CCT diagrams of tricalcium silicate
Part II: Influence of the Al$_2$O$_3$ content

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Abstract

This work studies the effect of the aluminum oxide content on the kinetics of thermal decomposition of tricalcium silicate, or C$_3$S, the main component of Portland cement. The experimental results allowed the construction of novel continuous cooling transformation (CCT) diagrams, showing the effect of the Al content on the C$_3$S stability, under continuous cooling.
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1. Introduction

The Portland cement is a hydraulic cement produced by pulverizing clinkers [1]. The Portland clinker, is composed of, approximately, 50–70% of tricalcium silicate (3CaO·SiO$_2$—known as C$_3$S), 15–30% of dicalcium silicate (2CaO·SiO$_2$—known as C$_2$S), 5–10% of tricalcium aluminate (3CaO·Al$_2$O$_3$—known as C$_3$A) and 5–15% of tetracalcium aluminoferrite (4CaO·Al$_2$O$_3$·Fe$_2$O$_3$—known as C$_4$AF) [2–4]. The industrial production of the clinker uses a mixture of limestone, clay and, if necessary, bauxite and iron ore, which is fired at temperatures around 1450 °C [2–4].

The hydration and curing properties of Portland cement, as well as its mechanical properties under service, strongly depend on its tricalcium silicate content [2–4]. C$_3$S is a metastable compound below 1250 °C, which decomposes into dicalcium silicate and free lime: 3CaO·SiO$_2$ → 2CaO·SiO$_2$ + CaO, upon cooling [2–4]. Its large amount in the clinker is obtained by the fast cooling rate of the material in the industrial process.

Tenório et al. [5] investigated the influence of the cooling rate on the C$_3$S decomposition, for pure C$_3$S samples heated at temperatures in excess of 1400 °C. That work showed that practically all of the C$_3$S is decomposed at 870 °C, for a cooling rate of 0.5 °C/min and that, for a cooling rate of 10.0 °C/min, less than 20% of the C$_3$S is decomposed at

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870 °C. These results showed that a larger amount of C_3S may decompose during the cooling cycle than what was observed in the isothermal experiments made by Mohan and Glasser [6].

In the clinker, C_3S presents a variety of impurities, at about of 3 or 4%, incorporated as solid solutions [2–4]. The major impurities are Mg, Fe and Al, which are natural constituents of the industrial raw materials. The C_3S impure form, present in the Portland clinker, is known as alite.

This paper studies the effects of Al_2O_3 additions over the C_3S stability and presents novel continuous cooling transformation (CCT) diagrams for the C_3S decomposition in the presence of this compound.

A previous paper [7] was devoted to the study of the effect of Fe_2O_3 content on the C_3S decomposition. C_3S samples with 0.5 and 0.8% of Fe_2O_3 additions were submitted to continuous cooling from 1450 °C, at different rates. For a cooling rate of 10 °C/min, it was shown that 0.5% of Fe_2O_3 addition increases the amount of CaO, produced by decomposition of C_3S, from 5.5% in a C_3S pure sample [5] to 16%, while 0.8% of Fe_2O_3 addition increases the CaO content to 18% [7]. For the smallest cooling rate studied, 1 °C/min, it was observed that the CaO content in samples reaches 23 and 24% for the 0.5 and 0.8% of Fe_2O_3 additions, respectively, while for a pure C_3S sample this content is around 22% [5].

2. Experimental procedure

Samples of pure C_3S were prepared according to the procedures described by Tenório et al. [5]. These procedures follow the method described by Odler and Dörr [8] where it is shown that the pure C_3S synthesis needs successive thermal cycles of a calcium carbonate and gel silica mixture.

The produced pure C_3S samples were powdered and doped with 0.8 and 2.0% of Al_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 (0.1N) titration in neutralized glycol ethylene [9]. The weight percent of decomposed C_3S was calculated from the relation $C_3S \Rightarrow CaO + C_2S$. The extrapolation of these data generated CCT diagrams for the decomposition of doped C_3S upon cooling. The CCT diagrams of alite with Al_2O_3 additions were compared to CCT curves for pure C_3S and for C_3S doped with iron.

