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Effect of the clinker composition on the threshold limits for Cu, Sn or Zn

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ABSTRACT

The threshold limit corresponds to the maximum amount of trace element that could be incorporated into clinker whilst reaching the limit of solid solution of its four major phases (C_3S, C_2S, C_3A and C_4AF). For Cu, Zn or Sn, these threshold limits in a standard clinker (65% C_3S, 18% C_2S, 8% C_3A and 8% C_4AF) were equal to 0.35, 0.7 and 1 wt.% respectively (Gineys et al., in press). This paper presents the effect of the clinker composition on these threshold limits. Laboratory made clinkers having different mineralogical compositions was characterised by XRD and SEM. Results showed that the threshold limits for Cu, Zn or Sn were consistent. The threshold limit for Sn was affected by the Bogue content in interstitial phases. On the other hand, the threshold limit for Zn was affected by the Bogue content in C_3S of clinker while that of Cu was unaffected by any modifications of clinker composition.

1. Introduction

In a previous study [1], the authors defined for a given clinker (65% C_3S, 18% C_2S, 8% C_3A and 8% C_4AF) the maximum content of trace elements (Cu, Sn or Zn) that could be incorporated into clinker while reaching the limit of solid solution of its main phases. For each trace element, the threshold limit is reached when the formation of a new compound and/or the decrease in content of one of the clinker phases is observed by X-ray diffraction (XRD).

These results revealed that the threshold limit for Sn was associated with the formation of a new compound identified as Ca_2SnO_4. The threshold limits for Cu and Zn were associated with a decrease in C_3S and C_3A contents, respectively. Indeed, Cu changed the crystallisation process and affected the formation of C_3S. Thus, a high content of Cu in clinker induced the decomposition of C_3S into C_2S and free lime. Zn, affected the formation of C_3A. A tremendous reduction of C_3A content due to the formation of $Ca_6Zn_3Al_4O_{15}$ was observed in clinker. The threshold limits for Cu, Zn and Sn in clinker were equal to 0.35, 0.7 and 1 wt.%, respectively. Finally, the results indicated that C_2S is less affected by the presence of these trace elements.

The reported threshold limits could be used by the cement industry to calculate the maximum amount of waste that could be valorised into the clinkering process as raw materials and/or alternative fuels. However, these values were obtained for a standard clinker composition and a generalisation of these results for different clinker compositions is required.

The subject of this paper was to investigate the effect of the clinker composition on these mono-elemental threshold limits. Thanks to previous results [1], it was possible to predict trends about the evolution of the threshold limits versus the clinker compositions. Thus, the threshold limit for Cu seems to be affected by the C_3S content of the clinker while the threshold limits for Zn and Sn could be affected by the interstitial phase content. Consequently, the study concerning the effect of the clinker composition on the threshold limits was conducted by testing two different parameters:

- the first one is the content in the interstitial phases (C_3A and C_4AF),
- and the second is the content of silicates and more particularly that of C_3S.

Here, we are presenting the results about the effect of the clinker composition on the threshold limits for Cu, Sn or Zn. Clinkers with different mineralogical compositions were synthesised in the laboratory and the influence of the threshold limits of each trace element was investigated by X-ray diffraction and scanning electron microscopy. The threshold limit was defined in the same way of Gineys et al. [1].

2. Materials and methods

The effects of the Bogue content in C_3S and interstitial phases on the threshold limits were studied individually. It means that, during the determination of the effect of the Bogue C_3S content on the threshold limit, the Bogue content in the interstitial phase is still constant (i.e. 8% C_3A and 8% C_4AF). Similarly, when studying the effect of the Bogue interstitial phase content on the threshold limits, the Bogue content in C_3S is kept constant (i.e. 65%).

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The effect of four different clinkers compositions on the threshold limits for Cu, Zn and Sn was investigated. Table 1 summarises the mineralogical composition (according to Bogue formula and Rietveld analysis) of the four clinker compositions obtained after sintering. The first clinker composition, noted as R, is the reference clinker (65% C_3S, 18% C_2S, 8% C_3A and 8% C_4AF) which served to determine the initial threshold limits [1]. The compositions T1 and T2 were established to test the effect of a decrease in the Bogue C_3S content on the threshold limits. They contain respectively 57.8 and 49.7% C_3S i.e. a decrease in the Bogue C_3S content of 7 and 15% points. The Bogue contents of interstitial phases were both fixed at 8% C_3A and 8% C_4AF. Finally, the clinker composition, noted as T3, was chosen in order to test the effect of a decrease in the Bogue content of interstitial phases on the threshold limits. It contains 65.2% C_3S, 26.6% $_2S$, 4% C_3A and 4% C_4AF i.e. a decrease in the Bogue interstitial phases by 50%.

