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The effect of foreign ions on the reactivity of the $CaO-SiO_2-Al_2O_3-Fe_2O_3$ system
Part I. Anions

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Abstract

The subject of this paper is the effect of foreign anions on the reactivity of the $CaO-SiO_2-Al_2O_3-Fe_2O_3$ system. One reference mixture and seven modified mixtures, prepared by mixing the reference sample with 1% w/w of chemical grade CaF_2, $CaHPO_4$, $Ca_3(PO_4)_2$, CaS, $CaCl_2$, $CaSiF_6$, or $CaSO_4$ were studied. The effect on the reactivity is evaluated on the basis of the free lime content (fCaO) in samples sintered at 1200°C and 1450°C. All the added compounds — except for the PO_4^{3-} are found to improve the reactivity of the quaternary system, even at 1200°C. According to their volatility at 1450°C, the added compounds can be subdivided in three groups of low (SO_4^{2-}, HPO_4^{2-}), moderate (PO_4^{3-}), and high volatility (S^{2-}, Cl^-). All samples have a final mineralogical composition, which corresponds to the structure of a typical clinker. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: $CaO-SiO_2-Al_2O_3-Fe_2O_3$; Mineralizers; Anions; fCaO; Volatility

1. Introduction

The $CaO-SiO_2-Al_2O_3-Fe_2O_3$ system is of great importance to cement chemistry, since more than 95% of the various Portland and aluminous cements are based on compounds containing Ca, Al, Si, and Fe oxides. Representation of this quaternary system exhibits certain difficulties, owing to its complexity and the unavoidable superimposition of phase fields [1].

The incorporation of foreign ions in the cement raw meal and their effect on the clinker formation and cement properties have been broadly discussed during the last years. Minor elements in clinker primarily come from the raw materials and fuel used in cement making, as well as the widely used auxiliary materials such as blast furnace slag, fly ash, silica sand, spent catalysts, and industrial by-products. Additional sources of minor components could be the refractories, chains, and grinding media such as liners and grinding balls [2].

According to the literature, the effect of minor components on clinker formation can be separated in terms of their ability to act as fluxes and/or mineralizers. Such components may lower the temperature of the first liquid phase formation and/or increase the amount of the melt (fluxes), accelerate the rate of the reactions occurring in the solid state, within the liquid phase, or at the liquid–solid interface (mineralizers), alter the viscosity and surface tension of the melt, and affect both crystal growth and morphology. The technological consequences are evident: changes in the reactivity and burnability of the raw materials, formation of new phases in altered amounts, differentiation of hydraulic activity and properties of produced cements, opportunities for energy conservation, and saving as well as alterations–precautions during clinker manufacture due to the high volatility of some compounds.

The literature on the effect of minor components on the reactivity of cement raw meal is of variable detail. Application of fluorine both as mineralizer and flux is widely known and has been reported in a number of studies. Fluorspar (CaF_2), added to cement raw mix, reduces the free lime content (fCaO) of clinkers prepared at temperatures between 1200°C and 1450°C, increases the formation

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of C_3S, improves burnability, and lowers clinkerization temperature by 50–100°C, depending on raw mix composition [3–5]. CaF_2 lowers the alite formation temperature by improving solid-state diffusion and reducing liquid phase viscosity and surface tension. The amount of fluorine in the raw mix has to be limited to less than 2.0% because it may have a negative effect on the cement properties [4,6]. Since fluoride is volatile, it is present in the gases and circulates in the kiln. In the cooler region of the kiln, condensation and reaction with excess CaO to form CaF_2, occurs.

Calcium and alkaline silicofluorides, are much more effective in stabilizing β-C_2S than the simple fluorine anion and they have been found to be effective mineralizers and fluxes [6–8].

Natural gypsum ($CaSO_4 \cdot 2H_2O$) was also used as mineralizer, alone or together with CaF_2. Generally the CaF_2 effect seems to be stronger than that of $CaSO_4$ [5]. In practice, sulfate addition to the raw mix is limited because of the restrictions concerning the SO_3 content in the cement and its volatility, which causes the formation of build-ups in the kiln and the preheaters. A procedure for predicting sulfate distribution in clinker has been developed and the data have been published in the literature [9]. An optimum addition of 6.0% $CaSO_4$ has been reported [10,11]. The mineralizer combination of CaF_2–$CaSO_4$ shows the most promising results with an estimation of 10.0% energy conservation compared with the traditional process [5,12].

