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SULFATE-CONTAINING CEMENTS

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Annotation

It's like a division phosphoanhydrite into two components, it is possible to determine the composition of the raw material mixture and clinker using the formulas we have developed, and according to the composition of the clinker, in turn, the necessary decomposition stump of $CaSO_4$ of the raw mixture.

Key words

phosphoanhydrite , sulfate-containing, sulfoaluminate module, sulfosilicate module, SAS cements, calcium aluminoferrites , chemical composition of components, aluminous-sulfoaluminate-belite , magneto-belite , magneto-sulfoaluminate-belite .

To create sulfate-containing effective cements, the process of formation of sulfate-containing polymineral clinkers was studied in detail and a method for calculating sulfate-containing raw material mixtures in the phase composition of clinker was developed [1-5].

Methods for calculating raw material mixtures and phase composition of sulfate-containing clinkers. We have developed formulas for calculating alumina-belite, alumina-sulfoaluminate-belite, magneto-belite, magneto-sulfoaluminate-belite, sulfoaluminate-belite, sulfoaluminate-silicate in sulfoaluminate-silicate with an excess of unbound clinker anhydrite and the presence of alite and without it. Knowing the chemical composition of sulfate-containing clinkers, these formulas can be used to calculate their mineralogical composition. When processing phosphoanhydrite into sulfate-containing cement and sulfur dioxide, there is no limestone in the raw material mixture, i.e., a two-component raw material mixture is obtained. However, in this case, the raw mixture cannot be calculated as a two-component one, since the phosphodehydrate does not decompose completely (70 ... 90%). Therefore, in the calculations, we conventionally divided phosphoanhydrite into decomposed and undecomposed. The preserved $CaSO_4$ should form sulfominerals, and its excess should be given in bound form to increase the physical and mechanical properties of the resulting cement. Thus, by conditionally

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dividing phosphoanhydrite into two components, it is possible to determine the composition of the raw material mixture and clinker according to the formulas we have developed, and by the composition of the clinker, in turn, the necessary decomposition of the $CaSO_4$ raw material $_{mixture}$.

The developed methods were the basis for designing the composition of clinkers and raw mixtures and controlling the processes of their preparation.

Next, a chemical-analytical technique was proposed for determining the quantitative mineralogical composition of clinkers, which made it possible to monitor the progress of mineral formation [1, 4, 6,] . When developing the calculation of raw material mixtures for all possible sulfoclinkers and their mineralogical compositions, we proceeded from the following:

1) the clinker contains no C_3A, C_5A_3 , $C_{12}A_7$ and C_2AS

2) the clinker contains SiO_2, in the lead C_3S, C_2S or $2(C_2S)CaS0_4$ (for convenience of calculation, $2(C_2S)$. $CaSO_4$ can be conventionally represented as $2C_2S+CaSO_4$);

3) the clinker contains Al_2O_3 in the form of $C_4A_2S(3CA+CaSO_4)$ and $C_4AF(CA+C_3F)$;

4) gypsum, introduced into the charge in sufficient quantities, prevents the formation of high-alumina alumina ferrites calcium, causing the appearance of C_4A_3S and C_4AF in the product. Consequently, iron oxides in clinkers are in the form of $C_4AF(CA+C_3F)$ [8-11] .

Based on the above and using the necessary transformations to find the KH (the coefficient of saturation of silica with calcium oxide to the composition $3CaO*SiO_2(C_3S)$) of sulfate-containing clinker, the final expression was obtained:

$$KH = \frac{C_0 - 0{,}55A_0 - 1{,}05F_0 - 0{,}7(\bar{S}_0) - 1{,}18(P_0)}{2{,}8S_0} \qquad (1)$$

where S_0, C_0 , A_0 , F_0 , $\bar{S}_0$ and P_0 . the content, respectively, of SiO_2 , CaO, Al_2O_3, Fe_2O_3, SO_4, and P_2O_5 in the raw mixture.

The value of 1,18 P_o must be taken into account in the case when phosphogypsum is used as a raw material component (the content of P_2O_5 in phosphogypsum reaches 3%).

