



CCT diagrams of tricalcium silicate Part I. Influence of the Fe_2O_3 content

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Abstract

This work studies the effect of the iron oxide content on the kinetics of thermal decomposition of tricalcium silicate, or alite, the main component of Portland cement. The experiments allowed the construction of novel continuous cooling transformation (CCT) diagrams, showing the effect of the Fe content on the alite stability, under continuous cooling.

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1. Introduction

The clinker of Portland cement is produced from a mixture of limestone, clay and, if necessary, bauxite and iron ore. The properties of Portland cement are directly related to the concentrations of its major phases, i.e., alite, belite, the ferritic phase and the aluminate phase [1,2]. These phases are the result of the firing of the mixture, with high contents of CaCO_3 , SiO_2 , Fe_2O_3 and Al_2O_3 . The firing process reaches

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temperatures between 1450 and 1500 °C, followed by quenching to produce a clinker with high alite contents, which is milled with gypsum, to make the cement.

The properties of Portland cement are directly related to the concentrations of its major phases, i.e., alite, belite, the ferritic phase and the aluminate phase. Alite, with the composition $3\text{CaO}\cdot\text{SiO}_2$, known as C_3S , should be the major component of the clinker after processing, once its hydration produces the high yield strengths of cured cement. Belite, with the composition $2\text{CaO}\cdot\text{SiO}_2$, known as C_2S , is the first lime and silica complex, formed during the heating process. It presents higher stability at low temperatures than C_3S , so that it tends to be formed again during the cooling cycle, from the decomposition of alite into belite and free lime [1,2]. The aluminate phase appears mainly with the composition $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, known as C_3A , and the ferritic phase appears with the composition $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$, known as C_4AF [3,4]. These phases melt at the high temperatures of the firing process, forming a liquid phase that embeds the C_3S and C_2S grains. The ferrite and alumina contents affect the alite stability, and, consequently, the reactivity of the cement.

Upon heating, the raw meal undergoes free water evaporation, release of the clay water, calcination and, finally, clinkering, which occurs between 1300 and 1450 °C. Clinkering consists of the melting of the aluminate and ferrite phases, followed by the formation of belite crystals and their transformation into alite, in the presence of the molten phases. The transformation temperatures may be altered by the heating rates, once Altun [5] showed that higher heating rates enable clinkering at lower temperatures. During the cooling cycle, the liquid phase solidifies and part of the alite content decomposes into belite and free lime. Hong et al. [6] studied the effect of high cooling rates on the mineralogy of industrial clinker, however, there is no detailed work in the literature describing the influence of the cooling rates on the properties and composition of the clinker.

The weight of the clinker is composed by, approximately, 50–70% of C_3S , 15–30% of C_2S , 5–10% of C_3A and 5–15% of C_4AF [1–4]. During the heating process of a mixture of calcium carbonate and silica, for the formation of pure alite [7], the C_2S formation occurs between 1100 and 1200 °C, and C_3S formation begins at 1400 °C, continuing up to temperatures as high as 1500 °C. Temperatures in excess of 1500 °C are usually employed to obtain pure alite [7], because the reactions occur by solid state diffusion, leading to low reaction rates.

Tenório et al. [7] showed that up to 20% of the alite may be decomposed already after 30 min at 1000 °C, depending on the cooling rate. A much larger amount of alite may decompose during the cooling cycle from the firing temperature [7], than what is observed in the isothermal experiments made by Mohan and Glasser [8].

Due to the compositions of the limestone, clay and, eventually, bauxite, in the mixture, the industrial clinker contains many other elements [9,10], including Fe and Al, which form C_3A and C_4AF . The C_4AF phase appears between 1100 and 1250 °C, and the C_3A phase at around 1100 °C [1,2]. At temperatures close to 1300 °C, the C_3A and the C_4AF phases begin to melt, forming a liquid phase that embeds the C_2S crystals, enhancing the C_3S formation, once the reaction begins to occur with diffusion in the presence of liquid. The diffusion rate, hence the formation of alite, is related to the amount and viscosity of the liquid phase. Antón et al. [11] studied the liquid phase sintering of ceramic matrix composites, made from Portland cement, but the individual effects of each component on the clinkering reaction have not yet been investigated.

This paper studies the effects of Fe_2O_3 additions over the alite stability and presents novel continuous cooling transformation (CCT) diagrams for the alite decomposition in the presence of this compound.