Calcium chloride ($CaCl_2$) increases the alkali volatilization and accelerates the lime combination, resulting in increased clinker production [13]. The $CaCl_2$-containing melt has a good ability to readily dissolve oxides, particularly CaO. Besides, the addition of $CaCl_2$ reduces the fCaO content, acts as a mineralizer, and lowers the firing temperature by 50–100°C.

Calcium phosphate ($Ca_3(PO_4)_2$) is used in combination with $CaSO_4$ and CaF_2 especially in the production of aluminophosphate cements. Generally, it decreases the viscosity of the melt and modifies the crystalline structure [14].

Despite the extensive literature, it is difficult to draw any comparative results concerning the effect of foreign ions on the reactivity of cement raw meal, since a wide range of materials and techniques have been applied. In the present paper, the effect of selected anions on the reactivity of the $CaO{-}SiO_2{-}Al_2O_3{-}Fe_2O_3$ system is studied. The volatility of the added compounds and the modifications of the structure of the sintered samples are also discussed. Another part of this work concerning the relative effect of foreign cations will be published soon.

2. Experimental

One reference mixture, 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, was prepared. Quartz and aluminum oxide were ground to a particle size less than 90 μm and then they were intensively mixed with Fe_2O_3 and precipitated $CaCO_3$ in a laboratory swing mill for 1 h. Homogeneity was ascertained by measuring the loss of ignition (LOI) on three separate samples of the mixture. The results indicated that LOI values were very close to the estimated one (34.99%), certifying a good homogeneity of the raw mix. Table 1 shows the chemical and the mineral composition (according to Bogue) of the reference mixture after it was sintered at 1450°C.

Table 1
Chemical and mineral composition of the reference mixture after thermal treatment at 1450°C

Clinker chemical composition		Clinker mineral composition (according to Bogue)	
Oxide	wt.%	Mineralogical constituent	wt.%
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

Seven modified mixtures were prepared by mixing the reference sample with 1% w/w of chemical grade CaF_2, $CaHPO_4$, $Ca_3(PO_4)_2$, CaS, $CaCl_2$, $CaSiF_6$, or $CaSO_4$. When necessary, the added compounds were ground in order to have the same fineness with the reference sample. Calcium salts were used in order to avoid the effect of foreign cations on the reactivity of the mixture.

All the samples were pressed to form pellets, then sintered at 1200°C and 1450°C for 30 min in an electrical furnace and cooled rapidly in air. The sintered pellets were ground and analyzed by the ethylene glycol method in order to determine the free CaO content, [15]. The samples were, also, examined using a Siemens D-5000 X-ray diffractometer with nickel-filtered Cu $K\alpha_1$ radiation ($\lambda = 1.5405$ Å) for the identification of the mineralogical phases formed during sintering.

The content of the added components in the sintered samples was determined in order to evaluate the volatility of these compounds at high temperature. The determination of Cl, S, and P was made according to Volhard [16], ASTM D5453-93 and ISO 6598/1985 (quinoline phosphomolybdate gravimetric method), respectively. Prior to measurement, all the samples were dissolved according to Maczkowski method with the exception of the sample containing $CaCl_2$, which was dissolved in 65% HNO_3.

3. Results and discussion

Table 2 shows the fCaO in all samples after the thermal treatment at 1200°C and 1450°C. Fig. 1 presents the ratio of fCaO in modified samples to the fCaO content in reference sample in relation to the added compound. The effectiveness

Table 2
The fCaO of the samples after thermal treatment at 1200°C and 1450°C

Sample	fCaO (%)	
	1200°C	1450°C
Reference	47.24	2.03
Reference + 1% CaF_2	41.74	0.34
Reference + 1% $CaSiF_6$	36.86	0.45
Reference + 1% $CaCl_2$	20.82	1.86
Reference + 1% $Ca_3(PO_4)_2$	50.71	2.31
Reference + 1% $CaHPO_4$	33.77	0.37
Reference + 1% CaS	30.13	0.51
Reference + 1% $CaSO_4$	24.83	0.31

of the anions in the reduction of fCaO can be expressed in the following decreasing order.

$$1200°C: \ Cl^- > SO_4^{2-} > S^{2-} > HPO_4^{2-} > SiF_6^{2-} > F^- > PO_4^{3-}$$

$$1450°C: \ SO_4^{2-} > F^- > HPO_4^{2-} > SiF_6^{2-} > S^{2-} > Cl^- > PO_4^{3-}$$

Most of these compounds are expected to affect mainly the formation and the properties of the melt and therefore change the reactivity of the mixture at high temperatures. However, a remarkable effect is also observed at 1200°C. Preliminary measurements showed that some of the added compounds, especially those containing Cl^-, F^-, and SO_4^{2-}, affect the temperature and the kinetics of calcium carbonate decomposition but further investigation is required on this subject.

