PHOSPHORUS EFFECT ON PHYSICAL AND MECHANICAL PROPERTIES: RELATION BETWEEN CLINKER MICROSTRUCTURE AND HYDRATION.

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ABSTRACT

Due to European cement industry efforts to reduce its energy consumption, cement plants commonly use alternative fuels in rotary kilns. The clinker burning process has proved to be safe and effective to valorize such alternative materials.

In that way, various types of waste are valorized as used tires, waste oils, oiled water, impregnated saw dust or animal meal. This last type of waste, widely used in cement industry since the ban on animal meal in 2001 all over Europe, is well known to bring supplementary phosphorous bearing compounds clinker minerals.

Two industrial clinker nodules containing 0.14 and 0.70 wt.% of P_2O_5 are compared before and after being hydrated in mortar samples cured in standard conditions (20°C, 65% RH) and in heat-cured conditions (60°C, 90% RH). Clinkers mineralogy are characterized with XRD, SEM, EPMA and TEM analysis. Hydrated mortar pastes are characterized with standard mechanical tests, SEM and TGA-MS analysis.

This coupled approach between microstructure of P_2O_5 distribution and hydration chemistry is discussed to propose a possible mechanism that explains mechanical and physical properties modifications observed between the samples.

1. INTRODUCTION

Quality control is a preoccupation of primary importance for cement producers. In that way European EN 197-1 standard , which classifies Portland cement in five classes (CEM I, CEM II, CEM III, CEM IV and CEM V) and defines required chemical and physical properties for cements and issued mortars, is the core of cement production quality system.

In parallel, ISO 14001 environmental management standard helps cement plants to control all parameters of the process that can negatively affect the environment. In particular, it allows using alternative fuels in the burning process in a totally safe and reliable

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way, starting from initial by-products characterization to atmospheric releases control (including kiln dusts, greenhouse gas emissions, dioxin, NO_x, and SO_2). Thus, nature and content of trace elements coming from the burning process are now more variable and need to be continuously monitored and analyzed to identify potential effects on cement properties.

Since 2000s, practical experience of cement industry in valorizing this new alternative fuel agrees that a content of 1 wt. % P_2O_5 in clinker is a maximum value under which clinker mineralogy and cement properties are not affected. Exceeding 1 wt.% P_2O_5, phosphate can enter and modify high temperature clinker reactions, reduce alite content and lead to C_2S-C_3P solid solution mineral reliance on β C2S normal mineral [1]. However, P_2O_5 contents of industrial cements can induce a sl ight retardation of cement setting [2] possibly due to chemical adsorption of phosphate ions onto anhydrous cement grains surfaces that can limit growth units and nucleation of CSH [3,4]. On the other hand, mechanical standard quality control tests do not exhibit strength development modifications. Taking this experience into account, we sampled two set of clinker nodules from daily production issued with different P_2O_5 contents. They are refereed as CK1 (low P_2O_5 content) and CK2 (high P_2O_5 content).

2. EXPERIMENTAL

2.1 Materials

The Portland clinker nodules samples used in this study were taken just after reciprocating grate clinker cooler in a Ciments Calcia Italcementi Group plant (France). Samples were ground to 80 μm for X-Ray Fluorescence (using PANalytical MagiX instrument) and to 40μm for quantitative Rietveld X-Ray powder Diffraction analysis (using PANaytical X'Pert instrument) . Obtained chemical and mineralogical data are given in (Table 1).

	CK1 sample (wt. %)	CK2 sample (wt. %)
XRF Analysis		
CaO	65.0	65.2
SiO_2	21.2	20.7
Al_2O_3	5.54	5.46
Fe_2O_3	3.16	2.82
P_2O_5	0.14	0.70
XRD analysis		
C_3S	58	59
C_2S	20	20
C_3A	3	3
C_4AF	15	14
Gypsum	3	3
Calcite	1	1

Table 1: Samples CK1 and CK2 chemical and mineralogical analysis.

