

Sulfomineral Hardening Processes

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Abstract

The rapid growth of strength, improvement of construction and technical properties of mixed high-strength cement is facilitated by; early crystallization of ettringite, the formation of a low-porous monolithic structure. This served as the basis for the development of technological parameters for the production of cement, based on sulphoclinkers and portlandcement

Keywords: sulfosilicate, hydrosilicate, calcium hydrosulfoaluminate, mineral formation, X-ray phase analysis, phosphogypsum, sulfocement, sulfoclinker.

Introduction

In terms of initial mechanical strength, the stone based on $C_4A_3\dot{S}$ is not inferior to the samples from CA. However, after 28 days of hardening in water, its strength begins to decrease and after a year it decreases by 15%. This phenomenon is apparently associated with the process of recrystallization of calcium hydrosulfoaluminate. A decrease in strength to 40% is also observed in CA, but we found that the addition of anhydrite (~ 20%) eliminates these structural defects [13 ... 15, 26 ... 28].

Sulfosilicates ($C_7S_3\dot{S}$, $C_5S_2\dot{S}$) harden much faster than C_2S . When 21 ... 28% of $CaSO_4$ fired at 1250° is added to β - C_2S , the mechanical strength of the samples in the first periods of hardening during storage in a humid environment and in water increases significantly, which, in our opinion, is due to the formation of a kind of strong crystalline gypsum intergrowth with calcium hydrosilicate. Adding 20% $C_4A_3\dot{S}$ to $C_7S_3\dot{S}$ and $C_5S_2\dot{S}$ causes an increase in their early strength by a factor of 7 ... 10 and their transformation into rapidly hardening cements.

Methods

Comprehensive physicochemical analyzes show that the high hydraulic capacity and strength of cements from sulfominerals are due to the formation of new forms of crystals of hydrates of type $3(CA) \cdot C\dot{S} \cdot nH_2O$ ($16 \leq n \leq 20$), $2(C_2S) \cdot mC\dot{S} \cdot mH_2O$ ($0,5 \leq m \leq 1$).

During hydrothermal treatment in an autoclave (8 atm) of slowly hardening silicate samples, their strength sharply increases, as a result, especially strong structures are created. With an increase in pressure to 15 atm, the strength of all samples increases significantly.

Physicomechanical tests of $C_5S_2\dot{S}$ and $C_4A_3\dot{S}$ with P_2O_5 additives show [13 ... 15] that $C_4A_3\dot{S}$, containing 0.5 ... 1% P_2O_5 , has a higher strength at all times of hardening than containing 3 ... 4% P_2O_5 , the strength of which is almost similar strength of pure $C_4A_3\dot{S}$ after 28 days of hardening (by 90 and 180 days, strength indicators decrease by 10 ... 15%). The presence of up to 4% P_2O_5 in $C_5S_2\dot{S}$ does not have a significant effect on the strength of 28-day-old samples, and in 90- and 180-day-old samples it slightly decreases in comparison with pure $C_5S_2\dot{S}$.

At a content of up to 1% MgO, the strength of samples from $C_4A_3\dot{S}$ practically does not change, with an increase in the amount of MgO to 2% or more, it decreases in the early stages of hardening, especially noticeable at 5% MgO. By the 3rd and 7th days, it is almost two times lower than that of pure $C_4A_3\dot{S}$. Subsequently, the strength of these samples increases rapidly and has approximately the same value as that of the reference samples. The absence of a strongly noticeable negative effect of MgO on the hardening of $C_4A_3\dot{S}$ is explained by the fact that it does not disturb the process of mineral formation. X-ray phase analysis found that MgO in the amount of 0.5 ... 5.0% does not prevent the formation of $C_4A_3\dot{S}$. The diffraction patterns have interplanar distances corresponding only to $C_4A_3\dot{S}$. At 3 ... 5% MgO under a microscope, along with $C_4A_3\dot{S}$ crystals with a refractive index slightly lower than the reference one ($N_{av} = 1.561$), phases with refractive indices $N_p = 1.720$ and $N_g = 1.736$ are observed, which belong to the spinel MgO, respectively. Al_2O_3 and free MgO.