3. Results and discussion

Figs. 1 and 2 show the amount of C_3S decomposed during the cooling cycle, from 1450 °C, for the temperatures of 1200, 1120, 1040, 960, 880 and 800 °C, of the samples with 0.8 and 2.0 wt% of Al_2O_3 additions (for the cooling rates of 10, 8, 5, 3 and 1 °C/min). The curves in Figs. 1 and 2 reveal that, below 960 °C, the rate of decomposition is independent of the cooling rate, because the lines are parallel. Between 1200 and 960 °C, higher cooling rates promote slower decomposition.
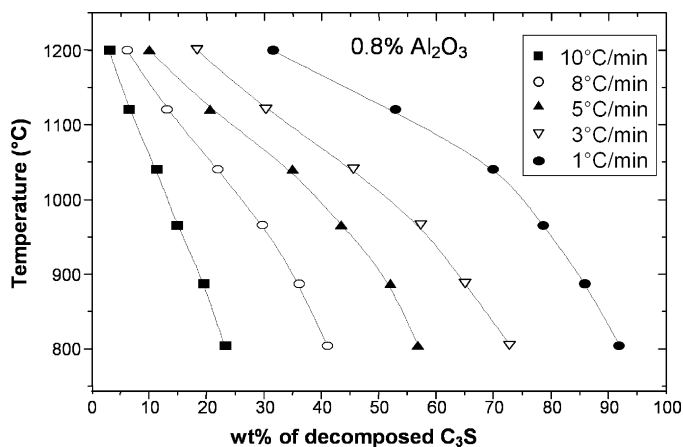

Fig. 1. Amount of decomposed C_3S, during cooling from 1450 °C, as a function of cooling rate, for C_3S samples doped with 0.8% Al_2O_3.
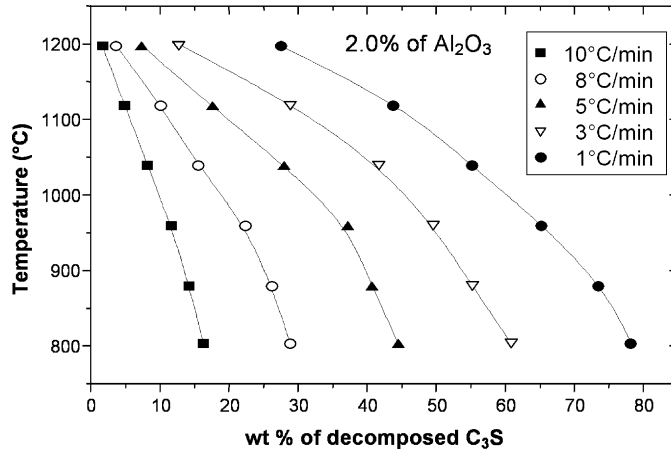
Fig. 2. Amount of decomposed C_3S, during cooling from 1450 °C, as a function of cooling rate, for C_3S samples doped with 2.0% Al_2O_3.

The decrease in the cooling rate from 10 to 1 °C/min resulted in a large increase in the amount of decomposed C_3S: from 23 to 92% in samples with 0.8% Al_2O_3 and from 16 to 78% in samples with 2.0% Al_2O_3. Once the rates of decomposition are all the same below 960 °C, this difference of more than 60% occurs above that temperature, which means that high cooling rates are crucial for temperatures above 1000 °C, for C_3S samples with the addition of aluminum oxide.

When compared to previous results [5,7], the addition of aluminum oxide shows an effect opposite to the addition of iron oxide, i.e., the addition of aluminum oxide decreases the C_3S decomposition while iron oxide increases it, for all the studied cooling rates. Fig. 3 shows this effect, for the cooling rate of 10 °C/min. The amount of CaO produced by the decomposition of pure C_3S at 800 °C is approximately 5.6% [5]; for an addition of 0.5% iron oxide, this value increases to around 16% and for an addition of 0.8% iron oxide, this value increases to around 18% [7]. On the other hand, for an addition of 0.8% aluminum oxide, the amount of CaO produced by the C_3S decomposition decreases to 5.2% and for an addition of 2.0% aluminum oxide, it decreases to 4.0%, as shown in Fig. 3. Aluminum oxide is an alite stabilizer, and its effect is opposite to the iron oxide effect, although less intense.

Figs. 4 and 5 show continuous cooling transformation diagrams, for alite with 0.8 and 2.0% Al_2O_3 additions, built with data extrapolated from Figs. 1 and 2, showing the dissociation of C_3S into C_2S and free lime, upon cooling from 1450 °C. The CCT diagrams show curves for amounts of decomposed C_3S between 10 and 70%.
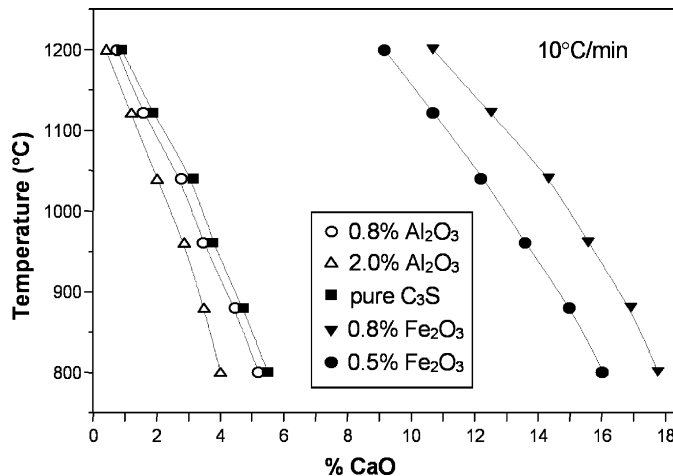

