates additional water outflow, as well as the growing effect of the system's constraint [6, 7].

Natural fillers fall into two general categories: one-component (e.g. quartz, feldspathic, carbonate) and two-component (e.g. carbonate-siliceous), which are frequently called binary. The latter are rather rare as their preliminary preparation for use requires special technology, so they have a scientific and practical value. We used a two-component filler in our work (flue dust from production of road construction materials) [16, 17]. This filler is an industrial product with crystal nano-size particles of calcium carbonate and microsilica. Nano-particles enable the filler to actively participate in physical and chemical processes due to their fractal size and high degree of self-arrangement [16, 17]. This is the main process involved in the formation of a stable structure and predetermined properties of multicomponent materials. At this point, new compounds are formed, such as calcium hydrocarboaluminate and low-base calcium silicate, therefore chemical reactivity of the filler is considerably higher than that of one-component micro-size fillers based on SiO_2 and CaCO_3 . Formation of new chemical compounds and development of a denser structure of the filled binder significantly increase the durability of cement compositions [16, 17].

Another promising area is practical application of sludge fillers containing chemically bound and adsorption water, in the production of construction materials [16, 17]. Sludge residues are quasi-solid bodies, inorganic polymers, and their properties are associated with strength properties of the structural grid, which, in its turn, is the quantity function of adsorption water. On the one hand, quasi-solid water serves as a link that ensures adequate deformation resistance of the whole system. Nano- and micro-size fillers combined with surface-active agents facilitates the formation of a close finely porous structure, making the cement rock less permeable for water and corrosive effects. Presence of adsorption-bound water is a significant factor in strengthening the contact layer of multicomponent raw mixtures, including decorative, finishing, and heat insulation solutions, etc. It should be noted, however, that introduction of fillers increases the total surface area of solid particles, thus increasing water demand of the mixture. The particles comprising the filler are characterized by fractal dimensions [16, 17].

Self-arrangement processes are associated with the pattern of particle motion and depend on their physical properties, as well as their collision and interaction properties. Their high ability for self-organization is based on their surplus of energy.

3 Results

Key technological operations in the production technology of non-autoclaved silicate products include preparation of the binder, mixing the binder and the filler, pressing the products and their further drying (temperature from 70⁰C). The binder is prepared by mixed grinding of the original components proportioned in the ratio of 5:7.

Further steam treatment of silica-lime binders is performed at the temperature of 90...100⁰C for 2 hours, water-solid ratio is maintained at 5...8. The prepared mixture is pressed at 40...60 MPa to form the product. After drying, compressive strength of the pressed products is 15...20 MPa; water absorption percentage is ~ 10%, frost resistance is - 35 cycles (meets the requirements of the Russian Standard GOST 379-2015 *Silicate Bricks, Stones, Blocks and Partition Blocks. General Specifications* [6, 7]. Analysis of the research shows, that preferred parameters for practical application are: pressure 54...56 MPa, pressing time 25-27 sec.

Studies of sludge over atomic structure by the low-angle neutron scattering method at the Membrane-2 diffractometer (B.P. Konstantinov Petersburg Nuclear Physics Institute, Gatchina) show that the particle size is 40-80 nm [17]. Regarding the content of basic oxides, mineral sludges fall into the categories with prevalence of: s-cations (Ca⁺², Mg⁺²), p- and d-cations (Fe⁺³, Cr⁺³, Al⁺³). Regarding the basicity factor, mineral sludges can be divided in two groups [16, 17].

The first one is comprised of ($M_0 > 1$) sludges consisting primarily of fine-grained crystalline CaCO₃, as well as hydroxide sludge where the amount of CaCO₃ and MgCO₃ prevails over metal hydroxide content. The second group is comprised of ($M_0 < 1$) aluminocalcium, aluminocalcine sludges and sludges of electroplating industry.

