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Abstract

Full Text

Chemistry

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On the Possibility of Directed Change in the Course of Mineral Formation in the System $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$

(Presented by Academician P. A. Rebinder on 30 X 1962)

To obtain Portland cement with high strength indices, it is very important to ensure, during firing, an increased content of highly active minerals and, correspondingly, a reduced content of weakly active minerals. Of the two calcium aluminates whose formation is possible in Portland-cement clinker— C_3A and C_5A_3 —the latter is more desirable, since, in comparison with C_3A , it gives considerably higher strength ⁽¹⁾. Likewise, of the two calcium silicates— C_2S and C_3S —the second is more desirable, because it surpasses C_2S in absolute strength and in rate of hardening.

It is known, however, that when mixtures consisting of CaCO_3 , Al_2O_3 , and SiO_2 are fired, in the process of binding calcium oxide with acidic oxides, as the temperature and duration of heating increase, CA is first formed from CaO and Al_2O_3 , which then passes into C_5A_3 and subsequently into C_3A ; analogously, from CaO and SiO_2 , C_2S is formed at first, which, upon reaching high temperatures, passes into C_3S . It is important to note that C_3A is formed at a lower temperature than C_3S ; thus, normally, saturation of silica with lime to C_3S is possible only after saturation of alumina to its most basic compound— C_3A .

We set ourselves the goal of determining whether it is possible to change the course of mineral formation in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ in a directed manner such that, after the formation of C_5A_3 , calcium oxide would proceed not to the formation of the less desirable C_3A , but to the saturation of C_2S in order to obtain highly active tricalcium silicate. To solve this problem we made use of the known observations on the instability of C_3A when it is heated with fluorides ⁽²⁻⁶⁾, as well as data on the considerable intensification of the formation of C_3S when fluorine-containing mineralizers are introduced into the raw mix ⁽⁷⁾.

Below are presented the results of experiments demonstrating the possibility of directed mineral formation in the system under consideration, namely the obtaining, from one and the same raw mix, instead of the normal composition— $C_3A + C_2S$ —of the more desirable composition— $C_5A_3 + C_3S$.

Fig. 1. X-ray diffraction patterns of mixtures of minerals $3C_3A + 4C_2S$, fired without an additive (a) and with an addition of CaF_2 (2% F) (b), with an addition of Na_2SiF_6 (2% F) (c)

Figure 1: Fig. 1. X-ray diffraction patterns of mixtures of minerals $3C_3A + 4C_2S$, fired without an additive (a) and with an addition of CaF_2 (2% F) (b), with an addition of Na_2SiF_6 (2% F) (c)

In the first series of experiments, two mixtures of the following compositions (in moles) were prepared from previously synthesized pure C_3A and pure C_2S : 1) $3C_3A + 4C_2S$ and 2) $3C_3A + 8C_2S$.

Each of these mixtures was divided into three equal parts. To the first of them no fluorides were added; to the second and third, CaF_2 and Na_2SiF_6 were added in an amount corresponding to 2% fluorine by weight of the mineral mixture. Mixtures without mineralizers were fired at 1400° , and those with mineralizers at 1300° .

The resulting clinkers were ground to the same specific surface area, approximately equal to $3000 \text{ cm}^2/\text{g}$. In the powders the content of free CaO was determined, and their strength on hardening was established by testing small specimens. X-ray patterns were also taken for the clinkers of composition $3C_3A + 4C_2S$.

Chemical analysis showed that the clinkers contained no free CaO . X-ray examination showed that, when the two-mineral mixture of composition $3C_3A + 4C_2S$ was fired without addition of fluorides, no changes occurred in its mineralogical composition: on the X-ray patterns—

Fig. 1. X-ray diffraction patterns of mixtures of minerals $3C_3A + 4C_2S$, fired without an additive (a) and with an addition of CaF_2 (2% F) (b), with an addition of Na_2SiF_6 (2% F) (c)

...corresponding to this clinker (see the lower X-ray diffraction pattern in Fig. 1), only diffraction maxima of interplanar spacings characteristic of C_3A and C_2S are visible. We see a completely different picture in the X-ray diffraction patterns taken from clinkers fired with an addition of fluorides. In this

case (see the two upper curves in Fig. 1), only diffraction maxima of interplanar spacings characteristic of C_5A_3 and C_3S are observed on the X-ray diffraction patterns. The lines of C_3A and C_2S are completely absent.

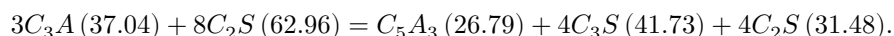
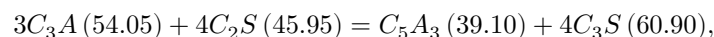
These data, as well as the absence of free lime in the sinters, convincingly show that, during firing of a mixture of two minerals— $C_3A + C_2S$ —in the presence of fluorides, a redistribution of lime between alumina and silica takes place. The addition of fluorine-containing compounds leads to decomposition of tricalcium aluminate, and as a result a more low-basic aluminate, C_5A_3 , is obtained, while the liberated calcium oxide combines with C_2S to form an increased amount of C_3S . The change in mineralogical composition occurs in accordance with the

following equations (the percentage contents of the initial and newly formed minerals are given in parentheses):

Table 1

Strength during hardening of two-mineral sinters obtained by firing without an additive and with fluoride additives

Additive	Amount of introduced F, %	Compressive strength limit, kg/cm ² , after 3 days	Compressive strength limit, kg/cm ² , after 7 days	Compressive strength limit, kg/cm ² , after 28 days
Sinter of initial composition				
$3C_3A + 4C_2S$				
Without additive	—	24	25	42
CaF_2	2	200	210	220
Na_2SiF_6	2	180	184	188
Sinter of initial composition				
$3C_3A + 8C_2S$				
Without additive	—	23	24	36
CaF_2	2	184	220	225
Na_2SiF_6	2	150	165	165



Such a substantial change in phase composition, caused by the fluoride additives, leads to a very great increase in the strength of the products obtained during their hardening. This is convincingly demonstrated by Table 1.

