On thermal effects of early structure formation of fluorogypsum composite binder

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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 construction gypsum G-5AII and sodium sulfate. The effects were assessed by temperature changes in the binder – water system. In order to compare processes of heat release in the studied gypsum-containing systems, the article presents results of analysis for the following ones: construction gypsum – water, fluorogypsum binder – water, fluorogypsum binder – construction gypsum – water and fluorogypsum binder – sodium sulfate – water. All processes of hydration and structure formation occurring in the system of fluorogypsum – water are accompanied by a change in temperature, which can be measured using differential microcalorimetry.

1. Introduction

In accordance with the modern international concept of combining state and market interests, as well as Federal laws 89-FZ “On production and consumption waste” and 184-FZ “On technical regulation”, work with industrial waste is being unified and regulated in order to ensure safety, resource conservation and full involvement of natural resources in the national economic turnover.

Significant need of Russian construction industry in resources resulted in development of a system of construction and technological utilization of industrial waste, which includes provision of biological and technospheric compatibility and environmental safety as well as assessment, testing, classification and regional accounting of waste as a source of raw materials for production of various items. The system also provides for standardization, rate making and technological forecasting as well as confirmation of compliance of developed construction materials with principles of complete utilization of waste [1 – 3]. To ensure required quality of industrial waste final products, it is necessary to scientifically substantiate composition and technological processes of production of building materials, taking into account structure formation optimization principles [4 – 6]. Effectiveness of creating science-based principles and technologies of structure formation depends on the efficiency of research of
industrial waste as potential raw material for production of special-purpose building materials, i.e. it is necessary to conduct testing, identification and assessment of waste according to functionality criterion.

In residential and public buildings construction, gypsum composite materials are widely used as finishing and walling materials. In Russian regions where there are no gypsum stone deposits, an alternative raw material for production of effective walling and finishing materials can be fluorogypsum (FG), a by-product of hydrofluoric acid production, consisting mainly of anhydrous calcium sulfate [5, 7]. The need to use fluorogypsum is an effective solution to the problem of integrated use of natural resources in construction materials production, reducing transfer of land for waste storage and pollution of the environment. Chemical and nuclear industries, as well as non-ferrous metallurgy, annually store more than half a million tons of sulphate-calcium waste (fluorogypsum). The reason for insufficient utilization of fluorogypsum raw materials in production of building materials is instability of its composition and properties, low activity and durability of hardened stone, and insufficient study of physical and chemical processes of structure formation of fluorogypsum in a powdered state. Therefore, it is necessary to systematize and develop a classification of fluorogypsum waste by chemical composition and physical and mechanical characteristics, followed by application of received data by forming territorial-industrial enterprises for production of construction materials and products using regional industrial waste, modern technologies and equipment [1, 3, 8].

For a more widespread use of fluorogypsum in building materials production, it is necessary to develop technologies to accelerate structure formation and increase composite binder strength. Emerging problems of utilization of fluorogypsum waste in building materials production are explained by lack of reliable data on the mechanism of hydration and structure formation of binders based on it. Available scientific data on hydration and structure formation, as well as factors affecting the strength of anhydrite construction compositions is debatable [9, 10]. To intensify processes of hydration and hardening of fluorogypsum compositions, it is necessary to accelerate formation of primary (nanodispersed) products of hydration by external energy influences. For a conscious and reasonable choice of external energy impact at an early stage of hydration processes development, it is necessary to establish changes in energy parameters in the fluorogypsum binder – water system using known laws and mechanisms. It is recommended to use the Gibbs equation, the combined equation of the first and second laws of thermodynamics [11]:

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

where $\Delta G$, $\Delta H$, $T \Delta S$ - free energy, enthalpy and entropy factors of the fluorogypsum – water system respectively;

$P \Delta V$ – work performed by the system when the volume changes, or energy required to make this change (compaction of mixture);

$\sigma \Delta s$ – work performed by the system when a new surface is formed, or energy released or absorbed when this change happens (mechanical dispersion of fluorogypsum);

$\mu \Delta n$ – work performed by the system or energy released or absorbed during formation of new chemical compounds and mutual changes in the amount of substance in the system, as well as changes in its phase composition (utilization of chemical additives, activators of hydration and hardening);

$\varphi \Delta q$ - work performed by the system when changing its electrical potential and amount of electricity in the process of changing ionic composition of the liquid or solid phase, when dispersing and forming a new surface (electrophysical, electrochemical impacts on the system);

$T$ – temperature of the system,

$\Delta S$ – change in entropy (degree of system disorder during dispersion).

