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АКТИВАЦИЯ ПРОЦЕССОВ ТВЕРДЕНИЯ ФТОРАНГИДРИТОВЫХ КОМПОЗИЦИЙ ХИМИЧЕСКИМИ ДОБАВКАМИ СОЛЕЙ НАТРИЯ

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В статье рассматриваются вопросы модифицирования фторангидритовых композиций химическими добавками солей натрия в виде сульфата, сульфита и сульфида натрия, а также их совместное воздействие на кинетику процессов структурообразования. Исследованы технологические, экологические, технологические аспекты применения активированных добавками фторангидритовых композиций. Проведенные эксперименты показали, что увеличение количества добавки сульфита натрия в количестве до 3% от массы фторангидрита приводит к повышению прочности образцов на сжатие в ранние сроки твердения (до 14 сут), использование добавки сульфата натрия формирует кристаллизационную структуру в более поздние сроки, поэтому рационально совместное применение добавок сульфата и сульфита натрия в количестве, не превышающем 3% от массы вяжущего. Формирование структуры твердения вяжущего с добавкой сульфида натрия осуществляется уже на ранних стадиях с образованием дополнительных структурообразующих веществ в виде сульфида кальция. Механизм раздельного действия индивидуальных добавок сульфата и сульфита натрия позволил выдвинуть предположение что, с одной стороны наиболее рационально использовать совместное воздействие сульфатных и сульфитных добавок, поскольку это не просто двойное действие добавок, а буферная смесь, а значит, механизм действия такой добавки будет подчиняться буферному действию. В системе будет поддерживаться постоянство строго определенного диапазона рН, которое определяет устойчивость новообразований, формирующих структуру твердения. А с другой - целесообразность введения добавки сульфида натрия и изучение его влияния на процесс структурообразования фторангидритовых композиций как при индивидуальном, так и при совместном действии с добавками сульфита и сульфата натрия. Введение добавки сульфида натрия приводит к образованию нерастворимого сульфида кальция, который может служить ядром для формирования иерархических организованных структур и способствовать кольматации пор, упрочняя структуру ангидритового вяжущего.

Ключевые слова: фторангидрит, сульфат натрия, сульфит натрия, сульфид натрия, дериватографический анализ, электронно-микроскопический анализ

ACTIVATION OF HARDENING PROCESSES OF FLUOROGYPSUM COMPOSITIONS BY CHEMICAL ADDITIVES OF SODIUM SALTS

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The article is devoted to modifications of fluorogypsum compositions by chemical additives of sodium salts in the form of sulfate, sulfite and sodium sulfide, as well as their combined effect on the kinetics of structure formation processes. Technological, ecological and technical aspects of utilization of fluorogypsum compositions activated by additives were investigated. Experiments have shown that an up to 3% increase in the amount of sodium sulfite additive leads to an increase in the compressive strength of samples at early stages of hardening (up to 14 days), whereas utilization of sodium sulfate additive forms a crystallization structure at later stages. Therefore, it is rational to combine sulfate and sodium sulfite additives in an amount not exceeding 3% of the binder's weight. The binder hardening structure formation with sodium sulfide addition at early stages results in production of additional structure-forming substances such as calcium sulfide. The mechanism of differentiated application of individual sulfate and sodium sulfite additives allowed to suggest that combined sulfate and sulfite additives utilization seems to be the most rational decision, due to the fact that it is not a mere individual additives' combination, but a buffer mixture, which means that the mechanism of such mixtures influence will be subject to the buffer action. The system will maintain a strictly defined pH range constancy, which determines stability of new growths, forming the hardening structure. However, using sodium sulfide as an additive and studying its impact on fluoroanhydrate compositions structure formation in both individual and combined with sodium sulfite and sodium sulfate forms appears to be as much reasonable. The combined Na_2SO_3-Na_2SO_4 additive activates hardening processes both at early and late stages. At the same time, columnar structures growing from the center to the periphery are formed, as indicated by electron-microscopic studies. Their growth stems from concentration gradient of SO_4^{2-}- and SO_3^{2-}- ions, which is in complete agreement with the other research data and is typical for both metal melts and cement systems solidification process.

