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Incorporation of trace elements in Portland cement clinker: Thresholds limits for Cu, Ni, Sn or Zn

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ABSTRACT

This paper aims at defining precisely, the threshold limits for several trace elements (Cu, Ni, Sn or Zn) which correspond to the maximum amount that could be incorporated into a standard clinker whilst reaching the limit of solid solution of its four major phases (C_3S, C_2S, C_3A and C_4AF). These threshold limits were investigated through laboratory synthesised clinkers that were mainly studied by X-ray Diffraction and Scanning Electron Microscopy. The reference clinker was close to a typical Portland clinker (65% C_3S, 18% C_2S, 8% C_3A and 8% C_4AF). The threshold limits for Cu, Ni, Zn and Sn are quite high with respect to the current contents in clinker and were respectively equal to 0.35, 0.5, 0.7 and 1 wt.%. It appeared that beyond the defined threshold limits, trace elements had different behaviours. Ni was associated with Mg as a magnesium nickel oxide ($MgNiO_2$) and Sn reacted with lime to form a calcium stannate (Ca_2SnO_4). Cu changed the crystallisation process and affected therefore the formation of C_3S. Indeed a high content of Cu in clinker led to the decomposition of C_3S into C_2S and of free lime. Zn, in turn, affected the formation of C_3A. $Ca_6Zn_3Al_4O_{15}$ was formed whilst a tremendous reduction of C_3A content was identified. The reactivity of cements made with the clinkers at the threshold limits was followed by calorimetry and compressive strength measurements on cement paste. The results revealed that the doped cements were at least as reactive as the reference cement.

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1. Introduction

In recent years, sustainable development and natural resources preservation have become global issues. The cement industry, which is known to consume a large quantity of raw material and energy, has integrated these issues to its development policy by promoting industrial wastes as raw materials and fuels in replacement for traditional materials used during the manufacturing process. The sources of alternative raw material are varied and provide the necessary ingredients for the raw mix (Ca, Si, Al and Fe). Blast furnace slag, fly ash, iron ores, mill scale, foundry sand, for example, can be used as alternative raw materials [1,2]. In addition, many plants use alternative fuels like scrap tyres, plastics, waste oils as substitutes for coal and petroleum coke [1,2]. However these wastes contain trace elements that could be incorporated into the cement phases during the clinkering process and could affect the technical and environmental properties of cement. Currently, the content of trace elements in Ordinary Portland Cement (OPC) is quite low (Table 1). Consequently, no effect on technical and environmental cement properties has been observed.

Although, the reuse of materials in cement manufacturing is currently considered as beneficial, cautions must be taken. Indeed, during the last decade, wastes valorisation has become a common practice in cement industry and the trace elements content in cement has increased [2].

Many studies have been conducted on the effect of trace elements in cement [3–12]. A literature review, detailed later in Section 2, shows that the data are still incomplete and often contradictory. A very important data, referred here as threshold limit, is still missing for numerous trace elements.

Before defining in more details the concept of threshold limit, it is necessary to recall some general notions of thermodynamics about the incorporation of trace elements into the clinker phases.

As described by Herfort et al. [13], the mechanism of action of the trace elements can be divided in two main steps depending on the amount of these elements.

- At low concentration, trace elements enter into the structure of the initial phases of the clinker (C_3S, C_2S, C_3A and C_4AF) and form different phase assemblages of solid solutions (C_3Sss, C_2Sss, C_3Ass, C_4AFss). At this step, no new phases are detected and the free energy (ΔG_{mix}) of these phase assemblages is lower than the combined free energy of the initial phases and the trace elements. The free energy of each phase could be defined as $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix.}$ ΔH_{mix} corresponds to the enthalpy of mixing and is due to

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Table 1
Average content in trace element in current Portland cement. [2].

Trace element	Average concentration in OPC, wt.%
As	0.0008
Cr	0.0068
Cu	0.0038
Ni	0.0045
Pb	0.0027
Sn	0.0003
V	0.0074
Zn	0.0164

the distortion of the crystal lattice. ΔS_{mix}, in turn, corresponds to the entropy of mixing and is responsible to the decrease in free energy. It should be noted that the effect on ΔH_{mix} and ΔS_{mix} can't be separated.

- When the content in trace elements increases, the presence of new phases is detected (by XRD for example). New phase assemblages must be considered compared to the original one. For example:

$$C_3Sss, C_2Sss, C_3Ass, C_4AFss \text{ and a X phase.}$$

Consequently, the threshold limit can be defined as the point between these two mechanisms and corresponds to the limit of solid solution of the clinker phases.

The determination of the threshold limit can be investigated by two different ways:

- The first one is to wait for a cement manufacturer's problem induced by trace elements and then investigate the threshold limit. Indeed, the use of animal meal as alternative fuel in cement manufacture induced in the past a decomposition of C_3S into C_2S and free lime. Following this problem, Girod-Labianca et al. [14] studied the effect of phosphorous on the main clinker phase and defined a threshold limit for P_2O_5 on clinker. It corresponds to the maximum amount of P_2O_5 that could be incorporated into clinker before the detection of α' C_2S. It is equal to 0.5 wt.%.
- The second way is to investigate the threshold limit for trace elements in order to prevent cement quality problems. The present work fits into this approach.