2. Experimental procedure

Pure alite powder, produced according to procedures described in Tenório et al. [7], was doped with 0.5 and 0.8% Fe_2O_3 . After doping, the mixtures were homogenized for 1 h, to produce five sets of six pressed discs, 3 mm high and 15 mm in diameter, for each composition. Each set was thermal treated at 1450 °C, for 20 min, and cooled at the rates of 10, 8, 5, 3 and 1 °C/min. For each cooling rate, one disc was quenched in alcohol from the temperatures of 1200, 1120, 1040, 960, 880 and 800 °C.

The CaO content was determined by chemical analysis, through HCl (0.1 N) titration in neutralized glycol ethylene [7]. The weight percent of decomposed C_3S was calculated from the relation $\text{C}_3\text{S} \Rightarrow \text{CaO} + \text{C}_2\text{S}$. The extrapolation of these data generated CCT diagrams for the decomposition of doped alite upon cooling. The CCT diagrams of alite with Fe_2O_3 additions were compared to the results presented by Tenório et al. [7] for pure alite.

3. Results and discussion

Figs. 1 and 2 show the amount of alite decomposed during the cooling cycle, from 1450 °C, for the temperatures of 1200, 1120, 1040, 960, 880 and 800 °C, of the samples with 0.5 and 0.8 wt.% of Fe_2O_3 additions, for the cooling rates of 10, 8, 5, 3 and 1 °C/min. All the curves in Figs. 1 and 2 are practically parallel to each other, revealing that, below 1200 °C, the rate of decomposition is independent of the cooling rate.

For both additions of iron oxide, the decrease in the cooling rate from 10 to 1 °C/min resulted in an increase in the amount of decomposed alite of around 30%. Once the rates of decomposition are all the same below 1200 °C, this difference of 30% occurs above that temperature, which means that high cooling rates are only crucial at high temperatures, i.e., the first 250 °C of cooling from 1450 °C.

The comparison of the curves for 0.5 and 0.8% iron oxide additions shows that such increase in its content results in an increase of approximately 6 wt.% of alite decomposition. The mixture with 0.5 wt.% Fe_2O_3 shows a minimum amount of decomposition of 37%, at 1200 °C and a cooling rate of 10 °C/min,

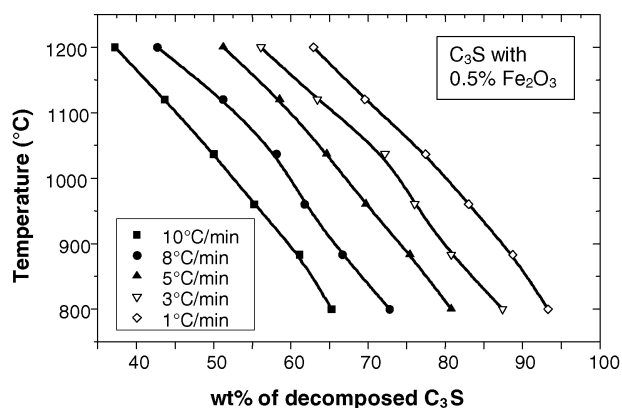


Fig. 1. Amount of decomposed alite, during cooling from 1450 °C, as a function of the cooling rate, for the alite samples doped with 0.5% Fe_2O_3 .

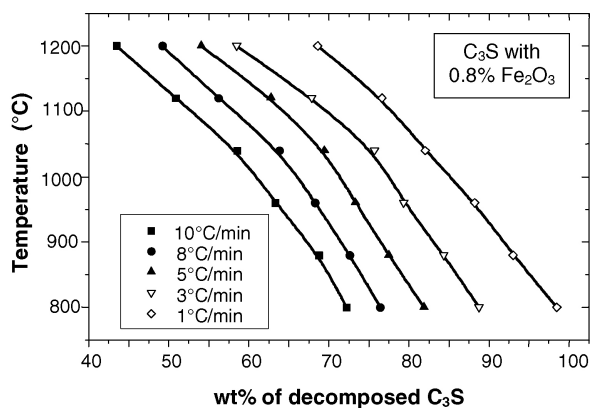


Fig. 2. Amount of decomposed alite, during cooling from 1450 °C, as a function of the cooling rate, for the alite samples doped with 0.8% Fe_2O_3 .

and a maximum decomposition of 94%, at 800 °C and a cooling rate of 1 °C/min. The mixture with 0.8 wt.% Fe_2O_3 shows a minimum amount of decomposition of 43%, at 1200 °C and a cooling rate of 10 °C/min, and a maximum decomposition of 98%, at 800 °C and a cooling rate of 1 °C/min.