2.2 Test methods

Experimental methods used for characterization of clinkers are respectively: SEM (Cambridge Stereoscan 360), EPMA (Cameca SX 100) and TEM (Phillips/Edax CM20/X-EDS equipped with Gatan camera). This set of methods allows identification of the different constituents at different scale (structure, texture and chemistry of the different mineralogical phases for qualitative but also for quantitative analysis). After mechanical testing, hydrated mortar pastes were characterized with TGA-MS (Netzsch QMS 403 C) and SEM (Cambridge Stereoscan 360).

2.3 Sample preparation

The sample preparation of clinkers nodules (CK1 & CK2) depends on the analytical methods used, but in term of comparative study, all the preparations have been performed using one sample of each. For TEM analysis the samples have been prepared in 2 ways: dry grinding, using a boron carbide mortar, to obtain a powder of $\varnothing <$ 10 µm and ultramicrotomy. Polished sections have been realized for SEM & EPMA analyses.

One kilogram of laboratory cement from each clinker nodules was manufactured with a closed circuit laboratory mill. The granulometry control of cements shows a refusal on the 40 µm sieve of 14.9% for CK1 laboratory cement and of 15.7% for CK2 one. Refusals on the 80µm sieve were of 1.5 and 1.2% for CK1 and CK2 cement respectively. Blaine specific surface area was of 3970 cm^2/g for each.

Hydrated samples were ground to 40 µm and analyzed through TGA-MS directly after mechanical testing thus avoiding using a time-consuming methanol methodology for stopping hydration of remaining anhydrous cement. SEM analysis were performed on carbon coated polished cross-sections of hydrated mortars.
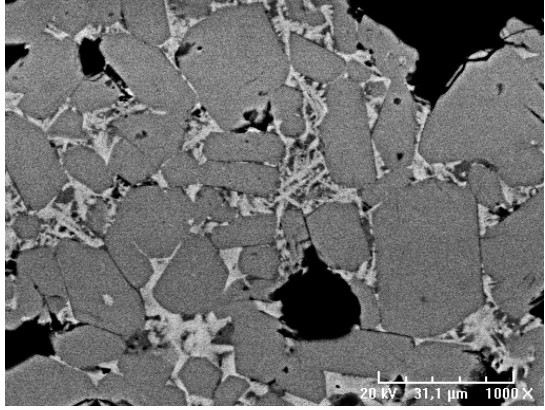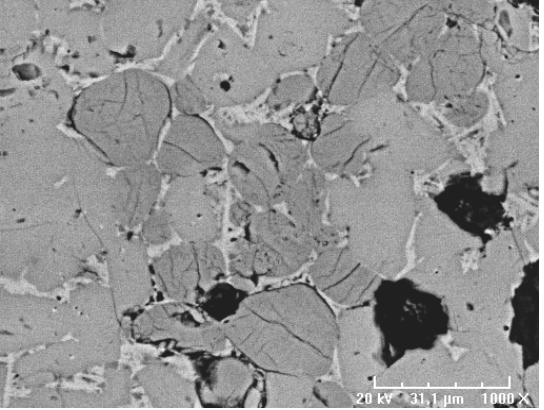

3. RESULTS AND DISCUSSION

3.1. Clinker microstructure characterization

XRF and XRD analysis of clinker nodules CK1 and CK2 show that mineralogy and chemical composition of clinkers are similar (see table 1). Nevertheless, P_2O_5 content is the main variable parameter between the two clinkers. CK2 rich P_2O_5 c linker (0.70 wt. % P_2O_5) corresponds to animal meal combustion process in the process and without animal meal combustion for CK1 sample (0.14 wt. %).

SEM and EPMA analyses (see tables 2,3) allow to detailed P_2O_5 distribution over clinker phases (analyses based on 10 shots onto 10 different crystal grains) ranging 0.1 to 1 (low-high at. %) in average. The EPMA results suggest that the phosphorus is preferentially distributed into the belite with a gradient from the surface to the core, confirmed by extensive analysis [5].

