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STUDY OF CLINKER DOPPED WITH P AND S COMPOUNDS

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Abstract

The sintering and the structure of clinkers, modified by the introduction of different ionic forms of sulfur and phosphorus into the raw mix, were examined. One reference synthetic mixture and 25 modified mixtures were prepared by mixing the reference sample with 0.5, 1.0, 1.5, 2.0 and 2.5% *w*/*w* of chemical grade $CaSO_4$, CaS, $Ca_3(PO_4)_2$, $CaHPO_4$ and $Ca(H_2PO_4)_2$. Free lime content in all samples was measured. The sintering reactions in samples were recorded by means of differential thermal analysis. The texture of the clinkers was examined using a scanning electron microscope and EDX. It is concluded that, despite of their relatively low doping concentration in the raw mix, P and S affect considerably its reactivity and the texture of the clinker. The various ionic forms of the same element (SO_4^{2-}, S^{2-} for S, PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ for P) exhibit a different and unequivocal effect on the reactivity of the synthetic raw mix and on the texture of the corresponding clinkers. S (in both forms) and P (added as HPO_4^{2-}) are mainly dissolved in the melt and they have a positive effect on the burnability of the raw mix. P (added as PO_4^{3-} or $H_2PO_4^-$) is preferentially accumulated in belite. In this case further stabilization of β-C_2S occurs and the binding of the free lime is hindered.

Keywords: cement, clinker, DTA, phosphorous, SEM, sulfur

Introduction

The incorporation of foreign ions into the cement raw meal and their effect on the clinker formation and cement properties have been broadly discussed during the last years. It has been found that small amount of inorganic additives can considerably affect the sintering process, the structure and the properties of clinker and that is why their effect was successfully described as a catalytic one [1–5].

Sulfur and sulfides from raw materials and fuel are oxidized and are incorporated into the solid phases as sulfates in clinker [2]. Sulfur, mostly in the form of natural gypsum ($CaSO_4 \cdot 2H_2O$) was used as mineralizer but in practice, sulfate addition in the raw mix is limited because of the restrictions concerning the SO_3 content in the cement.

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According to Taylor [6], in the CaO–C_2S^{**}–C_3P system, C_3S has a primary phase field, but at clinkering temperature of 1500°C, mixes with more than a few percent of P_2O_5 do not yield C_3S. Under oxidizing conditions phosphorus is highly soluble in C_2S phase in the form of P^{5+} ions, decreasing the amounts of alite, while under reducing conditions the major portion of P is reduced to P^{3+} [7]. PO_4^{3-} ions decrease the viscosity of the liquid phase [8], though Sychova and Anufriev [9] have reported the opposite phenomenon and it was attributed to the bigger size and lower mobility of PO_4^{3-} ions. According to Sychev and Volkonskii [10], the presence of P_2O_5 leads to a significant decrease in the surface tension of the melt. Low P_2O_5 levels (<1.0% *w*/*w*) have been reported to improve the burnability of the raw mix, and the alite formed exhibits higher hydraulic activity than ordinary alite [11]. Calcium phosphate ($Ca_3(PO_4)_2$) is used in combination with $CaSO_4$ and CaF_2 especially in the production of clinker and aluminophosphate cements [9].

In this paper, the sintering and the structure of clinkers, modified by the introduction of different ionic forms of sulfur and phosphorus, as minor elements in the raw mix, is examined. This work is part of a research project concerning the effect of foreign elements on the reactivity of the raw mix and on the properties of the cement.

Experimental

One reference mixture was prepared, composed of chemical grade $CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3 and having a composition very close to that of a typical cement raw meal. Table 1 shows the chemical and the mineral composition (according to Bogue) of the reference mixture, after sintering at 1450°C.

Table 1 Chemical and mineral composition (% *w*/*w*) of the reference clinker

Chemical composition		Mineral composition (according to Bogue)	
CaO	68.08	C_3S	65.0
SiO_2	22.81	C_2S	15.0
Al_2O_3	5.84	C_3A	10.0
Fe_2O_3	3.27	C_4AF	10.0

Twenty five modified mixtures were prepared by mixing the reference sample with 0.5, 1.0, 1.5, 2.0 and 2.5% *w*/*w* of chemical grade $CaSO_4$, CaS, $Ca_3(PO_4)_2$, $CaHPO_4$ and $Ca(H_2PO_4)_2$. The studied elements, phosphorus and sulfur, were introduced in the form of calcium salts, in order to avoid the side effects of foreign cations on the structure of the clinker. Several anionic forms of S and P elements were selected in order to examine the effect of different anionic species in the sintering process and on the reactivity of the cement raw mix.