Key words: fluorogypsum, sodium sulfate, sodium sulfite, sodium sulfide, X Ray diffraction, thermogravimetric analysis

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INTRODUCTION

Currently, a considerable amount of attention is paid to the search and scientific substantiation of effective ways to regulate the processes of structure formation of gypsum and gypsum-containing binders, including industrial waste [1-5].

Previously, we have shown that sulfate and sodium sulfite additives introduction leads to fluorogypsum compositions hardening process activation and to a significant increase in gypsum stone strength characteristics [6-7].

However, it is obvious that without identifying how the additives affect the processes under consideration, it is impossible to develop optimal compositions and production technology of fluorogypsum binders with increased performance.

The aim of the study is to research the effect of sulfate additives on the processes of structure formation of fluorogypsum binders.

EXPERIMENTAL METHOD

The research utilizes carbonate flour-neutralized fluorogypsum crushed in a ball mill to a 2000 cm^2/gr specific surface area. Water-solid ratio was selected to achieve 165 mm compositions fluidity in accordance with All-Union State Standard (GOST) 31377-2008 and comprised 43.0-46.0% by weight in different compositions. As the main criterion, the samples compressive strength value at early (3, 7 days) and late hardening stages (28 days) in small-scale samples obtained from fluorogypsum paste by injection molding, was selected.

The compressive strength test of the samples was carried out on an attested P-250 hydraulic press with a maximum force of 5 tons according to GOST 31733-2012.

Having analyzed the known anhydrite binders structure formation process regulating methods by means of introduction of activating additives [8-12], the authors proposed fluorogypsum binder properties regulation processing methods by means of same cation additives' introduction in the form of sulfate, sulfite and sodium sulfide.

The phase composition and structural parameters of the samples were studied using the CuK_α radiation of XRD-6000 diffraction meter. Phase composition, coherent scattering areas' sizes, internal elastic stresses ($\Delta d/d$) analyses were carried out using PCPDFWIN and PDF4+ databases, as well as the POWDER CELL full-profile analysis program [13]. Electron-microscopic studies were carried out using "Tesla BZ 301" scanning electron microscope with 4000x magnification at the age of 3 and 28 days of binders hardening [14].

RESULTS AND DISCUSSION

After the analysis of existent controlling methods of anhydrite binders' structure formation processes, the authors proposed components quantitative ratios and technological methods of introduction of additives with the same cation in the form of sulfate, sulfite and sodium sulfide [15-20].

The choice of sulfate additives is justified by their influence on the processes of calcium sulfates solubility for soluble anhydrite and crystalline primers. The additives increase the number of crystallization centers for extraction of new phases from supersaturated solutions and, as a consequence, increase the strength characteristics of the binder. The additives were introduced with the mixing water.

The results of experimental data on the effect of sodium sulfate and sodium sulfite additives showed that strength characteristics of samples with 2% sodium sulfite addition at an early stage (7 days) exceed the strength characteristics of samples with sodium sulfate addition. At the age of 14 days, the maximum value of compressive strength equal to 8.5 MPa was obtained, which was more than 2 times higher than the control samples strength. Compressive strength of samples with 2% sodium sulfate addition at the same age was 6.5 MPa. It was shown that by 28 days of age the strength of samples with 2% sodium sulfate addition reached 8.8 MPa, which exceeded the strength of samples with sodium sulfite addition. A combined introduction of additives in equal parts lead to an increase in strength both at early (7 days) and at later (28 days) stages. With introduction of additives in the amount of 3%, the compressive strength of samples decreased, however, the overall picture did not undergo any changes, so the introduction of more than 3% of additives is impractical.