On Figure 1, the different modes (Bright Field with X-EDS analysis, High Resolution with Fourrier Function Transform analysis) have been applied on nanometric crystals (black arrow). The X-EDS spectrum revealed the existence of a very few amount of P trapped into the C_3S nanocrystal. The HR image revealed the existence of atomic plane (large white circle) which has been measured by FFT at 0.324nm (small white arrows indicates the two diffracted spots corresponding to the fringes obtained in HR image. This distance belongs to the (312) atomic plane of C_3S. More measurements done onto several crystals of C_2S or C_3S exhibiting some P content never revealed any structural distortions of their atomic planes but some amorphous layer around the crystals. Consequently the TEM data show that the P_2O_5 is not under a new mineralogical phase but must be distributed around the C_2S in majority, sometimes into C_3S, without any structural modifications.

CK 1 (low P_2O_5 content)	CK 2 (high P_2O_5 content)
SEM image (BSE mode)	SEM image (BSE mode)

| SEM image (SE mode) | SEM image (SE mode) |
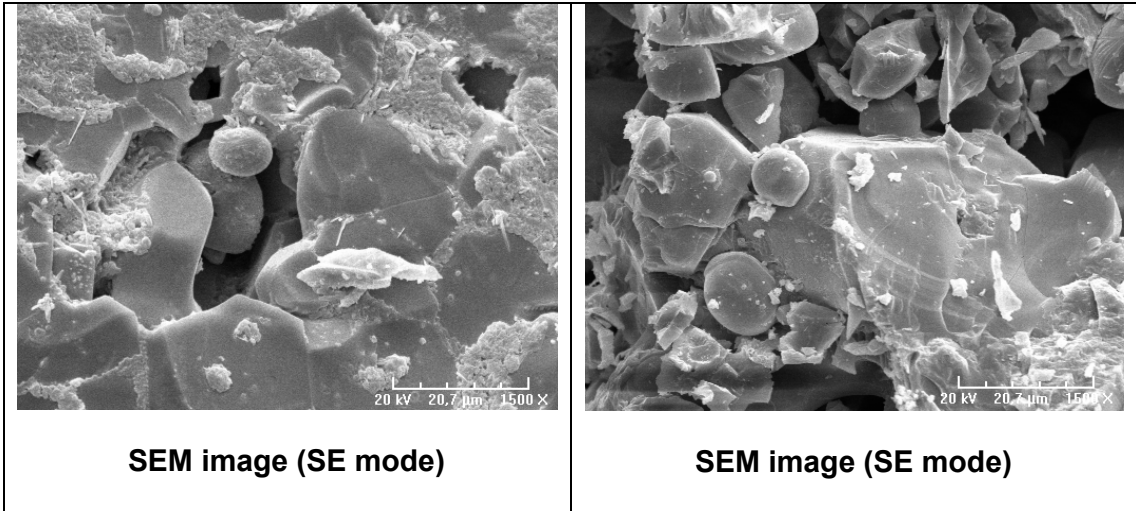
Table 2: SEM results of CK1 and CK2 clinker nodules.

