



## SULFOMINERAL CLINKERS BASED ON PHOSPHOGYPSUM (GYPSUM) AND VARIOUS CLAY MATERIALS

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### Abstract

The results of a comprehensive study of the liquid and solid phases of hydrating anhydrous minerals allow us to draw the following conclusion in dilute suspensions, highly basic hydrates are formed in the earliest periods of hydration and over time due to the formation of a dense shell consisting of hydrolysis products primary hydrates that are more stable under these conditions. The presence of  $\text{CaSO}_4$  in a mixture with  $\beta\text{-C}_2\text{S}$  significantly accelerates the main period of its hydration and promotes better crystallization of neoplasms.

**Keywords:** sulfo cement, sulfosilicate, hydration, of sulfosilicates, hydrosulfosilicate minerals, congruent composition, molar ratio, physico-chemical processes.

### 1. Introduction

Sulfur anhydrite introduced into the mixture in the form of  $\text{CaSO}_4$  has a strong mineralizing effect on the crystallization of clinker minerals of Portland cement. With an increase in the amount of  $\text{SO}_3$  from 0.5 to 2%, the crystallization of alite and belite improves - the crystals grow to significant sizes and acquire the correct shape. However, at the same time, defects appear in them: weak shading of belite crystals and porosity of alite crystals. In belite clinkers in the presence of  $\text{SO}_3$ , the content of active  $\beta\text{-C}_2\text{S}$  decreases by ~10%, and in alite clinkers in the presence of 0.5-1.5%  $\text{SO}_3$ , the amount of  $\text{C}_3\text{S}$  increases by 7% (abs) /138, pp.298-299/.

At a concentration of 0.5-1.5%  $\text{SO}_3$ , the actual mineralogical composition of sulfur-containing clinkers is characterized by an increase in the amount of alite and the preservation of almost constant ratios of  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$ . The presence of even small amounts of  $\text{SO}_3$  contributes to the stabilization of  $\text{C}_3\text{S}$  in the monoclinic form, and  $\text{C}_2\text{S}$  in the  $\alpha'$  form. The alumoferrite phase is approaching  $\text{C}_6\text{A}_2\text{F}$  /138, p.190/ in composition.

In the presence of  $\text{CaCO}_3$ , the following intermediate compounds are formed at the low-temperature firing stage:  $2(\text{CaO}\cdot\text{SiO}_2)\cdot\text{CaCO}_3$  - spurrit,  $3(\text{CaO}\cdot\text{Al}_2\text{O}_3)\cdot\text{CaSO}_4$ ,  $2(2\text{CaO}\cdot\text{SiO}_2)\cdot\text{CaSO}_4$ , as well as double salts on the contact of  $\text{CaCO}_3$  with alkali





sulfates /74/. As a result, the interaction temperature of  $\text{CaCO}_3$  and  $\text{SiO}_2$  decreases by  $38-80^\circ\text{C}$ .

The crystallization of minerals in belite clinkers ( $\text{KN} = 0.67$ ) becomes clearer when  $0.5\text{ SO}_3$  is added to the charge. The crystals of belite have mostly a rounded shape with dense, clear edges. With an increase in the amount of  $\text{SO}_3$  up to 3%, they often take an indefinite shape, often there are accretions, the edges of crystals sometimes with growths, the surface acquires shading, the color of etching is zonal. The refractive indices of belite in clinkers with the addition of 3%  $\text{SO}_3$ , as well as with a small number of fins (5%) are lowered and correspond to the indicators of  $\alpha'$ -C2S.

According to X-ray analysis, in the presence of 0.5-2%  $\text{SO}_3$  in the composition of the charge, the C2S lines do not undergo significant changes. This can be explained by the fact that the substitution of the  $(\text{SiO}_4)_4^-$  by  $(\text{SO}_4)_2^-$  complex in C2S due to the proximity of the sizes of the radii of the ions  $r(\text{SiO}_4)_4^- = 3.05 \text{ \AA}$ ,  $r(\text{SO}_4)_2^- = 2.95 \text{ \AA}$  does not significantly affect the crystal lattice of the mineral /138, pp.191-192/.

Thus, with a small amount of calcium sulfate (rarely more than 10%) in the charges designed to produce C3S, C2S, C3A, C4AF and  $\text{CaCO}_4$  acts as a stabilizer of  $\beta$ -C2S, prevents the resorption of alite, reduces the viscosity of the clinker melt /213, 214, p.9/. The processes occurring in the charges designed to produce sulfated cements differ from the processes occurring during the firing of conventional Portland cement charges. The presence of gypsum (10% or more) causes a decrease in the clinker firing temperature to  $1300-1350^\circ\text{C}$ , prevents the formation of hydraulically inert helenite (when obtaining alumina-belite cements from kaolin clays and substandard bauxite), accelerates the binding of lime /3, 5, 6, 14, 25, 26, 28-39, 65, 112, 156, 215-217/. At the same time, anhydrous calcium sulfoaluminate is formed in the charge. Regardless of the  $\text{CaO}:\text{Al}_2\text{O}_3$  ratio, the same compound is always formed in the presence of gypsum. With an increase in temperature ( $1350-1450^\circ\text{C}$ ), calcium sulfoaluminate decomposes.