With an up to 3% increase in the amount of sodium sulfide additive, compressive strength of samples at the age of 28 days increased to 14.8 MPa, whereas with an up to 4% additions amount strength of the samples decreased both at the early (7 days) and late stages of hardening (28 days).

To distinguish mechanism of structure formation process in a binder with additives, physical and chemical tests the results of which at the age of 28 days are presented in Fig. 1 were carried out.

Based on the nature of cleavage, samples without additives at the age of 3 days were represented by a gel-like mass, with an initial stage of structure formation; by 28 days of age, loose crystals of hardened fluorogypsum possessing large pores were formed. Columnar crystals of calcium sulfate dihydrate were practically absent (Fig. 1a). In the samples with sodium sulfate addition the formation of a close-packed arrangement of calcium sulfate dihydrate crystals was present. However, in the pores there were small new growth crystals, which hinted at a slow formation of structure-forming substances (Fig. 1b).

In the samples with sodium sulfite addition (Fig. 1c) there were needle-shaped crystals of calcium sulfate dihydrate, with penetration of large new growth crystals into pores, which indicated a rapid exchange process in the system of «fluorogypsum – additive (Na_2SO_3) – water», strengthening the anhydrite stone structure.

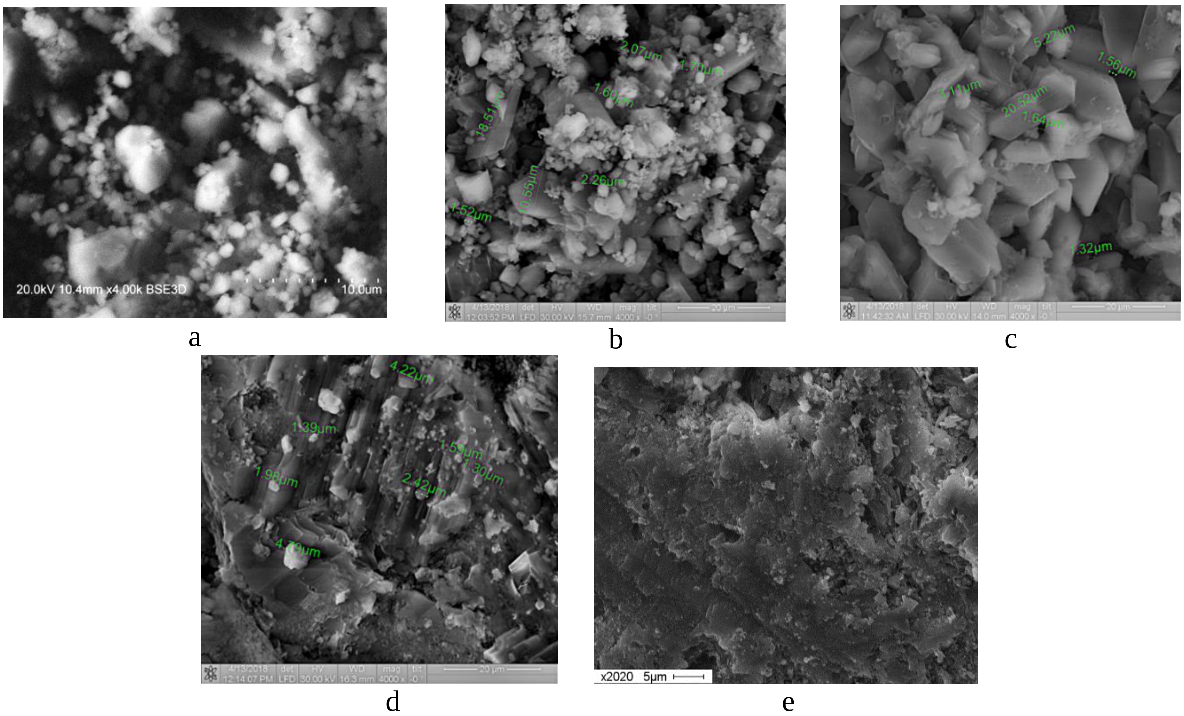

Fig. 1. The results of electron microscopic studies of hardened binder samples with additives at the age of 28 days of hardening with a magnification of 4000 times: a) without additives; b) sodium sulfite; c) sodium sulfate; d) sodium sulfide; e) sodium sulfate and sodium sulfite additions