We introduced the new concept of sulfosilicate modulus (n_s), which shows that silicon oxides are bound by sulfate to the composition of minerals $2(C_2S)*CaSO_4$ in the presence of free (unbound) $CaSO_4$ and without it:

$$n_s=(\bar{S}_0-0{,}21(A_0-0{,}64F_0))/(0{,}667S_0)=(\bar{S}_0-0{,}261A_0+0{,}166F_0)/(0{,}667S_0) \qquad (2)$$

where $0,261=SO_3/(3Al_2O_3)$ is the weight ratio of SO_3 to Al_2O_3 in the mineral $3(CA)CaSO_4$; $0,64=Al_2O_3/Fe_2O_3$ - weight ratio of Al_2O_3 to Fe_2O_3 in the mineral $4CaO*A1_2O_3$ Fe_2O_3.

Since in the raw mixture for 1 wt. parts of the third component account for the weight. parts of the first component and weight. part two, we can write the following equalities:

$C_0=(xC_1+yC_2+C_3)/(x+y+1)$; $S_0=(xS_1+yS_2+S_3)/(x+y+1)$

$A_0=(xA_1+yA_2+A_3)/(x+y+1)$; $F_0=(xF_1+yF_2+F_3)/(x+y+1)$;

$S_0=(xS_1+yS_2+S_3)/(x+y+1)$; $P_0=(xP_1+yP_2+P_3)/(x+y+1)$

Substituting the indicated values into formulas (1) and (2), we obtain a system of two linear equations with two unknowns:

$x[C_1 -2,8S_1*KH-0,55A_1-1,05F_1-0,7S_1-1,18P_1]+y[C_2 -2,8S_2*KH-0,55A_2-1,05F_2-0,7S_2-1,18P_2]=2,8S_3*KH+0,55A_3-1,05F_3-0,7S_3-1,18P_3-C_3$;

$x[C_1 -0,667S_1\ n_s -0,261A_1+0,166F_1]+y[S_2 -0,667S_2\ n_s-0,261A_2+0,166F_2]=0,667S_3n_s +0,261A_3 - 0,166F_3-C_3$.

For convenience of calculations, we will accept the following abbreviations:

$a_1 = C_1-2,8S_1\ KH -0,55A_1-1,05F_1-0,7S_1-1,18P_1$;

$b_1 = C_2-2,8S_2\ KH -0,55A_2-1,05F_2-0,7S_2-1,18P_2$;

$c_1 = 2,8S_3\ KH +0,55A_3+1,05F_3+0,7S_3+1,18P_3-C_3$;

$a_2 = S_1-0,667S_1n_s-0,261A_1+0,166F_1$;

$b_2 = S_2-0,667S_2\ n_s-0,261A_2+0,166F_2$;

$c_2 = 0,667S_3\ n_s+0,261A_3-0,166F_3-S_3$

Substituting these notations into linear equations, we get:

$a_1 x+b_1 y=c_1$;

$a_2 x+b_2 y=c_2$.

We solve a system of two equations with two unknowns:

$x=(c_1b_2-c_2b_1)/(a_1b_2-a_2b_1)$; $y=(a_1c_2-a_2c_1)/(a_1b_2-a_2b_1)$.

Taking KN equal to 0,67 and changing n_s in the range of 0…3,5, it is possible to calculate the raw material mixtures for producing alumina-belite, sulfoaluminate-belite, SAS, SAS cements with excess anhydrite, Portland cement, sulfoaluminate containing Portland cement.

If it is necessary to take into account the decomposition process of $CaSO_4$ in the chemical composition of the sulfate-containing component, part of the SO_3 can be considered as p.p.p. (this amount depends on the firing conditions, the design of the furnace, the chemical composition of the components, therefore it is determined experimentally for each specific case).

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To obtain stoichiometric quantities of Al_2O_3 . and 50% in the raw mixture in order to form the compound C_4A_3S in the composition of sulfoaluminate-belite clinker, we introduced a sulfoaluminate module (p_S), expressing the concept attitude SO_3: Al_2O_3.