The firing products of $C_5S_2\dot{S}$ mixtures containing magnesium oxide harden poorly. Even in the presence of 1% MgO, the strength of the samples becomes lower than the strength of pure $C_5S_2\dot{S}$. Samples with 3 ... 5% MgO show strength two times lower than $C_5S_2\dot{S}$ without MgO addition, and by 90 days they are destroyed. This is explained by the fact that under these conditions the complete formation of $C_5S_2\dot{S}$ does not occur; low-basic calcium silicates CaO appear. SiO_2 , $3Ca \cdot 2SiO_2$ with poor hydraulic activity.

The strength characteristics of samples $C_4A_3\dot{S}$ with and without 0.5% Na_2O are almost the same. With an increase in its amount to 3%, the strength after 3 and 7 days of hardening decreases by 10 ... 20%, which is explained by a decrease in the amount of $C_4A_3\dot{S}$ formed in the firing products and the appearance of calcium aluminates CA, C_5A_3 , as well as unbound $CaSO_4$. By the 28th and 90th days of hardening, the strength of these samples approaches the strength of pure $C_4A_3\dot{S}$, since by this time calcium aluminates formed in the presence of Na_2O begin to actively exhibit astringent properties. At 4 ... 5% Na_2O , the strength of the samples in the first day of hardening decreases even more, since the amount of the resulting $C_4A_3\dot{S}$ continues to decrease, but by 28 and 90 days it approaches the strength of pure $C_4A_3\dot{S}$.

The strength of $C_5S_2\dot{S}$ samples with 0.5 ... 1% Na_2O is close to the strength of pure $C_5S_2\dot{S}$. In this case, an insignificant dilution of $C_5S_2\dot{S}$ into C_2S and $CaSO_4$ is observed. With an increase in the content of Na_2O to 2 ... 4%, the strength of the samples is almost 2 times lower compared to the strength of pure $C_5S_2\dot{S}$, up to 5% - almost 3 times. This is due to the fact that at a high Na_2O content in the charge, as shown by X-ray phase analysis, $C_5S_2\dot{S}$ almost completely decomposes into C_2S with the release of a large amount of $CaSO_4$.

The presence of up to 2% Cr_2O_3 in clinker does not affect the physical and mechanical properties of $C_4A_3\dot{S}$, $C_5S_2\dot{S}$, 3% causes a slight decrease in strength.

With an excess of $CaSO_4$, the strength of $C_4A_3\dot{S}$ at 1 and 3 days of age is leveled, with the exception of samples with the addition of 15% $CaSO_4$, the strength of which is somewhat higher. At 20 and 25% $CaSO_4$ content, the physical and mechanical properties of the mineral deteriorate sharply.

In samples with additives from 0 to 30% and more $CaSO_4$, the strength of $C_5S_2\dot{S}$ changes little. This type of strength gain is maintained during the considered hardening period.

Results

The test results showed that the introduction of $Na_2O + P_2O_5$ leads to a slight decrease in strength by 3 and 7 days, and $MgO + P_2O_5$ - to 3 days, at other times a slight increase in strength is

noticeable. At 3% MgO + 2.0% P₂O₅ + 2% Na₂O, there is a slight increase in strength indicators, which is explained by the high efficiency of the mineralizing effect of additives, as a result of which conditions are created in C₃S₂S̄ for the formation of C₃S due to the decomposition of CaSO₄.

The joint presence of Na₂SiF₆ and P₂O₅ additives causes an increase in the strength of C₄A₃S̄. At 2.5% Na₂SiF₆ + 1% P₂O₅ and 3% Na₂SiF₆ + 2% P₂O₅, the strength of the samples reaches its maximum value: by 28 and 90 days of hardening in water, it is almost 1.5 ... 2 times higher than the strength of pure C₄A₃S̄. An increase in the amount of Na₂SiF₆ to 3% or more leads to a decrease in the strength of the samples, although it remains higher than that of pure C₄A₃S̄.

Conclusion

The greatest amount of water binds sulfominerals with a high content of Na₂SiF₆ and P₂O₅ additives by 28 days. They exhibit a relatively high hydraulic activity, which is little dependent on the firing temperature. Such additives, considered as complex, facilitate clinker sintering and improve the quality of the cement. Most of them are found in phosphogypsum, so that it can be used economically as one of the main components of sulfo cements.

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