Рис. 1. Результаты электронно-микроскопических исследований образцов затвердевшего вяжущего с добавками в возрасте 28 сут. твердения при увеличении в 4000 раз: a) без добавок; b) с добавкой сульфита натрия; c) с добавкой сульфата натрия; d) с добавкой сульфида натрия, e) с добавками сульфата и сульфита натрия

The microstructure of samples with sodium sulfide addition (Fig. 1d) was represented by close-packed arrangement of calcium sulfate dihydrate crystals, with embedded crystals of the formed calcium sulfide. Electron-microscopic studies have shown that under the influence of sodium sulfide, a more finely dispersed, but at the same time more porous structure of gypsum stone was formed, which is explained by some puffing of the construction mixture. With an increase in additives concentration, formation of a loose disordered structure of gypsum stone with mainly tabular and platelet crystals morphology was observed. The most close-packed arrangement of crystals was observed in samples with combined sulfate and sodium sulfite additives introduction (Fig.1e).

According to derivatographic studies (Fig. 2) the main endothermic effects were caused by removal of crystallization hydrated water at the temperature of 133.4 °C, decomposition of portlandite at the temperature of 449 °C and rearrangement of crystalline lattice accompanied by formation of insoluble anhydrite (610.9-719.2 °C). In samples with sodium sulfate addition there was an endoeffect shift towards higher temperatures (141 °C compared to 133.4 °C in samples without additives) at the age of 3 days. In samples with sodium sulfite and sodium sulfide addition, endothermic effect shift was more prominent. The maximum shift was observed in the samples with combined addition of sulfate and sodium sulfite, which was accompanied by an increased samples strength at the early stages of hardening. At the same time, the magnitude of endothermic effect produced by insoluble anhydrite decreased, though the amount of chemically bound water increased from 0.58 to 1.8 and 2.1 with sodium sulfide addition and combined addition of sodium sulfate and sulfite. At the age of 7 days, there was an even more significant endothermic effect shift caused by removal of crystallization hydrate water from 140.5 °C in the binder samples without additives to 151.5 °C in samples with sodium sulfite addition, which indicates an accelerated process of samples structure formation with this additive at the age of 7 days. Dynamics of hydration processes persisted with the age of the samples. At the age of 14 days double endothermic effects were observed. At the temperature of 143 °C for samples without additives; 146 °C in samples with sodium sulfate additives; 150 °C in samples with sodium sulfite addition; 149 °C in samples with sodium sulfide addition; 147 °C in samples with combined addition of sodium sulfate and sulfite, which indicates the formation of a stronger structure in samples with additives. Double endothermic effects at these temperatures are explained by the fact that by this hardening stage complex compounds and double salts, such as hydroglauberite ($Na_{10}Ca_3(SO_4)_8 \cdot 6H_2O$) [21], which provide binders microstructure densification have been formed, which is consistent with X-ray phase analysis data and microscopic methods of investigation. Endothermic effect maximum temperature of 150.7 °C was observed during combined addition of sulfate and sodium sulfite.

According to radiographic researches, it is established that formation of fluorine anhydrate binder hardening structure with sodium sulfate addition occurs due to the formation of dihydrate. With the introduction of Na_2SO_3 additive fluorine anhydrate binder structure formation process is intensified and calcium sulfate dihydrate is formed. The main structure-forming components are presented in Table.