| EPMA image (BSE mode) | Aluminum cartography |

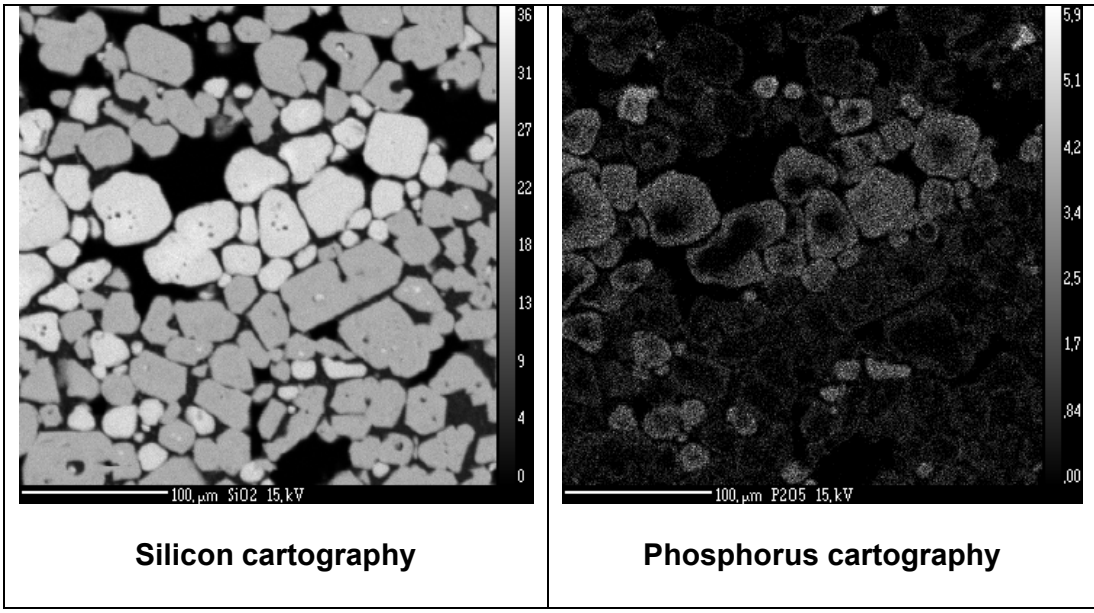| Silicon cartography | Phosphorus cartography |
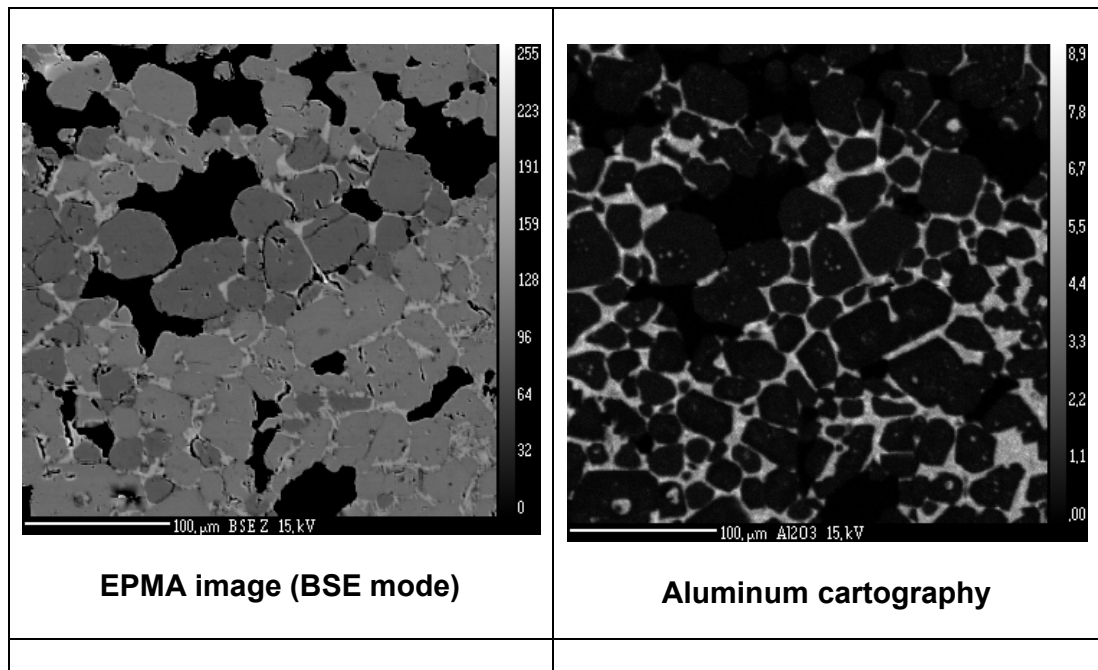
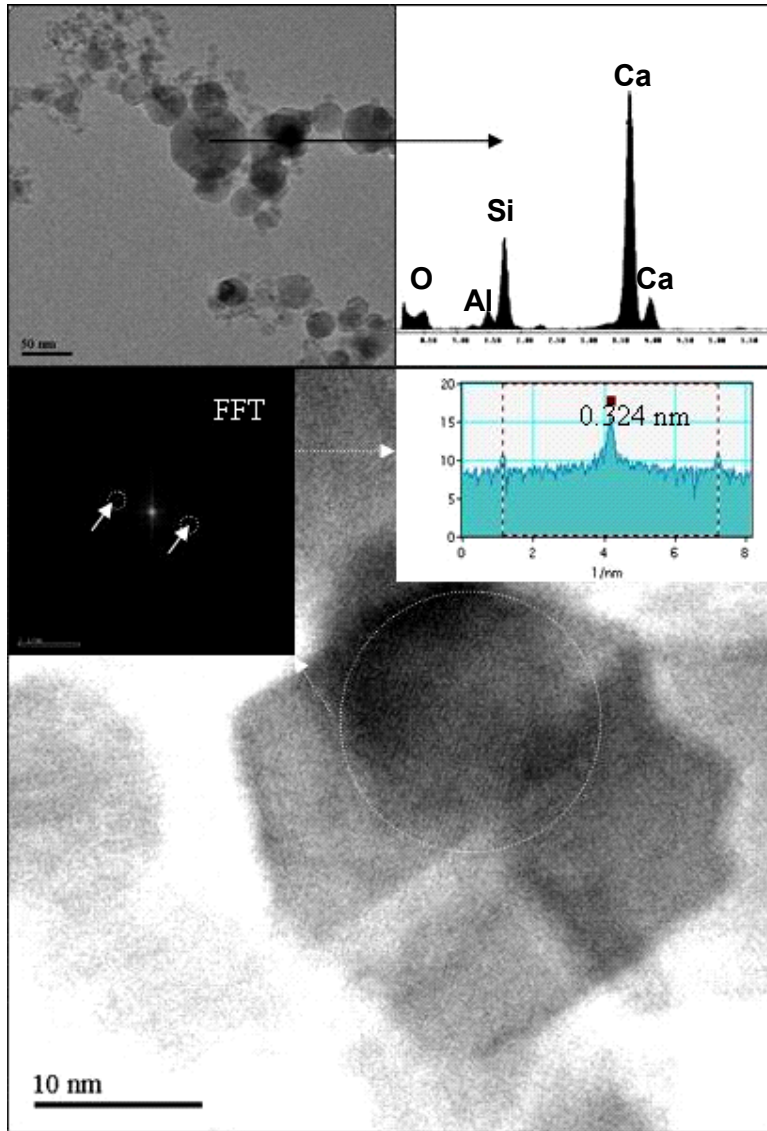Table 3: EPMA results of CK2 clinker nodules.