In cements containing Fe_2O_3 , not the entire amount of Al_0O_3 enters into the reaction of formation of C_4A_3S. According to some data, calcium aluminoferrites interact with $CaSO_4$ only when the A:F molar ratio in it is greater than one. In this regard, the expression for p_s can be modified as follows:

$p_s = SO_3 / (Al_2O_3 - 0{,}64Fe_2O_3)$

For C_4A_3S with a molar ratio SO_3 : Al_2O_3 = 1:3, the value ρ_S is 0.26. Then the formulas will take the following form:

$a_1 = C_1 - 2{,}8S_1 KH - 0{,}55A_1 - 1{,}05F_1 - 0{,}7S_1 - 1{,}18P_1$;

$b_1 = C_2 - 2{,}8S_2 KH - 0{,}55A_2 - 1{,}05F_2 - 0{,}7S_2 - 1{,}18P_2$;

$c_1 = 2{,}8S_3 KH + 0{,}55A_3 + 1{,}05F_3 + 0{,}7S_3 + 1{,}18P_3 - C_3$;

$a_2 = S_1 - p_s (A_1 - 0{,}64F_1)$;

$b_2 = S_2 - p_s (A_2 - 0{,}64F_2)$;

$c_2 = p_s (A_3 - 0{,}64F_3) - S_3$.

When KN is greater than 0,67, free lime is present. However, when calculating the charge, it is not always possible to accurately determine the amount of free CaO oxide in the designed clinker, since under synthesis conditions, along with C_2S, C_3S is also formed . When KN is less than 0,67, the composition of sulfate-containing clinker, along with saturated 2CaO * SiO_2 , or 2(2CaO SiO_2) CaSÓ$_4$, necessarily contains less saturated 3CaO $2SiO_2$, CaO SiO_2 . since there is a lack of lime,

It has been established that in sulfate-containing raw material mixtures, sulfate acts as a flux, and therefore, when firing mixtures designed to form the calculated amount of C_3S and C_2S as in SAB or SAS, clinker formation is completed mainly at a temperature of 1300°C or lower .

Knowing the chemical composition of sulfoaluminate-containing Portland cement clinker, it is possible to calculate the content of the main components of clinker using V.A. Kind's method.

Taking into account that 1% SiO_2 , combining with 2,8% CaO, forms 3,8% C_3S, and with 1,87% CaO – 2,87 C_2S , the content of C_3S and C_2S can be calculated;

$C_3S = 4{,}070CaO - 7{,}600SiO_2 - 2{,}239Al_2O_3 - 4{,}287Fe_2O_3 - 2{,}851SO_3$;

$C_2S = 8{,}600SiO_2 + 1{,}689Al_2O_3 + 3{,}235Fe_2O_3 + 2{,}150SO_3 - 3{,}070CaO$.

The number of remaining compounds (C_4A_3S, C_4AF, $CaSO_4$ bond) is determined in the same way as in previous cases. Formulas for calculating the

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content of clinker minerals are also valid when firing in the stability temperature range C_4A_3S.

By changing the value of KN, it is not difficult to obtain a clinker composition with different contents of C_2S and C_3S. If at KH=1, i.e., with complete saturation of silica to C_3S , there will be no C_2S in the clinker composition, then at KH = 0,67 - C_3S. The lower the KN, the more C_2S and less C_3S in the clinker .

To calculate a three-component raw mixture, you must also specify the KN and one of the modules (n_s or p_s). In this case, the sulfosilicate module should be specified in the case of a raw material mixture with a large amount of sulfate-containing materials, i.e., calculated for the formation of sulfoaluminate silicate clinker without excess $CaSO_4$ and with its excess. In the case of raw mixtures with less calcium sulfate and more alumina, i.e., designed for the formation of sulfoaluminate-belite clinker (i.e., containing $C_{12}A_7$) or expanding sulfoaluminate Portland cement, it is recommended to specify the sulfoaluminate module when calculating a four-component mixture it is necessary to specify KN, one of the modules (n_s or p_s) and, accordingly, an alumina or silicate module.