The action of foreign ions on the properties and the structure of the melt is complicated. Generally, it is believed that certain admixtures, when dissolved in the melt, can affect the acid–base equilibrium $[MeO_4]^{5-} \leftrightarrow [MeO_6]^{9-}$ of the amphoteric elements (Al^{3+} and Fe^{3+}) in the melt. The same authors argue that the displacement of this reaction to the left favors the formation of a network built from MeO_4^{5-} and silicon tetrahedra that leads to the increase of the melt viscosity, while $[MeO_6]^{9-}$ is more mobile and promotes the decrease of the viscosity. The surface tension of the melt may, also, be affected by ions having high surface activity, like SO_4^{2-} [17,18].

Sulfur compounds, especially $CaSO_4$, seem to be very effective mineralizers, though the opposite phenomenon was also reported [19]. The fCaO is reduced by 36–47% at 1200°C and 75–85% at 1450°C in samples containing CaS or $CaSO_4$. Since the greater effect is shown at the final stage of the sintering, it may be associated with the formation and the properties of the liquid phase. The formation of intermediate compounds containing S has been reported to increase the liquid amount and reduce its viscosity and surface tension and therefore promote the combination of free lime [5]. Sulfate ions were also found to affect the dynamic equilibrium between the different coordination forms of amphoteric Al and Fe oxides and favor the formation of FeO_6^{9-} and AlO_6^{9-}, which is generally related to the reduction of the melt viscosity [17].

The well-known mineralizing effect of CaF_2 is confirmed. Fluorine ions do not seem to have a remarkable effect at 1200°C, but they, drastically, reduce the free lime at high temperature. The fCaO content was reduced by 12–22% at 1200°C and 83–78% at 1450°C in samples containing CaF_2 and $CaSiF_6$, respectively. The increase in the rate of the solid state reactions, due to the easy diffusion of F^-, and the acceleration of the clinkering reactions, due to the lower viscosity of the melt, are the basic reasons that explain the above results.

In the case of CaS–$CaSO_4$ and CaF_2–$CaSiF_6$, the effect of the anion does not seem to be relevant to the kind of the compound, which is added. However, the effect of P is completely reversed in relation to the used compound. Thus, the addition of $Ca_3(PO_4)_2$ causes a negative effect on the reactivity of the mixture, while the addition of $CaHPO_4$ causes a positive one. This effect was also recorded in the past [20]. Additional measurements made in our laboratory,

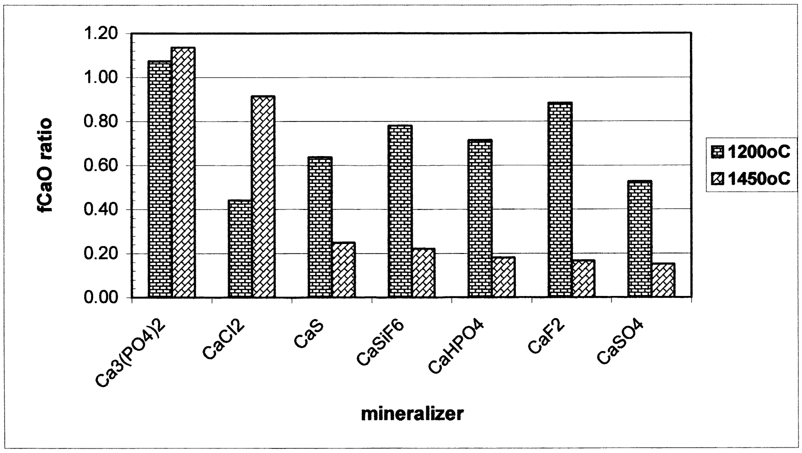

Fig. 1. Ratio of fCaO content in modified samples to fCaO content in reference sample in relation to the added compound.