Results of enthalpy and entropy factors energy components analysis offer an opportunity to determine possible impacts on the fluorogypsum – water system for management of complex physical and chemical processes of hydration and structure formation of fluorogypsum compositions. The given article presents results of a research on energy changes in fluorogypsum composition of normal
consistency with introduction of various chemical additives ($\mu\Delta n$). The effects were assessed by temperature changes in the binder – water system.

2. Materials and methods
Hydration and structure formation of fluorogypsum composite binders occurs with release of heat, with quantitative determination of which in kinetics, additional scientific data can be obtained to explain the mechanism of this process. During the research, instrumental determination of heat release during early structure formation of fluorogypsum composite binders was performed using the differential micro-calorimeter (DMC) [11-13] based on temperature difference between dry powder (reference sample) and a fluorogypsum composition with a given water content located in two thermally insulated calorimetric cells (CC). Temperature sensors (resistance thermometers) are located in the cells and connected via a balanced bridge circuit and an analog digital converter to a computer, which allowed controlling change in temperature difference between calorimetric cells over time.

In both cells, an equal amount of dry fluorogypsum is poured by weight and compacted to the same volume. In the reference cell, the binder remains dry, and a calculated amount of water is added into the other cell. When water is introduced into the cell with binder, the heat of wetting and hydration is released, the value of which is determined by the temperature difference between the cells during early structure formation.

The following materials were used in the research: powdered fluorogypsum with a specific surface area of 400 m$^2$/kg neutralized with limestone flour. The mineralogical composition of fluorogypsum is represented by the following components: CaCO$_3$ – 5.91%, CaF$_2$ – 6.86%, CaSO$_4$ 2H$_2$O – 18.67 %, CaSO$_4$ – 68.56 % [7-8]; construction gypsum G-5AII (All-Union Standard (GOST) 125-2018) and sodium sulfate as hardening activator (GOST 6318-77). During the research, gypsum paste of normal density was used with content of construction gypsum and sodium sulfate in the amount of 20% and 2%, respectively, of the weight of fluorogypsum.

3. Results and discussion
The results of heat release kinetics research during early structure formation of fluorogypsum binder are shown in Figures 1 – 4. In order to compare processes of heat release in the studied gypsum-containing systems, the following systems’ analysis results are presented: construction gypsum – water (Fig. 1), fluorogypsum binder – water (Fig. 2), fluorogypsum binder – construction gypsum – water (Fig. 3) and fluorogypsum binder – sodium sulfate – water (Figure 4). The first intensive heat release maximum is caused by a decrease in surface energy of the solid phase and release of wetting heat. The driving force of interaction of the binder with water is determined by the value of the total thermal effect of two components: thermal effect of hydration $Q_h$ and thermal effect of destruction and dispersion of the crystal lattice $Q_d$ of binder particles:

$$\Delta Q = Q_h + (-Q_d)$$

The heat of hydration is positive, since formation of a bond between two ions is always accompanied by a decrease in enthalpy. The process of crystal lattice destruction, accompanied by disruption of bonds in the crystal always occurs with absorption of heat and the $Q_d$ value will always be negative.

Duration of heat release depends on activity of the binder and sample weight. In addition, intensity of reactions of binder interaction with water is determined by value of total thermal effect of hydration and thermal effect of dispersion of minerals’ crystal lattice. When adding water to the binder, the released hydration heat spent on increasing temperature of the system, is sharply decreased during subsequent dispersion as a result of absorption of this heat ($Q_d > Q_h$). Thus, the process and mechanism of interaction of gypsum-containing systems with water can be assessed by alternations in temperature differences of dry and wet materials over time. The unity and contrast of processes of hydration and dispersion of building gypsum are shown in the character of the first heat release curve maximum, in which after intensive heat release associated with the wetting process, processes associated with
expenditure of heat for dispersion begin to prevail. In this case, dispersion processes in the gypsum – water system cease during the induction period of hydration (Fig. 1).