Figure 1: TEM images of CK2 clinker nodules using BF mode, RTF and X-EDS analysis

3.2. Mortars physical and chemical characterization

Mechanical strength tests:

Laboratory CK1 and CK2 cements were mixed in mortar pastes using CEN Standard sand and water primarily to the requirements of EN 196-1 standard. Each batch consists of 450 ± 2 g of cement, 1350 ± 5 g of sand and 225 ± 1 g of water (i.e. water/cement ratio 0.50). After mixing, mortars are disposed in the three-gang prism mould to prepare 40 x 40 x 160 mm mortar prisms. Two moulds were prepared for each clinker. One of the two was cured according standard EN 196-1 standard curing conditions (20°C and RH>90% for first 24 hours of

specimens in the mould; then 20°C in water for 27 days for three prisms before compressive strength determinations).

The other three-gang prism mould was heat-cured in curing cabinet for 5 hours at 60°C and 90% RH. Prior to this heat-curing cycle, mould was put at 20°C and 65% RH for 30 minutes. A cooling period of 30 minutes in same conditions was also adopted at the end of the heat-curing cycle. Such curing conditions are representative of rapid cycles used in precast concrete industry.

Flexural strength (mean value of three measurements) and compressive strength (mean value of six measurements) obtained for CK1 and CK2 mortars in these two different conditions of curing are given in table 4.

	CK1 mortar (low P_2O_5 content)	CK2 mortar (high P_2O_5 content)
28 days, 20°C Flexural Strength	8.1 MPa	9.2 MPa
28 days, 20°C Compressive Strength	64.4 MPa	69.5 MPa
5 hours, 60°C, 90% RH Flexural Strength	3.0 Mpa	2.9 MPa
5 hours, 60°C, 90% RH Compressive Strength	18.1 MPa	13.2 MPa

Table 4 – Flexural and compressive strength of CK1 and CK2 mortars after28 days in standard curing conditions and after heat-cured conditions.