Table 3
Volatility of doping anions at 1450°C

	Doping anion				
	Cl as $CaCl_2$	S as $CaSO_4$	S as CaS	P as $Ca_3(PO_4)_2$	P as $CaHPO_4$
Volatility (%)	30.96	6.17	27.13	16.77	10.19

show that the fCaO of the mixture is strongly related to the $PO_4{}^{3-}$ content and a negative effect is observed if the $PO_4{}^{3-}$ content exceeds 0.75% in the starting mixture. Besides, preliminary measurements showed that the effect of P varies depending on the ionic form of the added P compounds. This was not expected, since these forms are not stable at high temperature and the P content is approximately the same in all of them. Further investigation is needed on this subject.

The addition of $CaCl_2$ had an unexpected effect on the reactivity of the mixture. As it is shown in Table 2 and Fig. 1, the addition of $CaCl_2$ reduces by 50% the fCaO at 1200°C, but has only a marginal positive effect at 1450°C. The TGA measurements show that, in the presence of $CaCl_2$, the decomposition of calcium carbonate starts at much lower temperature (approximately 70°C lower than in the reference sample). XRD measurements show, also, some indications for the formation of Ca–Al–Cl–O solid solutions at 1200°C. Therefore, the increased rate of fCaO combination at 1200°C, can be attributed to the accelerated decomposition of calcium carbonate and the incorporation of CaO in new Cl-containing phases. This positive effect is diminished at 1450°C, probably because of the decomposition of these intermediate compounds and the liberation of CaO.

The XRD studies, conducted in clinkers that were burned at both 1200°C and 1450°C, showed that the diffraction patterns correspond to a structure of a typical clinker, obtained at the above temperatures. The dominant phases were well crystallized giving peaks at the common 2θ values. There are some indications concerning the formation of new phases with the contribution of the added anions, e.g., $Ca_{12}Al_{14}O_{32}Cl_2$ for the clinker with $CaCl_2$, $Ca_4Si_2O_7F_2$ in the clinker with $CaSiF_6$, or $Ca_{12}Al_{14}F_2O_{32}{-}Ca_{10}Si_3O_{15}F_2$ phases in the case of CaF_2. Further investigation is required in order to identify completely the new compounds that may be formed with the incorporation of the added ions and the temperature limits for the formation and decomposition of relative intermediate phases.

Table 3 presents the percentage of the element that has been volatilized during the thermal treatment. Based on these data, the anions can be subdivided into the three categories of low, moderate, and high volatility:

$$\begin{aligned}&\text{low volatility}: \ SO_4^{2-},\ HPO_4^{2-};\\ &\quad\text{moderate volatility}: \ PO_4^{3-};\\ &\quad\text{high volatility}: \ S^{2-},\ Cl^{-}.\end{aligned}$$

Our attempt to measure the F content in the sintered samples, using an ion selective electrode, gave erratic results. However, the detection of F-containing compounds in the samples (XRD) indicates that considerable amount of this element is still present in the samples after the sintering.

Chloride ion has a high volatility. In industrial practice, volatile chlorides react readily with alkalis so that the alkali level in the clinker is often reduced when chloride is present. In some cases, $CaCl_2$ is added in the kiln feed for accelerating both alkali volatilization and lime reaction [2,13,21,22].

$SO_4{}^{2-}$ and S^{2-} anions show a different behavior, as far as their volatility is concerned, a fact that is in relevance with the different form of each ion. Sulfates are quite stable compounds at high temperature. Sulfides and sulfur are oxidized and, although they are incorporated into the solid phases, some sulfur always escape as SO_2 and participates in the alkali cycle in the kiln [2,10,23,24].

Phosphorus, added as $HPO_4{}^{2-}$ and $PO_4{}^{3-}$, has low and moderate volatility, respectively. According to the literature, P-containing compounds show low volatility during the sintering [2,25].

It must be noted that the thermal treatment of the samples was performed as a batch operation in a laboratory electrical furnace. In industrial practice the volatile compounds participate in the so-called alkali cycle and their final content in the sintered sample may be significantly different.

4. Conclusions

From the present study the following conclusions can be drawn concerning the effect of selected anions on the reactivity of the $CaO{-}SiO_2{-}Al_2O_3{-}Fe_2O_3$ mixture:

- Compounds containing S or F improve the reactivity of the mixture and accelerate the CaO combination, especially during the final stage of the sintering. Cl-containing compounds improve the reactivity at 1200°C but have only a marginal positive effect at higher temperatures. P-containing compounds have a complicated effect, which needs further investigation.
- Based on their volatility at 1450°C, the added compounds can be subdivided in three groups of low ($SO_4{}^{2-}$, $HPO_4{}^{2-}$), moderate ($PO_4{}^{3-}$), and high volatility (S^{2-}, Cl^{-}).

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