The second series of experiments was carried out by us in order to show that directed mineral formation can be achieved not only when firing mixtures of

ready-made minerals, but also when firing raw mixes of the corresponding composition. For the experiments, two raw mixes were prepared from chemically pure calcium carbonate, silica gel, and aluminum hydroxide, calculated so that after firing they would give (under conditions of normal mineral formation) clinkers of the same two compositions as those adopted in the first series of experiments: 1) $3C_3A + 4C_2S$ and 2) $3C_3A + 8C_2S$.

The raw mixes were fired without additive and with an addition of fluorides according to the regime adopted in the first series. After preparation, the clinkers were ground to a specific surface corresponding to $3000 \text{ cm}^2/\text{g}$. No free CaO was found in the clinkers. X-ray diffraction examination showed that the process of mineral formation during firing of raw mixes without an additive and with a fluoride additive proceeds quite differently, as a result of which the phase composition of the fired products is different. The clinker of calculated composition $3C_3A + 4C_2S$, when obtained from a raw mix without fluorides, consisted only of C_3A and C_2S . Conversely, clinkers of the same initial calculated composition, when fired with fluoride additives, contained no C_3A or C_2S ; on the X-ray diffraction patterns of these clinkers, only diffraction maxima of interplanar spacings characteristic of C_3S and C_5A_3 were visible. The data of Table 2 show that the strength of clinkers obtained with fluorides very greatly exceeds the strength of the corresponding clinkers fired without fluorides. This is also, although indirect, nevertheless weighty evidence of the directed course of mineral formation during firing.

From the foregoing it is clear that the principal distinctive feature of directed mineral formation is the circumstance that, in the presence of fluorides, calcium oxide combines (after formation during firing—

...material C_5A_3 and C_2S) not with pentacalcium trialuminate, but with dicalcium silicate. For an additional verification of this, we decided to carry out a third series of experiments. A mixture of the following composition (in moles) was prepared from previously synthesized C_5A_3 , C_2S (in the γ -modification), and $CaCO_3$: $C_5A_3 + 4C_2S + 4CaCO_3$.

The amount of $CaCO_3$ in the indicated mixture was deliberately taken such that it would be sufficient either for the complete conversion of all C_5A_3 into C_3A , or for the complete conversion of C_2S into C_3S . The experiments were to show with which mineral— C_5A_3 or C_2S — CaO would combine during firing of the indicated mixture without fluorides and with the addition of fluorides.

Table 2

Strength during hardening of clinkers fired without additive and with an addition of fluorides

Additive	Amount of introduced F, %	Compressive strength, kg/cm ² after 3 days	Compressive strength, kg/cm ² after 7 days	Compressive strength, kg/cm ² after 28 days
Clinker of calculated composition				
3C ₃ A + 8C ₂ S				
Without additive	—	21	24	39
CaF ₂	2	160	185	207
Na ₂ SiF ₆	2	150	165	188
Clinker of calculated composition				
3C ₃ A + 8C ₂ S				
Without additive	—	19	23	35
CaF ₂	2	150	175	200
Na ₂ SiF ₆	2	120	115	155

After preparation, the mixture was divided into three parts, to two of which CaF₂ and Na₂SiF₆ were added (calculated as 2% fluorine relative to the expected weight of the fired product).

The firings were carried out according to the regime adopted in the first series. Free CaO was not found in the clinkers. In an X-ray examination of the radiograph of the clinker obtained without the addition of fluorine-containing compounds, only diffraction maxima of interplanar spacings characteristic of C₃A and C₂S were detected. This indicates that normally (i.e., in the absence of fluorides) CaO combines preferentially with C₅A₃, and not with C₂S. On the radiographs taken from clinkers with additions of CaF₂ and Na₂SiF₆, only diffraction maxima of interplanar spacings characteristic of C₃S and C₅A₃ were visible; maxima characteristic of C₂S, C₃A, and CaO were absent. Thus, during firing of the charge with an addition of fluorides, CaO combines preferentially with C₂S, and not with C₅A₃. Mechanical tests confirmed the above-described features of mineral formation during firing of a charge of composition C₅A₃ + 4C₂S + 4CaCO₃ without additive and with an addition of fluorides: in the latter case the strength proved to be considerably higher than in the former.

The results of the third series of experiments once again clearly show that the presence of fluorine-containing mineralizers in the fired charge, as it were, imposes a prohibition on the formation of the highly basic calcium aluminate of composition C_3A , and, conversely, promotes the more rapid formation, at lower temperatures, of tricalcium silicate.

The general conclusion on the basis of the three series of experiments carried out is that introduction into the raw mix of fluorine-containing additives in the proper amount (of the order of 1-2%, calculated as fluorine) makes it possible to effect a directed change in the course of mineral formation during firing, leading to the production of high-strength, rapidly hardening minerals C_5A_3 and C_3S , instead of the low-strength and slowly hardening C_3A and C_2S .

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