Analysis of early structure formation of anhydrite binders from secondary raw materials using microcalorimetry

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Abstract. This article presents results of a research on changes in energy parameters of fluorogypsum composition of normal consistency with introduction of various additives (μΔn) such as sodium sulfate and sodium sulfite. Activity of binder in interaction with water was defined as the sum of thermal effect of hydration and thermal effect of dispersion of fluorogypsum crystal lattice. In order to compare processes of heat release in the studied gypsum-containing systems, the article presents results of analysis for the following ones: fluorogypsum binder – water, fluorogypsum binder – sodium sulfate – water and fluorogypsum binder – sodium sulfite – water. Research has shown that processes of hydration during by development of alternating exothermic and endothermic effects in systems containing fluorogypsum binders.

1. Introduction
Taking into account significant needs of construction industry in material resources, Russia has developed a system of construction and technological utilization of industrial waste which includes ensuring environmental safety, as well as assessment, testing, classification and regional accounting of waste as a source of secondary raw materials for manufacturing products, component and technological forecasting; rationing, standardization of construction materials with maximal use of secondary raw materials [1, 2, 3]. Efficiency of secondary raw materials’ usage depends on how much they are studied as potential raw materials for production of specific building materials.

In construction of buildings, alternative gypsum-containing secondary raw material – fluorogypsum – from chemical, nuclear and non-ferrous metallurgy enterprises can be used as finishing and wall material [4, 5]. The reason for slow introduction of fluorogypsum raw materials in production of construction materials is instability of its composition and properties, low activity and strength of the hardened stone, as well as insufficient knowledge of physical and chemical processes of its structure formation. Therefore, firstly, it is necessary to systematize and develop its classification by most important parameters and characteristics, and then distribute obtained data among the forming territorial-industrial complexes for production of construction materials [1, 3, 6].

Existing problems of utilization of fluorogypsum waste in production of construction materials are related to ambiguousness of available data on the mechanism of hydration and structure formation of binders based on it [7, 8]. As a rule, to intensify processes of hydration and hardening of anhydrite binders hardening activator additives are used. Identification of mechanisms of hydration and
hardening processes that commence with introduction of additives is important for understanding processes of transition of the system to a colloidal state at first, and then to a crystalline one. For an efficient selection of external energy impact at an early stage of hydration process development, it is necessary to analyze alternations in energy parameters in the fluorogypsum binder – water system using known laws and tools. It is recommended to use Gibbs equation, the combined equation of the first and second laws of thermodynamics [9]:

$$\Delta G = \Delta H - T \Delta S = P \Delta V + \sigma \Delta s + \mu \Delta n + \phi \Delta q - T \Delta S,$$

where $\Delta G$, $\Delta H$, $T \Delta S$ – free energy, enthalpy and entropy factors of the fluorogypsum binder – water system accordingly.

Results of analysis of enthalpy and entropy factors’ energy components help to select probable impacts on the fluorogypsum – water system managing complex physical and chemical processes of hydration and structure formation of fluorogypsum compositions. This article presents results of the research of energy parameter alternations in fluorogypsum composition of normal consistency after introduction of various chemical additives ($\mu \Delta n$). The energy released or absorbed during formation of new chemical compounds and changes in its phase composition are analyzed.

2. Research methodology and applied materials
Hydration of fluorogypsum binders is accompanied by heat release, which is spent on dispersion of particles over a long period of time and increase in entropy of the system. It is inefficient to use existing microcalorimeter designs to control system temperature changes, since they allow determining only the total amount of heat generated by the system. During the research, instrumental determination of heat release during early structure formation of fluorogypsum composite binders was performed using a differential microcalorimeter (DMC) [9-12] based on temperature difference between dry powder (reference sample) and fluorogypsum composition with a given water content located in two thermally insulated calorimetric cells. The DMC design allows using the principle of differential thermal analysis (DTA), which helps to control temperature difference between calorimetric cells over time. The resulting hydration heat is determined by temperature difference between the cells.

The following materials were used in the research: powdered fluorogypsum with a specific surface area of 400 $m^2/kg$ neutralized with limestone flour. Mineralogical composition of fluorogypsum is represented by the following components: $CaCO_3 - 5.0\%$, $CaF_2 - 6\%$, $CaSO_4 \cdot 2H_2O - 10.0\%$, $CaSO_4 - 79.0\%$. Sodium sulfate (GOST 6318-77) and sodium sulfite (GOST 5644-75) were used as hardening activators. During the research $W/T=0.46$ fluorogypsum binder with content of sodium sulfate and sodium sulfite in the amount of $2\%$ of the weight of fluorogypsum was used.

3. Research results
Changes in temperature difference in the fluorogypsum binder – water system during hydration and hardening over the first 72 hours are given in Figures 1 – 3. The first intensive maximum of heat release in the fluorogypsum binder – water system (Figure 1) is due to a decrease in surface energy of the solid phase and release of hydration heat. Activity of binder in interaction with water is determined by the sum of thermal effect of hydration and thermal effect of dispersion of fluorogypsum crystal lattice with $Q_d > Q_h$. After contact of fluorogypsum binder without additives with water, wetting temperature is $1.7^\circ C$, minor bursts of dispersion and crystallization are apparently associated with the presence of soluble form of calcium sulfate in fluorogypsum.

In this system, there is a cyclical repetition of processes of dissolution and crystallization of accumulated products every 24 hours during 3 days (Figure 1). Heat release kinetics of fluorogypsum binder with addition of sodium sulfate is also cyclical (Figure 2). After binder’s contact with water, intense heat generation occurs during first minutes, and then the heat is spent on dispersion. Long second induction period of the binder with addition of sodium sulfate which lasts about 15 hours is apparently associated with dissolution of developed double salts. The processes of dissolution and crystallization are also cyclical. In all systems (Figures 1 – 3), after a temperature decrease in
induction period, during which entropy factor prevails, temperature increases after a certain period of
time due to release of crystallization heat.

Figure 1. Kinetics of dissipation of the composition: fluorogypsum-water over 72 hours

Heat release kinetics of fluorogypsum binder with addition of sodium sulfite also has cyclical
character, with dispersion process lasting about 3 hours and crystallization process lasting about 15 –
20 hours. With addition of sodium sulfite dissolution processes intensify and heat release processes are
much faster (Figure 3). Formation of primary hydrated particles and their subsequent association due
to coalescence is manifestation of binding properties of fluorogypsum binder.

Figure 2. Kinetics of dissipation of the composition: fluorogypsum-sodium sulfate-water over 72 hours
Figure 3. Kinetics of dissipation of the composition: fluorogypsum-sodium sulfite-water over 72 hours

Thus, it has been shown that processes of hydration during the first 72 hours are accompanied by development of alternating exothermic and endothermic effects, which is indicative of intermittence of processes developing in systems containing fluorogypsum binders.

4. Conclusion

Analyzing hydration and structure formation processes of fluorogypsum binders with additives of sodium salts, it is necessary to take into account energy components of enthalpy and entropy factors, accompanied by alternations in temperature, which can be measured using differential microcalorimetry. Mechanism of fluorohydrite binder hydration according to heat release kinetics is manifested in periodic topochemical colloidization of hydrating substances and subsequent crystallization of developed hydration products.

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