According to the research results in samples containing 2% Na_2SO_3 solution, the main structure-forming substances that provide early strength of fluoroanhydrate binder with sodium sulfite addition were calcium sulfite and calcium sulfate dihydrate.

Studying the samples with Na_2SO_4 (2%) addition, it can be assumed that formation of fluorogypsum binder hardening structure with sodium sulfate addition occurs due to calcium sulfate dihydrate formation.

Analysis of the results shows that a possible mechanism of additives activating impact can be explained in the following way. All the activators under analysis affect structure and energy state of water (grouting fluid) due to the disturbance of water dissociation chemical equilibrium with formation of H^+ and OH^- ions, a significant impact on this process is produced by the activator concentration, which determines the solution hydrogen index value. An excess of SO_4^{2-} or SO_3^{2-} anions, which acidifies the environment due to sulfuric H_2SO_4 (sulfurous H_2SO_3) acid formation, affects solubility and the mechanism of anhydrous calcium sulfate ($CaSO_4$ II) hydration and its modifications.

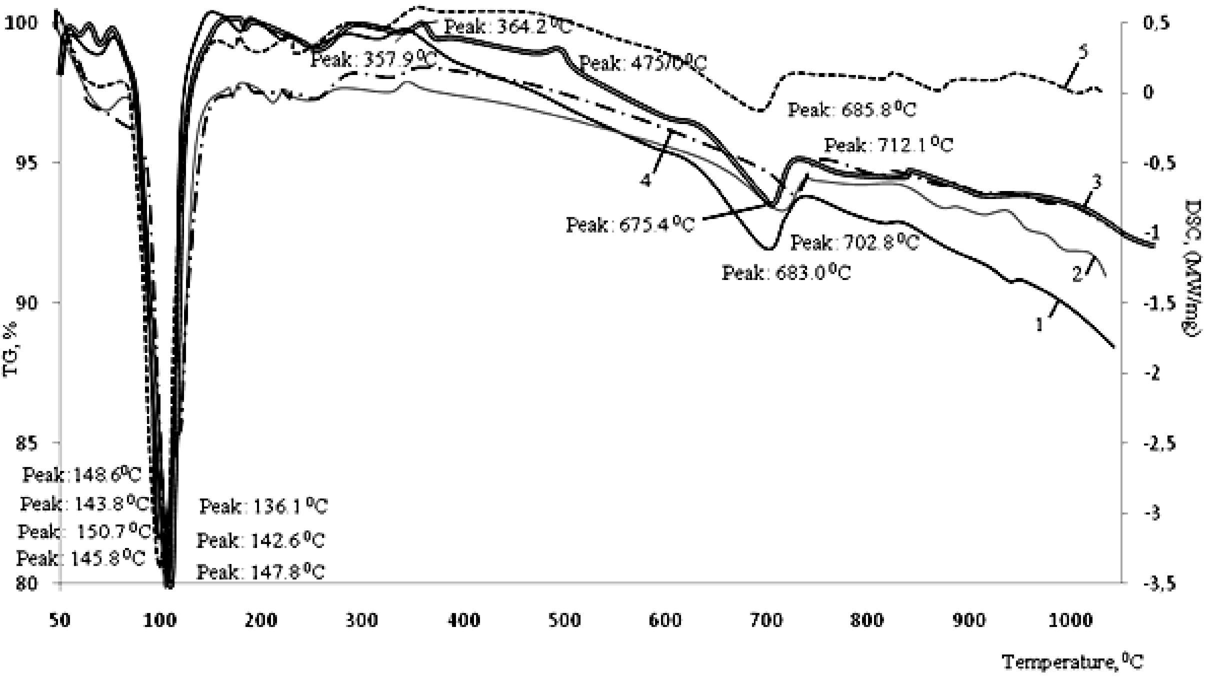

Fig. 2. Derivatograms of hardened binder samples at the age of 28 days 1 – reference sample; 2 – sodium sulfat; 3 - sodium sulfit; 4 - sodium sulfide; 5 - sodium sulfat + sodium sulfit