Formation in the presence of sulfur  $\text{C}_4\text{A}_3\hat{\text{S}}$ , characterized by high intensity of hydration and hardening in the initial terms /3, 9, 69, 112, 156/, as well as  $\text{C}_{12}\text{A}_7$ , it causes an increase in the strength of sulfur-containing cements. According to our data, the optimal amount of  $\text{CO}_3$  contributing to the greatest increase in strength is that which is sufficient for the complete conversion of calcium aluminates into  $\text{C}_4\text{A}_3\hat{\text{S}}$ , in alumina-belite cement it is not enough for the complete binding of  $\text{Al}_2\text{O}_3$  in the raw mixture. To obtain an active fast-hardening high-strength cement and a uniform increase in its strength, it is necessary to introduce  $\text{CaSO}_4$  into the raw material mixture in an amount sufficient to completely bind  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , respectively, in  $\text{C}_4\text{A}_3\hat{\text{S}}$  and  $\text{C}_5\text{S}_2\hat{\text{S}}$ , and the presence of a significant excess of  $\text{CaSO}_4$  /3, 69, 125, 218-





222/. The amount of excess  $\text{CaSO}_4$  depends on the content of  $\text{C}_4\text{A}_3\hat{\text{S}}$  in the clinker: the more of it, the more  $\text{CaSO}_4$  should be. The optimal amount of  $\text{SO}_3$  in cement, which helps accelerate its uniform hardening, depends on the type and amount of  $\text{C}_4\text{A}_3\hat{\text{S}}$ ,  $\text{C}_{12}\text{A}_7$  in the binder, on the content of  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{F}$ ,  $\text{P}_2\text{O}_5$ , as well as other factors.  $\text{C}_4\text{A}_3$  coexists with  $\text{C}_5\text{S}_2\hat{\text{S}}$  and  $\text{C}_4\text{AF}$  at a temperature of  $1200^\circ\text{C}$  /73/. I. V. Kravchenko and T. V. Kuznetsova /70, 83, 85-87, 89/ believe that the presence of  $\text{C}_{12}\text{A}_7$  in clinker is necessary to obtain active sulfoaluminate-belite cement. Calcium sulfoaluminate and calcium sulfosilicate arise as intermediates in the formation of cement minerals in the combined process of cement and sulfuric acid production. Desulfurization of raw flour does not occur until significantly higher temperatures are reached than those that are common for this process /223/. Obviously, it is necessary to reconsider the existing view of the role of gypsum in mineral-forming processes. Gypsum is not only a mineralizer that accelerates the process of mineral formation, but also a component of the charge that causes the appearance of new compounds -  $\text{C}_4\text{A}_3\hat{\text{S}}$  and  $\text{C}_5\text{S}_2\hat{\text{S}}$  /35/. It is also necessary to note the positive effect of free anhydrite in clinker on the properties of future cement /3, 69, 125, 219, 220, 224, 225/.

The use of high-intensity firing processes leads to the search for ways to accelerate solid-phase reactions, and the need to reduce energy consumption - ways to synthesize non-graphite clinkers /226/. One of the ways to reduce energy consumption during clinker formation may be the choice of raw compositions that ensure the synthesis of intermediates with a positive thermal effect. By replacing up to 50%  $\text{CaCO}_3$  with a melt ( $\text{CaSO}_4$ ), it is also possible to reduce the firing temperature and the proportion of  $\text{CaCO}_3$ , the dissociation of which will require minimal energy consumption. T. Nakamura, D. Sudo and Sh. Akiava /42/ reports that widespread kaolin clays with a high content of  $\text{SiO}_2$  as a clay component are suitable for the production of expanding cement clinker.

To study the progress of mineral formation in raw mixtures on the basis of model systems -  $\text{As}\hat{\text{S}}$  and different raw materials we used, in addition to model systems, 12 episodes of mix that contains the source components in different ratios based on different carbonate, clay and sulfate materials (tab.16). The charge was prepared based on receipt of three types of binders consisting of  $\text{C}_4\text{A}_3\hat{\text{S}}$ ,  $\text{C}_{12}\text{A}_7$ ,  $\text{C}_2\text{S}$ ,  $\text{C}_5\text{S}_2\hat{\text{S}}$ ,  $\text{C}_4\text{AF}$ ;  $\text{C}_4\text{A}_3\hat{\text{S}}$ ,  $\text{C}_5\text{S}_2\hat{\text{S}}$ ,  $\text{C}_4\text{AF}$  and in some cases, with some excess  $\text{CaSO}_4$  after binding of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , respectively, in  $\text{C}_4\text{A}_3\hat{\text{S}}$  and  $\text{C}_5\text{S}_2\hat{\text{S}}$ . Within each series, several charges differing in the value of  $n\hat{\text{S}}$  were studied. Clinkers with  $n\hat{\text{S}}$  less than one were classified as sulfoaluminate-belite, with  $n\hat{\text{S}}$  equal to or greater than one - as sulfoaluminate-silicate.





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