SEM results:

No difference has been noticed at the microstructural level between the two mortars. The mortar worked out with cement with low content of P_2O_5 contains more portlandite that than this elaborated with cement with high content of P_2O_5. The calcium silicate hydrates (CSH) present in the two mortars have the same morphology (see Fig. 2) and chemical composition (determined by X-EDS analysis).

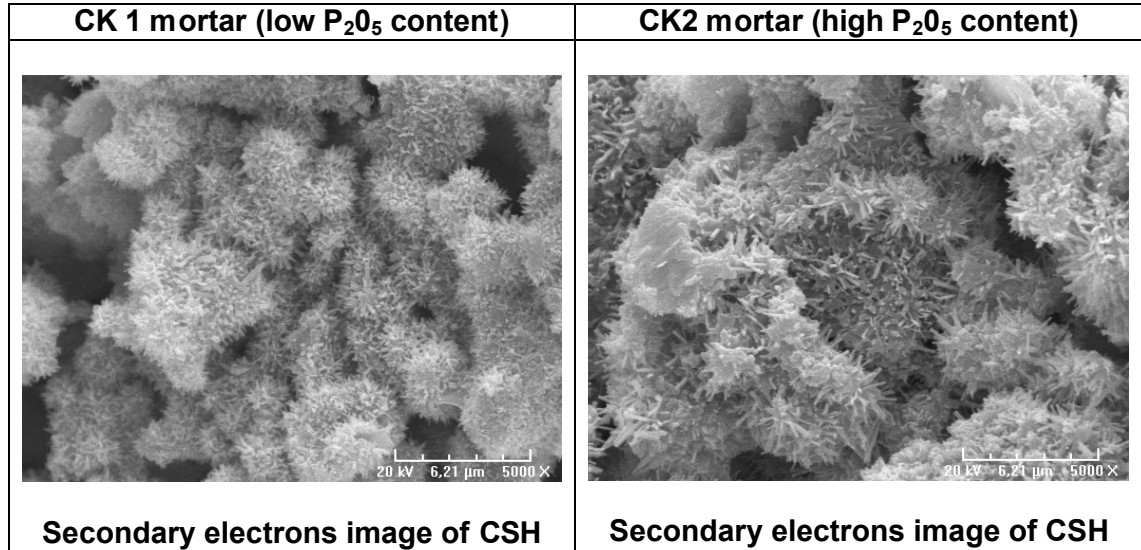| CK 1 mortar (low P_2O_5 content)	CK2 mortar (high P_2O_5 content)
Secondary electrons image of CSH	**Secondary electrons image of CSH**

Figure 2: SEM images of hydrated mortars.

DTA-TG results:

DTA-TG results show a portlandite content in 60°C heat-cured samples of 3.0 wt. % in CK1 mortar sample (low P_2O_5 clinker) and of 2.4 wt. % in CK2 mortar sample (high P_2O_5 clinker) , confirming previous mechanical results obtained on heat-cured samples (see table 4).

3.3 Coupled analysis of results and discussion

The results of this study lead us to emphasize the Phosphorous distribution in clinker minerals, potential impact on cement hydration and mechanical properties of mortars.

Phosphorus diffusion:

SEM, EPMA and TEM results clearly show the Phosphorus distribution around belite grains of clinker. The presence of a chemical gradient of Phosphorus from the outside surface to the core underlines a diffusion process occurring during the final crystals growth. As an hypothesis we have to consider the thermal mechanisms occurring during clinkerization. Indeed, animal meals are introduced inside the kiln. The temperature reached in the kiln transform animal meals into at plasma which comes in contact with belite grains already formed in the first part of the furnace. Elementary phosphorus can then diffuse in minerals at very hot temperature following by a quenching of clinker which is able to generate some amorphous phase around the minerals