The curves for the decomposition of pure alite, from Tenório et al. [7], present a minimum amount of decomposition of only 9%, at 1200 °C and a cooling rate of 6 °C/min, and a decomposition of 92%, at 880 °C and a cooling rate of 1 °C/min; for the cooling rate of 10 °C/min, the maximum alite decomposition observed by Tenório et al. [7] reached only 19% at 880 °C. This suggests that the addition of iron oxide is critical in raising the alite decomposition for high cooling rates, close to those used in the industrial practice, but does not show such strong effect for low cooling rates. This can be understood if the iron oxide is taken as a catalyst of the alite decomposition reaction; lower cooling rates provide higher amounts of thermal energy for the reaction and minimize the effect of the Fe_2O_3 added.

Figs. 3 and 4 show continuous cooling transformation diagrams, for alite with 0.5 and 0.8% Fe_2O_3 additions, built with data extrapolated from Figs. 1 and 2, showing the dissociation of pure alite in belite and free lime, upon cooling from 1450 °C. The CCT diagrams show curves for amounts of decomposed C_3S between 50 and 85%.

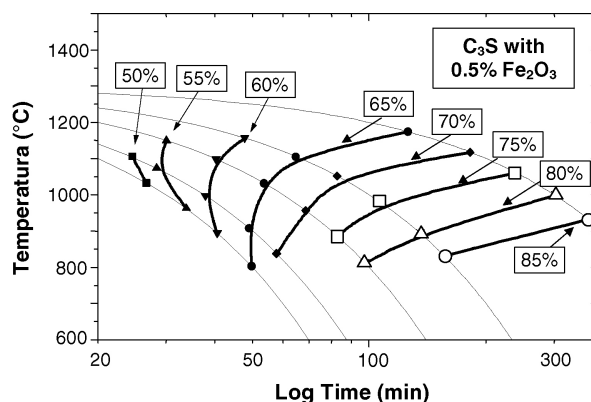


Fig. 3. CCT diagram for alite with 0.5% Fe_2O_3 added, cooled from 1450 °C, at the cooling rates of 10, 8, 5, 3 and 1 °C/min.

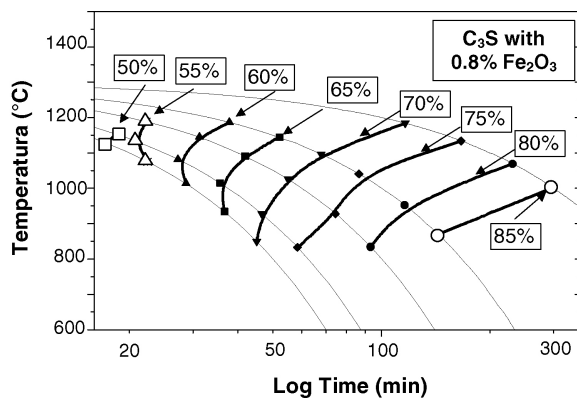


Fig. 4. CCT diagram for alite with 0.8% Fe₂O₃ added, cooled from 1450 °C, at the cooling rates of 10, 8, 5, 3 and 1 °C/min.

The CCT diagrams for alite decomposition with iron oxide additions show periods of time for the transformation considerably smaller than the value reported by Tenório et al. [7] for pure alite. The 50% alite decomposition curve occurs at approximately 100 min for pure alite [7], at 25 min for alite with 0.5% Fe₂O₃ and at around 15 min for alite with 0.8% Fe₂O₃. All times are considerably shorter than those observed by Mohan and Glasser [8], who built a time–temperature transformation (TTT) diagram with only 10% of decomposed alite at 1000 °C after 5 h. The CCT diagrams show that up to 80% of the alite may be decomposed after 100 minutes at 800 °C, if iron oxide is added.

The divergence in behavior between the TTT and curves CCT is a consequence of the fact that the TTT curves are built from isothermal experiments, whilst the CCT curves are built from continuous cooling experiments, and the high temperatures at the beginning of the process supply the decomposition with high amounts of thermal energy. When iron oxide is added to the alite, it catalyzes the nucleation of CaO and C₂S at the surface of the C₃S crystals, enhancing the decomposition kinetics.