4 Discussion

Thus, the occurring mechanical syneresis of liquids and rearrangement of aggregates result in a gradual increase of the volume fraction of the solid phase finely-dispersed component [6, 7]. Upon reaching small distances between the particles under the influence of the concentration factor, wedging forces, as well as gradual transition of the particles into the area of constrained state and further into the area of the closest potential well, come into action. The area where the solid phase reaches critical concentration coincides with the occurrence of percolation condensation front that divides the contact area into two: the dynamic membrane area and the capillary-porous body area [6, 7]. The percolation area gradually shifts to the volume phase area. In the process of percolation, solid phases of unreacted particles act as fillers in the micro-system and do not form phase contacts. With the pressing pressure up to 50-60 MPa, incomplete coalescence of particles occurs at the level of colloidal particles of gel masses, as the most active ones in terms of energy [6, 7]. In the process of silica-lime mixture preparation, large hydrosilicate crystals, which have formed earlier, do not participate in the contact-condensation processes having been already crystallized, and simply act as an active filler for micro-pores. Gel matrix acts as binder matrix, and forms the basis for the main structure of semi-finished product to form under the influence of deformations. This is due to partial overlapping of porous clusters in elastic nodal points of the gel periodic grid [6, 7]. It is assumed that the density in such aggregates decreases towards the periphery, so their bond elements acquire partial translation and rotation motion ability, which causes interaction of cluster crystallites in their outer layers. This also allows for a more dense packing of some sol particles that have not joined the gel grid yet. When the aggregate concentration is critical, an infinite percolation graph (cluster) is formed on overlapping spheres, which should be associated with emergence of phase irreversible contacts in the most energy-intensive overlapping cluster areas, i.e. with

formation of the main structure of the semi-finished product [6, 7]. This mechanism of the main structure formation implies a sufficient supply of gel component in the system under pressure as a carrier of contact-condensation properties. This component is used both for coating of large crystals and filling the cavities remaining in the system. Viewing consolidation of unstable molding compound as a redistribution process of unstable binding phase between the drains and sources explains the principal difference of the part that pressing pressure plays for different compositions. For instance, in case of cement concrete that hardens under pressure, the gel layer developing through hydration of clinker particles has a relatively strong bond with the particle surface, so its motion abilities against the surface are highly constrained. Free water remaining in cavities feeds this gel layer in the process of further hydration of clinker grain, and thus produces constant wedging pressure that prevents the particles from transition to the constrained energy level. Taking into consideration that the solid phase density of the gel layer decreases towards the periphery, insertion (overlapping) of such grids one into another is to be expected. This overlapping will rise along with the increase of pressing energy. Although a higher concentration of the solid phase is observed in the overlapping area, this concentration is insufficient for the particles to break the wedge barrier and establish phase contacts, as the particles have no kinetic component. Such conditions are met only provided that free water stops feeding the gel. Drainage of the grain gel area due to water evaporation provides for creation of free volumes and enhances the probability of their filling. The role of external pressure in the process of strengthening will increase. However, the probability of such transition decreases due to the increase of critical shear stress. In the latter case, there is a highly filled unstable phase between the contacting grains in the cavities; this phase has a weaker bond with the structural elements and, in case above-critical stress occurs, it squeezes into the neck cavities where it condenses and repacks, so finally this provides the conditions for a percolation phase transition [6, 7].

Among recommendations for composition design of multi-component binders and materials on their basis, based on the data analysis, the following should be highlighted:

1) compositions must be multicomponent, while the components must partially remain in their unstable active form, and the other part must constitute crystalline compounds. The basis for hardening is formed by unstable components containing Al_2O_3 , SiO_2 , as well as basic oxides that form a group of varying reactivity with alkaline oxides;

2) reactivity of multicomponent binders depends largely on the surface reactivity, therefore fillers in micro-disperse state are preferred;

3) products on the basis of such mixtures and solutions should be manufactured by pressing or hyperpressing in order to ensure the contact between the particles under conditions of water deficit (including free water) in the system;

4) hardening conditions also play a major role, so it is preferable to perform this process in low temperature environment ($\sim 80 \dots 105^\circ \text{C}$);

5) nano-disperse modifiers that form a monolith structure after pressing and fill spaces between the particles play a positive role. Nano-fillers should have a chemical reactivity under the conditions of pressing.

5 Conclusion

Studies of mutual coordination and kinetics of skeleton formation of construction composite materials, modeling its probability structure are among the least explored areas of contemporary Materials Science.

Therefore, potential energy gain facilitates its transition into kinetic energy, which will repack the particles and increase their concentration. If we prepare the mixture using the separate technology scheme suggested by V.I. Solomatov, pressing silicate, cement

compositions following the strengthening scheme described above will give a greater effect of pressure [1, 6 - 8]. The mixtures of interest are characterized by a well-developed interface area between separate phases and minerals, which requires strength improvement between separate structure elements. The primary mechanism of directed structure formation at interface boundaries of these binders are nano-, ultra- and micro-disperse particles with high absorption and adhesion properties, which are primarily intended to strengthen the contact area (one of the key structural units of multicomponent binders). This factor, in particular, enabled us to select the materials for experimental research.