The concentration range chosen is however still representative of the average mineralogical composition of a Portland cement clinker (Table 2).

2.1. Materials

Clinkers were prepared by mixing analytical grade reagents of $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3, MgO and K_2O. To prepare the doped clinkers, trace elements were introduced into the raw meal in the form of oxide (CuO, SnO_2 or ZnO). The raw mixes were homogenised and pressed at 5 kN into pellets (height = 23 mm, diameter = 40 mm) to obtain a more regular clinkering process. Pellets were placed in alumina crucible and fired up to 1450 °C at a rate of 10 °C/min. After 45 min of burning to the clinkering temperature, the clinker was slowly cooled in the furnace. The clinker was ground until to a Blaine specific surface area between 4500 and 5000 cm^2/g. In our experimental conditions, the atmosphere inside the furnace was oxidant.

A standard without trace elements was synthesised for each new clinker composition (T1, T2 and T3) in order to observe the effects of trace elements on the clinker phases and compare them with those previously observed for the reference clinker composition (R). Although, the clinker was slowly cooled in the furnace, no transformation of C_3S into C_2S and free lime was observed. Indeed small amounts of neighbour elements (Al, Fe and K) are incorporated into C_3S stabilised at lower temperature (Table 3).

2.2. Methods

The chemical composition of each doped clinkers after sintering was checked by X-ray fluorescence (Table 4) and corresponds to the bulk content of the doped clinkers. For clarity, all the doping concentrations were expressed as trace element weight percentage present in clinker.

The mineralogy of the clinkers was studied by the means of XRD. A Bruker D8 with Co Kα radiation (1.78 Å) was used. The X-ray patterns were acquired in the 2θ (5–100°) with a step of 0.019° and 3 s per step. The effects of trace elements on clinker phases were determined by using the height of the XRD peaks. The Rietveld quantification method was used to verify the mineralogical clinker compositions of the different standards. The analyses were conducted at the Research Center of Lafarge in Saint Quentin Fallavier.

The chemical composition of the clinker phases was investigated on polished sections with a Hitachi S-4300SE/N SEM operating in backscattered electron mode (20 keV) and equipped with a Thermo Scientific Ultradry EDS. To make the polished section, a piece of clinker was vacuum impregnated in epoxy resin and then polished with ethanol to avoid reaction with water. Finally the samples were carbon coated before observation.

Table 2
Average mineral composition (%w/w) for a clinker of Portland cement [2–4].

Clinker phase	C_3S	C_2S	C_3A	C_4AF
wt.%	50–70	15–35	5–12	5–12

3. Results and discussion

3.1. Effect of the clinker compositions on the threshold limits

3.1.1. Effect of the decrease in the C_3S content

In this part, all the results deal with the T1 and T2 clinker compositions. All the XRD patterns obtained for each doped clinker are summarised in Figs. 1, 2 and 3 (A, B and C).

The results, obtained for the clinkers doped with 0.35 wt.% Cu, (Fig. 1A, B, C) revealed that there is no decrease in its actual C_3S content and no formation of free lime. The threshold limit for Cu is therefore not affected by a decrease in the Bogue content of C_3S in clinker.

The XRD patterns, obtained for the clinkers doped with 0.7 wt.% Zn, (Fig. 2A, B, C) showed a decrease in its actual C_3A content. In addition, $Ca_6Zn_3Al_4O_{15}$ was identified in T2 doped clinker. It must be noted that γ-C_2S was also detected in both XRD patterns. A decrease in the Bogue C_3S content in clinker affected therefore the threshold limit for Zn and induced a decrease in its value. The presence of γ-C_2S in cement could have negative consequences particularly in lowering long-term strength as the γ-C_2S is relatively inert.

Table 1
Mineral composition (%w/w) of the different compositions of clinker tested (R = reference clinker, T1, T2 and T3 = new clinker compositions) determined according to Bogue formula and Rietveld analysis.

	R [1]		T1		T2		T3	
	Bogue	Rietveld	Bogue	Rietveld	Bogue	Rietveld	Bogue	Rietveld
C_3S	65	67.1	57.8	60	49.7	52.8	65	65.8
C_2S	18	17.9	25.2	24	33.4	31.4	26.6	27.0
C_3A	8	8.2	8	9.8	8	9.6	4	4.9
C_4AF	8	6.2	8	5.8	8	5.7	4	2

Table 3
Mineral composition (%w/w) of the phases of the reference clinker (R) measured by EDS.

	O	Mg	Al	Si	K	Ca	Fe
C_3S	28.55	0.44	0.72	11.84	0.1	57.35	0.93
C_2S	30.70	0.20	0.64	15.06	0.48	51.94	0.82
C_3A	30.55	0.29	8.53	6.50	0.45	50.66	2.84
C_4AF	27.66	0.59	8.71	4.43	0.08	43.68	14.66