Рис. 2. Дериватограммы образцов затвердевшего вяжущего (28 сут) 1 - контрольный образец; 2 - сульфат натрия; 3 - сульфит натрия; 4 - сульфид натрия; 5 - сульфат натрия + сульфит натрия

Table

Interplanar spacing of the corresponding compounds

***Таблица*. Межплоскостное расстояние соответствующих соединений**

Chemical compounds	Interplanar distance d, Å			
	Na_2SO_4 addition	Na_2SO_3 addition	Na_2S addition	Combined additives' influence
$CaSO_4$	3.8; 3.5; 2.85; 2.87; 2.33; 2.21; 2.09; 1.99; 1.75; 1.65; 1.49; 1.27; 3.8; 3.5; 2.22			
$CaSO_4 \cdot 2H_2O$	4.29; 2.88; 2.69; 2.5; 2.09; 4.29; 3.06; 2.69; 2.5; 2.22; 2.09; 1.9; 1.81; 1.87; 1.78; 1.66			
CaF_2	3.06; 1.65; 1.62			
$CaSO_3$	-	2.87; 2.09	-	2.87; 2.22
CaS	-		2.85; 2.00; 1.63; 1.28	
$Na_{10}Ca_3(SO_4)_8 \cdot 6H_2O$	4.659; 2.931	-	-	-

Therefore, in an acidic environment, there is an increase in anhydrite solubility and acceleration of calcium sulfate crystallization from solution with hydrate phase germs' formation.

It was discovered that sulfate activators affect grouting mixtures fluidity in different ways, for example sodium bisulfite ($NaHSO_3$) is characterized by the highest 26-27% water demand. Sodium hydrosulfite has a high reactive capacity for initial binders, stimulating exchange processes in the «fluorogypsum – additive – water» system.

Taking into account the presented experimental data, it can be concluded that, in case an early (up to 7 days) strength gain is required. It is more rational to use sodium sulfite addition. Otherwise, sodium sulfate addition is more appropriate.

Introduction of sodium sulfide additive leads to insoluble calcium sulfide formation according to the scheme: $Na_2S + Ca(OH)_2 \rightarrow CaS\downarrow + 2NaOH$, which by the law of colloidal chemistry can serve as a nucleus for the hierarchically organized structures formation and contribute to the pores colmatation, thereby strengthening gypsum stone structure [22].

CONCLUSION

The effectiveness of sodium salts as activators of the process of hardening of fluorogypsum binders has been proven.

It has been shown that the mechanism of action of additives reduces to accelerate the process of hydration of anhydrite and the formation of gypsum ($CaSO_4 \cdot 2H_2O$), of insoluble calcium sulfide (CaS), calcium sulfite ($CaSO_3$) as well as the formation of double salts of calcium such as hydroglauberite ($Na_{10}Ca_3(SO_4)_8 \cdot 6H_2O$). The substances obtained are insoluble in water and can serve as the nucleus of the micelle-forming colloidal structures that underlie the formation of structures.

It has been established that the strength of hardening structures and the physicomechanical characteristics of the anhydrite binder are significantly improved both at the early and late stages of hardening. The compressive strength of samples with the addition of 2% sodium sulfate at the early age (7 days) exceeds the strength characteristics of control samples and samples with the addition of sodium sulfate. By 28 days of age, the compressive strength of samples with the addition of sodium sulfate is 40% higher than the strength of samples with the addition of sodium sulfite. The joint introduction of additives in equal proportions leads to an increase in strength both at the early and late stages of hardening. When using an additive of sodium sulfide in an amount up to 3% by weight of the binder, the binder compressive strength of the samples increases both at the early and late stages of hardening.

Therefore, the experiments proved high efficiency of sodium salts addition in fluorogypsum activation processes, while the developed anhydrite binders compositions showed improved performance.

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