** Cement chemistry notation: C=CaO, S=SiO_2, A=Al_2O_3, F=Fe_2O_3, C_3S=3CaO·SiO_2 (alite), C_2S=2CaO·SiO_2 (belite), C_3A=3CaO·Al_2O_3 (aluminate), C_4AF=4CaO·Al_2O_3·Fe_2O_3 (ferrite)

All samples were pressed to form pellets, then sintered at 1450°C for 30 min in an electrical furnace and cooled rapidly in air. The unreacted lime (free lime, fCaO) was determined according to the standard ethylene glycol method. The sintering reactions in samples doped with 1.0% *w*/*w* of the above calcium salts were recorded by means of differential thermal analysis, using a Mettler–Toledo TGA/SDTA 851 instrument (T: 25-1500°C, rate: 10°C/min).

Mineralogical studies of the sintered samples doped with 2.5% *w*/*w* of the above additives were performed using a Siemens D-5000 X-ray diffractometer ($CuK_{\alpha1}$, λ=1.5405Å). Selected clinker nodules of the burned samples were examined using a Jeol JSM-5600 scanning electron microscope equipped with an Oxford Link ISIS 300 Energy Dispersive X-ray spectrometer (EDX).

Results and discussion

Burnability tests in modified raw mixes

Variations on the reactivity of the modified raw mixtures were evaluated on the basis of the unreacted lime (fCaO) content after sintering at 1450°C. Figure 1 presents the free lime content in the reference and the modified samples. As it can be seen from Fig. 1, both forms of S compounds strongly improve the reactivity of the raw mix. The variations are probably due to the different S content in the two compounds (44.4% in CaS, 23.5% in $CaSO_4$). However, the different ionic forms of phosphorus affect the reactivity of the raw mix in a variant way, even though the P content in $Ca_3(PO_4)_2$, $CaHPO_4$ and $Ca(H_2PO_4)_2$ is almost the same (20.0, 22.7 and 26.5% *w/w* respectively). The addition of $CaHPO_4$ has a positive effect while $Ca(H_2PO_4)_2$ causes a negative one on the binding of free lime and that of $Ca_3(PO_4)_2$ is intermediate.

DTA studies of modified raw mixtures

Thermal analytical methods have been widely used for the study of sintering and hydration reactions in cement [12–13]. Figure 2 presents the DTA curves of the reference sample and the samples containing 1.0% *w*/*w* $CaSO_4$, CaS, $Ca_3(PO_4)_2$, $CaHPO_4$ and $Ca(H_2PO_4)_2$. In all modified samples the reactions associated with clinkerization (1200–1450°C) were recorded, suggesting satisfactory burning and clinkerization of all samples.

The addition of the selected anionic species does not affect the decomposition of $CaCO_3$ in general. An exception was recorded in the case of $Ca(H_2PO_4)_2$, where the endset of the decomposition is shifted to higher temperatures (approximately by 77°C).

Differentiations concerning belite formation were recorded in raw mixtures doped with $Ca_3(PO_4)_2$ and $Ca(H_2PO_4)_2$, where the main stage of belite formation is shifted to higher temperatures in comparison to the reference. On the contrary, in the rest of the samples the opposite phenomenon was observed and the main stage of belite formation was shifted to lower temperatures in comparison to the reference.

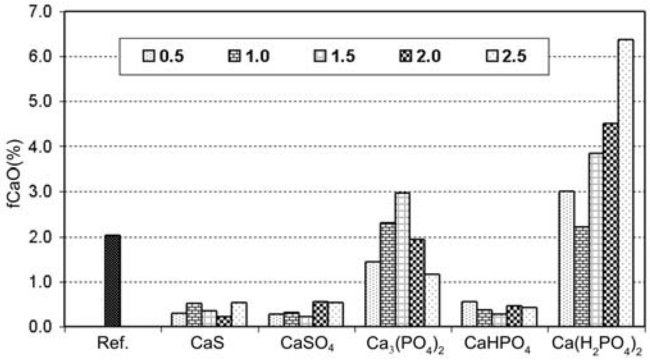

Fig. 1 Free lime content (%) of modified samples after thermal treatment at 1450°C, as a function of the doping concentration

Generally, it seems that despite their relatively low doping concentration in the raw mix, the addition of S and P compounds differentiates the sintering process of the synthetic raw mix. Their exact action is difficult to be explained in detail, due to the nature of the sintering process itself (reactions that proceed simultaneously, formation-decomposition of intermediate products, alterations of physicochemical properties).