Fig. 3. Amount of CaO produced by the C_3S decomposition, at a 10 °C/min cooling rate, for pure C_3S and C_3S with additions of Al_2O_3 and Fe_2O_3.
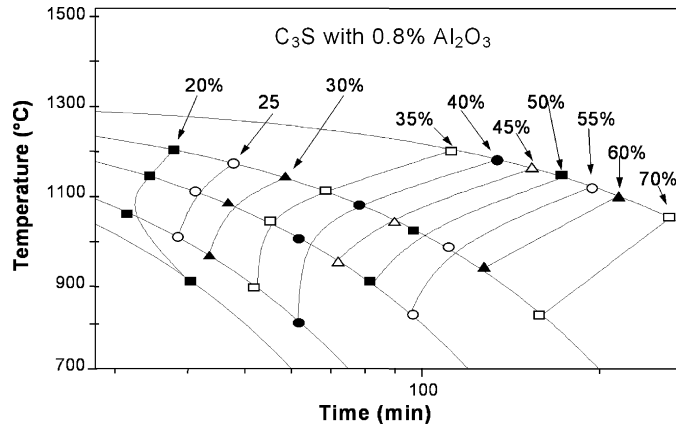
Fig. 4. CCT diagram for decomposition of C_3S doped with 0.8% Al_2O_3, cooled from 1450 °C at the cooling rates of 10, 8, 5, 3 and 1 °C/min.
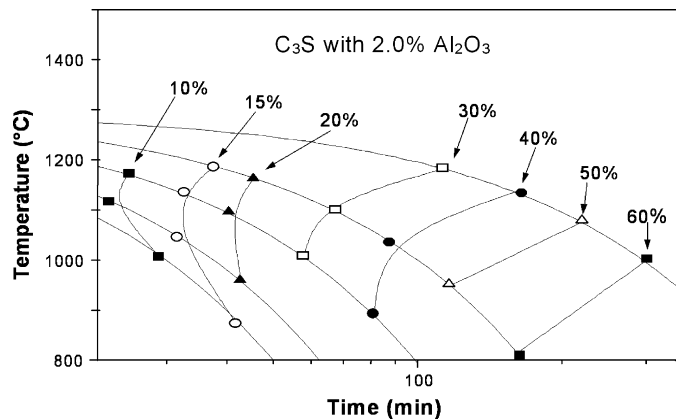

Fig. 5. CCT diagram for decomposition of C_3S doped with 2.0% Al_2O_3, cooled from 1450 °C at the cooling rates of 10, 8, 5, 3 and 1 °C/min.

The CCT diagrams for C_3S decomposition with aluminum oxide additions show periods of time for the transformation considerably larger than the value reported by Tenório et al. [7] for C_3S with iron additions, and also larger than the values observed for pure C_3S [5]. The 50% C_3S decomposition curve crosses the 1 °C/min cooling curve at approximately 100 min for pure C_3S [5], at around 20 min for C_3S with 0.8% Fe_2O_3 [7] and at 200 min for C_3S with 2.0% Al_2O_3.

All times are considerably shorter than those observed in the time–temperature-transformation (TTT) diagrams by Mohan and Glasser [6,10], with only 10% of decomposed pure C_3S at 1000 °C after 5 h. Such divergence in results is due to the fact that in this work the C_3S samples were fired at a temperature of 1450 °C, higher than the temperatures of the isothermal treatment of Mohan and Glasser, which supplied the decomposition with a larger amount of thermal energy.

4. Conclusions

Novel continuous cooling transformation diagrams were built, showing the dissociation of C_3S, with additions of aluminum oxide into C_2S and free lime, upon cooling from 1450 °C. It was observed that for C_3S with 0.8 and 2.0% added aluminum oxide, higher cooling rates promote slower decomposition, between 1200 and 960 °C. For both additions of aluminum oxide, the decrease in the cooling rate from 10 to 1 °C/min resulted in an increase in the amount of decomposed C_3S above 60%, twice as much as in the case of the addition of iron oxide, as measured by Tenório et al. [7]. The comparison of the curves for 0.8 and 2.0% aluminum oxide additions shows that such increase in its content

results in a decrease of approximately 1.2 wt% of C_3S decomposed. The CCT diagrams for C_3S decomposition with aluminum oxide additions show periods of time for the transformation larger than the value reported by Tenório et al. [5] for pure C_3S.

Acknowledgments

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