Cement hydration and mechanical strength development

Hydration of alite and belite minerals are known to produce CSH and portlandite hydrates. Nevertheless, these two major minerals of Portland clinker are also known to have very different hydration rates.
At 20°C after 28 days, about 75% of alite minerals react with water while only about 20% of belite ones react in the same time [2, 6, 7]. In these conditions, belite rate of hydration progress of about 0.7 % a day. K. Asaga and al. [7], quantify the effect of curing temperature increments from 0 to 80°C on clinker phase rates of hydration by means of quantitative X-Ray analysis. According to their measurements, one can assume that after 5 hours of curing at 60°C, about 50% of alite minerals hydrate, when in the same time about 10% of belite minerals hydrate.

Taking into account these information and our results on hydrated paste in standard and heat-cured conditions, we can understand that PO_4^{3-} ions concentrations in interstitial solutions of mortar pastes should be very different. From a chemical point of view, solubility products and complexation constants of Ca^{2+} ions by OH^- and PO_4^{3-} ions allow to establish predominance diagrams of precipitated phases in the $CaO-P_2O_5-H_2O$ system as given in [8]. The analysis of this diagram states that in basic solution, without PO_4^{3-} ions, $Ca(OH)_2$ portlandite precipitates in $CaO-H_2O$ cement like system while $Ca_{10}(PO_4)_6(OH)_2$ hydroxyapatite solid is more stable in presence of saturated PO_4^{3-} solutions in $CaO-P_2O_5-H_2O$ system. Then, the chemical equation that describes the reaction in $CaO-P_2O_5-H_2O$ system in higly basic solutions that we have in cement pastes is given in (Eq.1):

$$10\ Ca\ (OH)_2 + 6\ H_3PO_4\ \rightarrow\ Ca_{10}\ (PO_4)_6(OH)_2 + 19\ H_2O \quad (Eq.1)$$
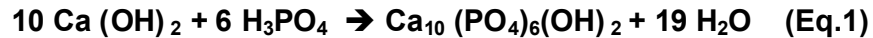
This reaction is a simple method used for obtaining synthetic hydroxyapatite [9] . Applying this result to our experiments, we can envisage that at room temperature during 28 days of hydration, the instantaneous PO_4^{3-} concentration in the interstitial pore solution is weak even in the P_2O_5 rich hydrated clinker. Thus, portlandite content formed from alite and belite hydration is high.

Inversely, on heat-cured samples, 10% of belite hydrate in few hours. Then, most of P_2O_5 distributed at outer surface of belite grains is released in pore solution in which local PO_4^{3-} supersaturation could lead to hydroxyapatite precipitation in substitution of a part of portlandite. This mechanism could be the major cause of the portlandite depletion observed by means of SEM and DTA-TG analysis on heat-cured P_2O_5 rich clinker CK2 sample. In the same time, heat curing conditions increase drastically the rate of precipitation of portlandite and CSH in few hours. Consequently, CSH precipitation and mechanical strength development in heat-cured conditions may be affected while ambient ones are not.

4. CONCLUSION

The aim of this study was to check the distribution of phosphorus in two industrial clinkers (0.14 and 0.70 wt. % P_2O_5) and to evaluate its effect on mechanical properties development at 20°C and 60°C. All the analytical techniques (EPMA, SEM, TEM and XRF) confirmed that phosphorus is mainly distributed into belite grains without any structural modifications. Mechanical strength tests of the two clinkers exhibit a very different behaviour at 20°C and 60°C: at 60°C the highest is the P_2O_5 content , the lowest is the mechanical strength whereas it is the reverse at 20°C. As an explanation to this difference, we suggest that thermal activation of belite dissolution at 60°C, boosts the release of P_2O_5 which precipitates as hydroxyapatite in substitution of a part of portlandite (3.0 wt. % of portlandite in low P_2O_5 clinker sample and 2.4 wt. % of portlandite in high P_2O_5 clinker sample, after heat-curing cycle). This reaction may reduce CSH growth and amount . Consequently, mechanical strength development after heat-curing cycle for P_2O_5 rich clinkers may be affected.

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