XRD studies of modified clinkers

All the samples sintered at 1450°C have the structure of a typical clinker. The dominant phases (alite, belite, calcium aluminate and ferrite) were well crystallized, giving peaks at the nominal 2θ values. Free CaO was detected only in samples doped with $Ca(H_2PO_4)_2$ and $Ca_3(PO_4)_2$, as it was expected on the basis of fCaO measurements (Fig. 1). The XRD patterns of the samples did not show any indications of formation of new phases, probably because of the extensive overlapping of the peaks and/or the low doping concentration.

SEM examinations of modified clinkers

The examination of modified clinkers by SEM led to the photographs presented in Fig. 3. The photos were selected to be representative as far as the distribution, size and form of alite and belite crystals were concerned. An evaluation of size and shape of clinker silicate minerals is presented in Table 2. With the point acquisition analysis of EDX, the composition of the principal phases was analyzed at five to eight points. Owing to instrumental limitations, accuracy in analyses of the minute grains in the interstitial phases proves difficult to achieve. In any case, the comparison of the point analysis in each clinker phase can lead to qualitative indications only concerning the distribution of the added elements in the individual clinker compounds.

The reference sample (Fig. 3a) has the texture of a typical clinker with compact prismatic alite crystals, small roundish belite grains and interstitial material having a fine-crystalline structure.

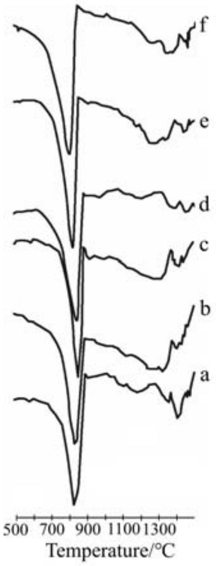

Fig. 2 DTA curves of the modified raw mixtures containing 1% *w/w* of the additive. a – Reference, b – $CaSO_4$, c – CaS, d – $Ca_3(PO_4)_2$, e – $CaHPO_4$, f – $Ca(H_2PO_4)_2$

The sintered samples containing 2.5% *w/w* $CaSO_4$, CaS or $CaHPO_4$ (photos 3b, 3c and 3d, respectively), have similar texture. Belite crystals are uniformly distributed as small roundish grains while alite grains dominate the sample's texture, as compact prismatic crystals of slightly rounded hexagonal outline. EDX elemental analysis showed that S and P are preferentially incorporated in the interstitial phase while small amounts are also found in belite.

The photo of the sample containing 2.5% *w/w* $Ca_3(PO_4)_2$, is given in Fig. 3e. Alite crystals are larger in size and have hexagonal elongated shape. Traces of phosphorus were detected by EDX analysis in the interstitial matrix, but remarkable concentrations of P were found in silicates and especially in belite.

Figure 3f presents the sample containing 2.5% *w/w* $Ca(H_2PO_4)_2$. Free CaO grains with a characteristic leaflet configuration are well recognized, close to clusters of C_2S grains. The coexistence of free lime and belite suggests that the reaction between CaO and C_2S has not come to an end. Probably, either alite is decomposed in the presence of high P_2O_5 levels (1.52% *w/w* in the raw mix doped with 2.5% *w/w* $Ca_3(PO_4)_2$, *vs.* 1.31% *w/w* in the raw meal with 2.5% *w/w* $CaHPO_4$ and 1.16% *w/w* P_2O_5 in raw mix doped with 2.5% *w/w* $Ca_3(PO_4)_2$) or belite is stabilized in such a way that further reaction with CaO is inhibited. The latter suggestion seems to be correct since EDX analysis showed that P is preferentially incorporated in calcium silicates and especially in C_2S. In addition, phase equilibrium studies for the CaO–C_2S–C_3P system suggest that phosphorus favors free lime formation by going into solid solu-

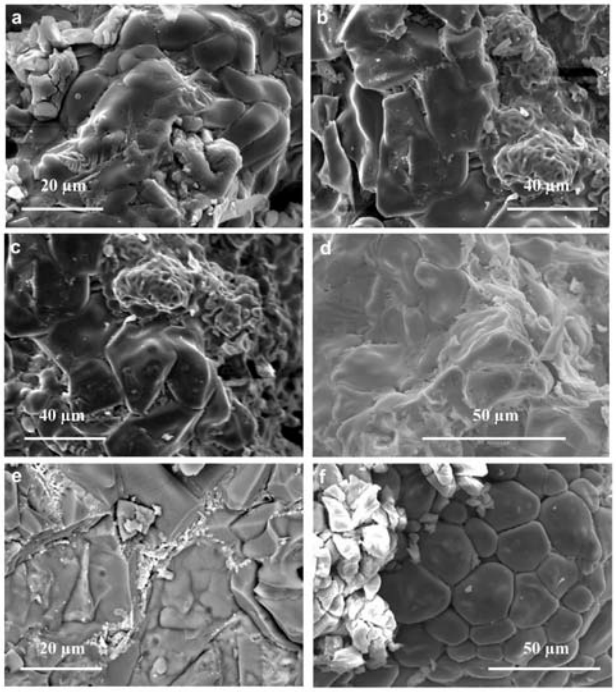

Fig. 3 SEM photos of clinkers. a – Reference, b – $CaSO_4$, c – CaS, d – $CaHPO_4$, e – $Ca_3(PO_4)_2$, f – $Ca(H_2PO_4)_2$