Prior experience in working with multi-component materials proves the feasibility of applying products of nano-technological origin. Positive influence of introducing secondary nano raw materials in the production of construction materials implies its relevance in the future, and encourages the search for new sources of waste generation [18 - 26]. Further rationale for technical and economic efficiency of manufacturing fillers of nano-technological origin in a working environment is required.

References

1. V. V. Babkov, V. N. Mokhov, S. M. Kapitonov & P. G. Komokhov, *Structure Formation and Destruction of the Cement Concrete* (Ufimskij poligrafkombinat, Ufa, 2002)
2. V. R. Falikman, *Industrial and Civil Construction* **1**, 31-34 (2013)
3. I. V. Melikhov, *Physical and Chemical Evolution of the Solid Substance* (BINOM. Laboratory of knowledge, Moscow, 2006)
4. A. I. Gusev, A. A. Rempel, *Nanocrystalline Materials* (Physmathlit, Moscow, 2001)
5. V. I. Roldugin, *Physics and Chemistry of the Surface* (Dolgoprudny: TCC INTELLIGENCE, Moscow, 2008)
6. Y. V. Sidorenko, *Modelling of Contact-Condensation Processes of Low-Basic Calcium Hydrosilicates Hardening: PhD Thesis* (SSUACE, Samara, 2003)
7. Y. V. Sidorenko, S. F. Korenkova, *Multi-Level Synergetic Approach to Formation of the Hardening Mechanism of Contact-Condensate Systems of The Silicate Type* (SSUACE, Samara, 2005)
8. Y. V. Sidorenko, S. F. Korenkova, *Solid State Phenom* **871**, 47 - 52 (2016)
9. H. Haken, *Secrets of Nature. Synergetics: the doctrine about cooperation* (Institute of Computer Science, Moscow-Izhevsk, 2003)
10. V. I. Roldugin, V. M. Zhdanov, *Adv. Colloid Interface Sci.* **98**, 121 - 215 (2002)
11. V. I. Vereshchagin, L. P. Rikhvanov, Y. S. Sarkisov, Y. F. Asoskov, A.P. Smirnov, *Tomsk Polytechnic University Proceedings* **315 (3)**, 12 - 15 (2009)
12. V. E. Romanenkov, E. E. Petyushik, *Physical and Chemical Bases Of Hydration Powder Media Hardening* (Belarusian Navuka, Minsk, 2012)
13. B. M. Dolgonosov, *J Colloid*, **63 (1)**, 39 - 42 (2001)
14. L. I. Loitsiansky, *Fluid and Gas Mechanics* (Drofa, Moscow, 2003)
15. P. V. Konarev, M. V. Petoukhov, V. V. Volkov, D. I. Svergun, *J. Appl. Cryst.* **39**, 277–286 (2006)
16. S. F. Korenkova, Y. V. Sidorenko, *IJAER* **10 (20)**, 40908 - 40913 (2015)
17. A. M. Guryanov, S. F. Korenkova, Y. V. Sidorenko, *MATEC*. **86**, 04011 (2016)
18. E. V. Romanova, *Solid State Phenom* **871**, 132-137 (2016)

19. E. V. Romanova, *J. Of Economy and entrepreneurship* **9 (74)**, 984 – 987 (2016)
20. E. V. Romanova, *MATEC* **73**, 07010 (2016)
21. T. Y. Vavilova, N. D. Potienko, I. V. Zhdanova, *Procedia Eng.* **153**, 938 - 943 (2016)
22. M. B. Djukic, G. M. Bakic, V. Sijacki Zeravcic, A. Sedmak, B. Rajcic, *Corrosion* **72 (7)**, 943 - 961 (2016)
23. D. Mailyan, L. Mailyan, *MATEC* **73**, 04020 (2016)
24. R. R. Bhargava, S. Hasan, *Applied Mathematical Modelling* **36**, 5741-5749 (2012)
25. L.G. Spiridonova, *Urban Construction and Architecture* **2 (19)**, 54-59 (2015). doi: 10.17673/Vestnik.2015.02.9
26. A.M. Fattakhova, *Urban Construction and Architecture* **2 (19)**, 60-66 (2015). doi: 10.17673/Vestnik.2015.02.10