It should be noted that the temperature difference between calorimetric cells during wetting is 3.6°C, the process is active compared to other systems, duration of dispersion and dissolution process is 18 minutes, after which process of crystallization of calcium sulfate dihydrate begins, accompanied by heat release. Duration of heat generation, dispersion, crystallization and cooling processes in construction gypsum is 2 hours. After contact of fluorogypsum binder without additives with water the wetting temperature is substantially less than in the first case, and is 1.7°C and minor bursts of dispersion and solidification are apparently associated with presence in fluorogypsum of soluble calcium sulfate. In this case, there is a cyclical repetition of processes of dissolution and crystallization of accumulated products after 1 day over the period of 3 days (Fig. 2).

The heat release kinetics of fluorogypsum binder with addition of building gypsum and sodium sulfate is also cyclical, and development of hydration and hardening processes occurs in the same way as in the cement – water system. With addition of building gypsum, dissolution processes are intensified, and the process of heat release is much faster (Fig. 3). Long second induction period of the binder with addition of sodium sulfate is probably associated with dissolution of formed double salts. The process of dissolution and crystallization is also cyclical. Duration of the first induction period is almost the same, while the temperature difference between CCs decreases: for neutralized binder by 1.35°C, with addition of sodium sulfate by 0.5°C, with addition of building gypsum by 0.7°C. After decrease in temperature in these systems the induction period which is dominated by entropic factor, after a certain period of time for all systems the temperature begins to increase again due to the heat of crystallization (Q.cr.). In
equilibrium the heat is consumed by dispersion, at the same time amount of heat spent on dispersion is higher than the amount of heat released during crystallization.

**Figure 2.** Dissipation kinetics of the composition: fluorogypsum – water over 3 days
During transition from colloid state to crystalline state, when primary products are combined into larger and more stable aggregates, density of hydrated products increases, which creates free volume and water and contributes to further flow of hydration processes. During this period, heat is also consumed by the processes of dispersion, however, the temperature difference remains positive: the ratio of enthalpy and entropy factors’ values in the fluorogypsum – additive – water system provides a negative value of the Gibbs energy for a long time, and different in direction thermal effects of particles’ crystallization (+) and surface dispersion (-), are the driving force of hydration process. Formation of primary hydrated particles of nanodispersed size and their subsequent blending due to coalescence is a sign of manifestation of binding properties in fluorogypsum binders.
Figure 4. Dissipation kinetics of the composition: fluorogypsum - sodium sulfate-water over 3 days

Thus, repeated pattern of fluorogypsum binder’s hydration without additives and with additives is the main feature that distinguishes it from construction gypsum, during hydration of which there is a complete dispersion of the binder and binding of almost all mixing water, and after that recrystallization processes with participation of primary products of hydration commence. Analysis of hydration mechanisms and fluorogypsum binders’ hardening according to kinetics of heat dissipation and results of physical and chemical methods of research [7-8] confirm that the most accurate theory of hydration is the theory of A.A. Baikov, in which the interaction of binder with water is accompanied by topochemical colloiding of initial hydration products.

4. Conclusion
When analyzing the processes of hydration and structure formation of fluorogypsum composite binders, it is necessary to take into account energy components of enthalpy and entropy factors of the Gibbs equation. All processes of hydration and structure formation occurring in the system of fluorogypsum – water are accompanied by a change in temperature, which can be measured using differential microcalorimetry. Processes of hydration and hardening are accompanied by occurrence of alternating exo- and endothermic effects during the entire period of interaction of binder and water, which indicates repeating pattern of fluorogypsum binder hydration processes, and this is the main feature that distinguishes it from calcium sulfate semi-hydrate. The mechanism of hydration of fluorogypsum binder according to the heat release kinetics is manifested in periodic topochemical colloiding of hydrating substances and subsequent crystallization of the formed hydration products. Duration and intensity of processes depend on the type and quantity of introduced activator additives, the effects of which should be evaluated using highly sensitive differential microcalorimetry and taken into account when developing scientifically based compositions and technologies for manufacturing effective building materials using fluorogypsum raw materials. This can solve the problem of construction and technological utilization of fluorogypsum raw materials in construction.
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