Fig. 5 shows the amount of CaO produced by the decomposition of alite, at a cooling rate of 10 °C/min, for pure alite [3] and for alite with additions of 0.5 and 0.8% Fe₂O₃. The addition of 0.5% of Fe₂O₃ increases the amount of CaO produced by the decomposition of alite, at 800 °C, from 5.5 to 16%, a value that reaches 18%, for 0.8% Fe₂O₃. Therefore, the addition of 0.8% iron oxide increases in up to 50.8% the amount of C₃S decomposed, which leads to a 63% increase for each 1.0% iron oxide added.

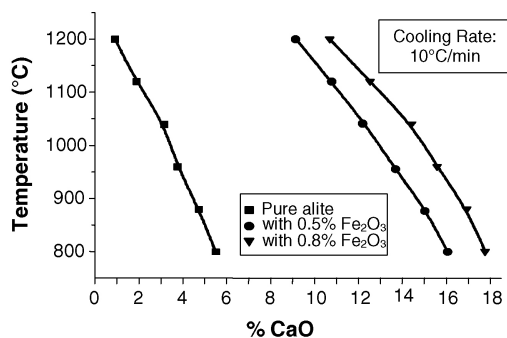


Fig. 5. Amount of CaO produced by the decomposition of alite, at a cooling rate of 10 °C/min, for pure alite and for alite with additions of 0.5 and 0.8% Fe₂O₃.

4. Conclusions

Novel continuous cooling transformation diagrams were built, for the tricalcium silicate system, showing the dissociation of alite, with additions of 0.5 and 0.8% iron oxide, into belite and free lime, upon cooling from 1450 °C. It was shown that, for iron oxide added alite, below 1200 °C, the rate of decomposition is independent of the cooling rate. For both additions of iron oxide, the decrease in the cooling rate from 10 to 1 °C/min resulted in an increase in the amount of decomposed alite of around 30%. The comparison of the curves for 0.5 and 0.8% iron oxide additions shows that such increase in its content results in an increase of approximately 6 wt.% of alite decomposition. The addition of iron oxide is critical in raising the alite decomposition for high cooling rates, close to those used in the industrial practice, but does not show such strong effect for low cooling rates. The CCT diagrams for alite decomposition with iron oxide additions show periods of time for the transformation considerably smaller than the value reported by Tenório et al. [7] for pure alite. When iron oxide is added to the alite, it catalyzes the nucleation of CaO and C₂S at the surface of the C₃S crystals, enhancing the decomposition kinetics. The addition of 0.8% iron oxide in pure alite increases in up to 48% the amount of C₃S decomposed.

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References

- [1] H.F.W. Taylor, Cement Chemistry, second ed. Academic Press, London, 1992.
- [2] F.M. Lea, The Chemistry of Cement and Concrete, third ed. Chemical Publishing Co., New York, 1970.
- [3] S. Gothenburg, 10th International Congress on the Chemistry of Cement, June 2–6 1997, 1997, pp. 287–294.
- [4] S. Gothenburg, 10th International Congress on the Chemistry of Cement, June 2–6 1997, 1997, pp. 569–580.
- [5] A. Altun, Cem. Concr. Res. 29 (4) (1999) 599–602.
- [6] H. Hong, Z. Fu, X. Min, Cem. Concr. Res. 31 (2) (2001) 287–290.
- [7] J.A.S. Tenório, S.S.R. Pereira, A.V. Ferreira, D.C.R. Espinosa, A.M. Barros, F.G.S. Araújo, REM—Revista Escola de Minas, vol. 57, 2003 (in Portuguese).
- [8] K. Mohan, F. Glasser, Cem. Concr. Res. 7 (1977) 1–8.
- [9] D. Stephan, R. Mallmann, D. Knofel, R. Hardtl, Cem. Concr. Res. 29 (1999) 1949–1957.
- [10] D. Stephan, R. Mallmann, D. Knofel, R. Hardtl, Cem. Concr. Res. 29 (1999) 1959–1967.
- [11] N. Antón, R. Gamboa, V. Amigó, J.M. Torralba, J. Eur. Ceram. Soc. 20 (12) (2000) 2215–2224.