With an ideal $p_{s\ value}$ (0,26), sulfoaluminate Portland cements of ordinary average composition require about 1% SO_3 in clinker or 2,4 wt. % gypsum (dihydrate) in the raw mixture. However, this is only possible if the roasting is carried out in the temperature stability range C_4A_3S. Therefore, expanding clinker is produced in a rotary kiln in the same way as ordinary Portland cement clinker, the only difference being that the temperature in the firing zone is not 1500°C, but about 1300°C or lower. If the temperature in the oven is 1300°C, then due to C_4A_3S and free lime the following reaction will occur [7]:

$C_4A_3S+6C \rightarrow 3C_3A+CS$.

In this case, the values of KN, C_3S, C_4A_3S will be lower than calculated and in order to obtain clinkers with actual KN and correspondingly higher contents of C_3S and C_4A_3S , it will be necessary to make adjustments.

As our studies have shown, in clinker, along with CA, calcium aluminate of the composition $C_{12}A_7$ is formed with a lack of calcium sulfate. In this case, the alumina remaining after the formation reaction of C_4AF and C_4A_3S binds with CaO to form calcium aluminate of composition $C_{12}A_7$.

The raw mixture is calculated using KN and p_s (sulfoaluminate module):

KN= $((C_0\text{-}0{,}94A_0(1\text{-}1{,}6\ p_s)\text{-}0{,}8\ F_0\ (1+1{,}2\ p_s)\ \text{-}0{,}7\ S_0\ \text{-}1{,}19\ P_0\ /\ 2{,}8S_0$

$p_s = S_0\ /\ (A_0\ \text{-}0{,}64\ F_0\ )$

When deriving the formula for calculating the three-component raw material mixture, we used the technique used earlier when calculating the sulfoaluminate-silicate raw material mixture:

$a_1 = S_1 - 2{,}8\, S_1 KN - 0{,}94A_1 (1-1{,}6\, p_s) - 0{,}8F_1 (1+1{,}2\, p_s) - 0{,}7S_1 - 1{,}19P_1$;

$b_1 = C_2 - 2{,}8S_2KH - 0{,}94A_2(1-1{,}6\, p_s) - 0{,}8F_2(1+1{,}2\, p_s) - 0{,}7S_2 - 1{,}19P_2$;

$c_1 = 2{,}8S_3KH + 0{,}94A_3(1-1{,}6\, p_s) + 0{,}8F_3(1+1{,}2\, p_s) + 0{,}7S_3 + 1{,}19P_3 - C_3$;

$a_2 = S_1 - p_sA_1 + 0{,}64F_1p_s$;

$b_2 = S_2 - p_s A_2 + 0{,}64F_2\, p_s$;

$c_2 = p_s A_3 - 0{,}64F_3\, p_s - S_3$

Substituting these abbreviations into linear equations, we obtain the following system of equations:

$a_1x + b_1y = c_1$; $a_2 + b_2 y = c_2$.

We solve them through determinants and after appropriate reductions and groupings we obtain the following values for x and y :

$x = (c_1b_2 - c_2b_1) / (a_1b_2 - a_2b_1)$; $y = (a_1c_2 - a_2c_1) / (a_1b_2 - a_2b_1)$.

of calcium sulfate, it is completely consumed in the formation of C_4A_3S. Based on the fact that each percentage of SO_3, SiO_2 and Fe_2O_3 gives, respectively, $7{,}6C_4A_3S$, $2{,}87C_2S$ and $3{,}043C_4AF$, to calculate the content of C_4A_3S and C_4AF (%) Let's see the formulas:

$C_4A_3S = 7{,}6SO_3$; $C_2S = 2{,}87SiO_2$; $C_4AF = 3{,}043Fe_2O_3$

Considering that every percent of Al_2O_3 forms $2C_4A_3S$, and C_4AF is associated with $0{,}64Fe_2O_3$. you can calculate the bound amount of Al_2O_3 in the minerals C_4A_3S and C_4AF

$A_{connection} = (\%C_4A_3S)/2 + 0{,}64\, F$.

Knowing that each percent of the remaining A_2O_3 forms $1{,}94C_{12}A_7$, we can calculate its amount in clinker:

$C_{12}A_7 = 1{,}94(A_{total} - A_{bond}) = 1{,}94(A - \%C_4A_3S /2 - 0{,}64F)$.

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