tions and displacing CaO from other compounds [6, 7]. The amount of belite and free lime seems to be higher in comparison with the other samples, a fact that was also confirmed by the chemical tests (Fig. 1) and the XRD studies.

Table 2 Size and shape of alite and belite grains in clinker with 2.5% additive

Sample	Alite		Belite	
	Size/µm	Shape	Size/µm	Shape
Ref.	20–30	compact, prismatic, with slightly rounded hexagonal outline	5–10	small, roundish
$CaSO_4$	20–60	large, compact, prismatic, with slightly rounded hexagonal outline	5–10	small, roundish
CaS	20–80	large, compact, polygonal, rather elongated, prismatic	5–10	small, roundish
$Ca_3(PO_4)_2$	40–100	large, elongated, compact, prismatic, angular	5–10	small, roundish
$CaHPO_4$	20–50	large, compact, polygonal, with slightly rounded outline	5–10	small, compact, roundish
$Ca(H_2PO_4)_2$	20–40	large, compact, prismatic, angular	10–20	larger in size, compact, round

An attempt to summarize the above remarks, is presented below:

- The various ionic forms of S and P (SO_4^{2-}, S^{2-} for S, PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^{-}$for P) affect the texture of the corresponding clinker, in a variant way. The same remark was also recorded for the burnability tests and cannot be disregarded as accidental.
- Both forms of S compounds (SO_4^{2-} and S^{2-}) exhibit a similar effect on the burnability and texture of clinker. However in the case of P compounds, the various ionic forms exhibit completely different influence. Concerning the burnability of raw mixtures, this effect is even reversed.
- According to the results of the elemental microanalysis in clinker, P, added as PO_4^{3-} or H_2PO^{4-}, is preferentially accumulated in belite and therefore affects its formation and stability. On the other hand, S (in both forms) and P (added as HPO_4^{2-}) are mainly dissolved in the melt.
- When the added elements are accumulated in belite, further stabilization of β-C_2S occurs and the binding of the free lime is hindered. When the added elements are dissolved in the melt, a positive effect on the burnability is observed, probably due to the alteration of the melt properties (viscosity and surface tension). In the first case, we observed the highest amount of bigger belite grains, as well as the highest levels of free lime. In the second case, the main texture characteristic is the big and rounded alite grains.
- The effect of variation in P may be attributed to the phase transformations of calcium phosphates upon heating. According to the literature, in the presence of calcium carbonate, $Ca(H_2PO_4)_2$, is transformed to $Ca_3(PO_4)_2$ at around 1000°C [15]. PO_4^{3-} levels greater than the solubility limit of P in C_3S phase (1.1% *w*/*w* P_2O_5) inhibit the crystallization process of pure C_3S and lead to a preferential formation of C_2S–P_2O_5 solid solutions and to a stabilization of C_2S polymorphs [7]. The above remarks probably explain the behavior of $Ca_3(PO_4)_2$ and $Ca(H_2PO_4)_2$. $CaHPO_4$, on the other hand, when heated, is transformed to $Ca_2P_2O_7$, which melts at 1280°C. At this temperature, the interstitial phase of clinker also melts and this explains why, in this case, P is mainly found in the interstitial phase ($Ca_3(PO_4)_2$ melts above 1600°C).

Conclusions

From the present study the following conclusions can be drawn:

- Despite their relatively low doping concentration in the raw mix, P and S affect considerably the reactivity of the raw mix and the texture of the clinker.
- The various ionic forms of the same element (SO_4^{2-}, S^{2-} for S, PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^{-}$ for P) exhibit a different and unequivocal effect on the reactivity of the synthetic raw mix and on the texture of the corresponding clinkers.
- S (in both forms) and P (added as HPO_4^{2-}) are mainly dissolved in the melt and they have a positive effect on the burnability of the raw mix.
- P (added as PO_4^{3-}or $H_2PO_4^{-}$) is preferentially accumulated in belite. In this case further stabilization of β-C_2S occurs and the binding of the free lime is hindered.

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