To prevent the same problems as those encountered for phosphorous, we choose to investigate the concept of threshold limits for four trace elements i.e. Cu, Ni, Sn or Zn that could possibly have deleterious effects if their content continues to increase in cement.

Firstly, we determined for a standard laboratory-made clinker the threshold limit of these four trace elements incorporated at different levels in the same specific clinker of a Portland cement and secondly the reactivity of cements made with the clinkers at the threshold limits. The effect of the trace elements on the clinker phases was investigated by X-ray Diffraction (XRD) and by Scanning Electron Microscopy (SEM). The reactivity of the doped cement paste was followed by isothermal calorimetry and also by the measurements of the compressive strength.

2. Literature review

The four trace elements studied in this paper, were chosen by virtue of their frequent presence in raw materials and fuels. As mentioned previously in the Introduction, a large number of studies have been conducted on the effect of trace elements in cement. Three main research topics were investigated:

- the effect on the stability and the reactivity of pure clinker phases [3–5],
- the effect on clinker particularly on the incorporation rate, the burnability and the sintering process and the mineralogy of the clinker phases [6–9],
- the immobilisation of trace elements in cementitious materials [10–12].

Here, a literature review focused on Cu, Ni, Zn and Sn is presented.

Cu can be found in large quantities in dust, galvanic sludge, iron industry wastes, iron ore and fly ash [2,15]. Although their melting points are respectively equal to 1326 and 1235 °C, CuO and Cu_2O are largely incorporated into the clinker phases [15]. In cement clinkering, CuO is known to act as mineraliser [16,17] because it decreases the melt temperature considerably (at least by 50 °C) and favours the combination of free lime. In clinker phases, Hornain [6] showed that Cu is mainly concentrated in the ferrite phase followed by alite, aluminate phase and belite. Moreover, for high intakes of Cu in clinker, several studies revealed the presence of a new phase rich in Cu and containing CaO [18,19]. The incorporation of Cu into the clinker seemed to have different effects on the grindability. For example, Tsivilis et al. [20] showed that an addition of 2 wt.% Cu had little effect on the grindability whereas Bhatty [9] showed that only 0.25 wt.% Cu decreased the grindability of the clinker. The effect of Cu on cement hydration was also studied [8,9,21]. The results indicated that Cu delayed the hydration particularly during the first days and affected in consequence the early compressive strength which decreased. After 28 days of hydration, the compressive strengths were slightly lower but the difference observed was less important than that observed for the early ages.

Finally, soluble salts of copper were known to delay cement hydration [22–25] and thus to decrease the early compressive strength. Kakali et al. [21] explained this delay in cement hydration by the formation of $Cu(OH)_2$ which covers the calcium silicates during the early ages.

Ni, like Cu, comes from wastes generated by iron industry, iron ore and fly ash [2,16]. In the kiln, Ni is quite non-volatile [15]. Ni is preferentially concentrated in ferrite phase, followed by alite, aluminate phase and belite [6]. For clinkers containing Mg, Ni is mainly incorporated into periclase [10]. Reports on the effect of Ni on the grindability of the clinker are conflicting. Bhatty [9] showed that 0.5 wt.% Ni introduced into clinker decreased the grindability. In contrast, Tsivilis et al. [20] indicated that 2 wt.% Ni did not affect the grindability of clinker. During the hydration, Ni seemed to have little effect on cement hydration and did not modify the compressive strength [9,30]. Stephan et al. [30] showed that even 2.5 wt.% Ni did not affect the cement hydration and its mechanical properties.

Soluble salts of nickel had different effects on cement hydration. For example, Miller [22] showed that soluble salts of Ni could act as accelerators and give high early strengths. Recently Gineys et al. [25] showed that Ni added as nitrate salt had little effect on cement hydration.

Zn can be found in a variety of sources. Secondary fuels like tyres, rubber and metallurgical slags contain a large part of Zn [2]. ZnO is easily incorporated into clinker [26]. In cement clinkering, Zn improves the formation of clinker by decreasing the clinkering temperature and favours the combination of free lime between 1000 and 1100 °C. The distribution of zinc into clinker phases is very contradictory. Knöefel [26], for example, showed that zinc is half concentrated into silicates and the remaining half into ferrite phase. In contrast, Hornain [6] showed that Zn was preferentially present in ferrite followed by alite, aluminate phase and belite. This result was in accordance with the studies of Bolio Arcéo et al. [27] and Barbarulo et al. [28]. In addition, they showed that a new phase, identified as $Ca_6Zn_3Al_4O_{15}$, was present when high intakes of Zn (>1 wt.%) were incorporated into clinkers. Boikova [29] showed that increasing additions of Zn modify the symmetry of C_3S from triclinic to rhombohedral. The incorporation of Zn into the clinker seems to have different effect on the grindability. For example, Bhatty [9] showed that 0.5% Zn had little effect on the grindability of the clinker whereas Tsivilis et al. [20] reported that an addition of 2 wt.% Zn

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