



Natural fluorapatite as a raw material for Portland clinker

Sonia Boughanmi^a, Islem Labidi^a, Adel Megriche^a, Mohamed El Maaoui^a, André Nonat^{b,*}

^a Université de Tunis El Manar, Faculté des Sciences de Tunis, UR11ES18 Chimie Minérale Appliquée, Campus Universitaire Farhat Hached, 2092 Tunis, Tunisie

^b Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS-Université de Bourgogne Franche Comté, BP 47870, 21078 Dijon Cedex, France

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ABSTRACT

The present work focuses on the mineralogy and the reactivity of clinkers made from the integration of natural fluorapatite in the raw meals with percentages ranging from 0 up to 15%. The samples were characterized by infrared spectrometry, X-ray diffraction and microscopy techniques. The distribution of phosphorous and fluorine into clinkers minerals was determined by MEB/EDS mapping. The mineralogical composition was determined by XRD/Rietveld and the samples reactivity followed by isothermal microcalorimetry. It has been found that fluorine stabilizes C_3S and β - C_2S which still are found with high levels of P_2O_5 . Cements obtained from up to 8% natural fluorapatite incorporation still present acceptable properties. Natural fluorapatite could have an important potential as decarbonised source of CaO contributing to decrease the CO_2 emission in cement industry.

1. Introduction

One of the highest man-made CO_2 emissions from industry is due to Portland cement production [1]. During clinkering, the main source of calcium, raw limestone, $CaCO_3$, is transformed into CaO, releasing CO_2 greenhouse gas that causes climate changes. Roughly 800 kg of CO_2 is emitted for every ton of Portland cement [2,3]. > 60% of them are due to limestone decomposition, the remaining part is produced by fuel combustion. Among others, one way to reduce the CO_2 emissions could be the use of none carbonated calcium sources. Such products are rare and more expensive. The replacement of all or part of the limestone must preserve the quality of the final cement without rising cost. Fluorapatite, $Ca_5(PO_4)_3F$ could be a potential candidate for this purpose. This material presents the advantage to yield very low CO_2 content, 0% for volcanic phosphate rocks and up to 6% into sedimentary francolite deposits. It is a very cheap and abundant mineral. High extraction occurs all around the world, we cite for example Morocco and Tunisia productions which reached in 2010, 30 and 8 million tons per year respectively. The purpose of this paper is to study the effect of P and F incorporation into Portland cement properties and to delimit the proportions which may be used. It is reported that phosphorous has an important impact on the melting properties of cement raw meal and affects the phase composition of clinker; P enters the C_3S and C_2S cells in substitution of Si in silicate tetrahedra and causes defects that change hydraulicity without annealing it. It has a distinctly negative effect on alite nucleation; when a high amount of P_2O_5 is incorporated, C_2S is stabilized and C_3S formation is inhibited [4–8]. On the contrary,

fluorine presents a positive effect on the rate of Portland clinker formation and a possibility of lowering the energy consumption in the clinker firing process [9–11]. Thus it could reduce significantly the heat consumption and fuel inputs. The effect of phosphorous is relatively well documented especially on laboratory made clinkers. It is generally agreed that phosphorous stabilizes α' - C_2S in such a way that the formation of alite is limited and free lime is remaining [5,6,8] [12–15]. The mechanism limiting the C_3S formation is not well understood. It was found that 1–2% phosphorous in clinker slows down the rate of hardening of cement [4] and above 2.25% the mechanical properties are completely destroyed [5]. However, a previous study on phosphorous containing industrial clinkers [16] shows that the properties could be preserved with 1% of P_2O_5 . If the substitution rate of limestone by fluorapatite is limited in such a way that the P_2O_5 content does not exceed 1%, it corresponds to 4% and also the CO_2 reduction will be about 4% (see Fig. 1). The effect of fluorite (CaF_2) is also well documented in literature. The addition of fluorite to the cement raw mix improves the burnability and lowers the clinkering temperature from 50 to 100°C depending on raw mix composition; for a given temperature in a wide range, it increases the formation of C_3S and reduces the free lime content of clinkers [9,11,17–19] by improving solid state diffusion and reducing liquid viscosity and surface tension [20]. The optimum fluorite content in term of performance of the cements should be close to 0.2 wt% F [21].

One thus could expect that fluorine partly balances the deleterious effect of phosphorous. This was investigated in the present work by studying the effects of the substitution of a part of the limestone in the

* Corresponding author.

E-mail address: andre.nonat@u-bourgogne.fr (A. Nonat).

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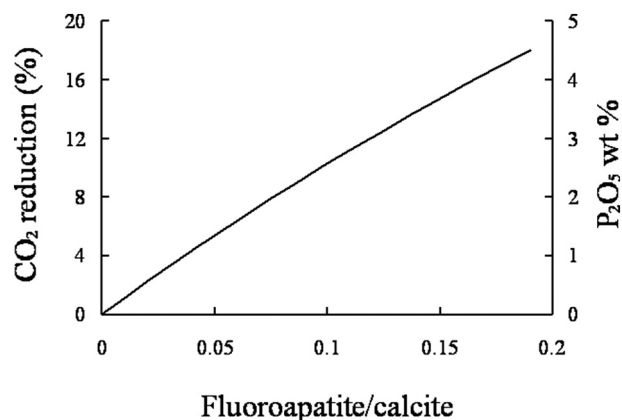


Fig. 1. Expected CO₂ reduction and P₂O₅ clinker content in function of the fluorapatite calcite ratio in the raw mix.

raw materials of laboratory made clinkers by natural fluorapatite (natural FAp) on their mineralogy and the reactivity of the cements. The substitution rate ranged from 0 to 15 wt% natural FAp. The clinkers were characterized by infra-red spectrometry, X-ray diffraction and optical and electronic microscopy. The distribution of phosphorous and fluorine into clinker minerals was determined by MEB/EDS mapping. The level of the free lime was determined by ethylene glycol extraction method. Finally the hydration process of the cements was controlled by isothermal calorimetry.

2. Materials and methods

2.1. Clinker samples preparation

2.1.1. Raw materials

Artificial raw meals for laboratory experiments were prepared by mixing the natural fluorapatite (natural FAp) with pure commercially available limestone, silica, alumina and iron oxide. The fluorapatite comes from Tunisia; its composition is given in Table 1. SiO₂ (ground quartz), Al₂O₃ (corundum), CaCO₃ (calcite) are provided by Prolabo and Fe₂O₃ (hematite) by Sigma-Aldrich. 12 raw mixtures were prepared in such a way that CaO and SiO₂ contents remain constant taking into account CaO, SiO₂, Al₂O₃ and Fe₂O₃ coming from the natural fluorapatite. As a consequence, the Al₂O₃ and Fe₂O₃ content decreases with the increase of FAp. The composition of the raw meals is given in Table 2 and their particle size distribution in the Supplementary Information file associated to this paper. Whatever the FAp content the particle size distributions of the raw meals are similar. All grains are smaller than 90 μm with 43 μm < D-90 < 50 μm. The expected chemical compositions of the clinkers are given in Table 3. The maximum P₂O₅ and F contents are above the limit generally accepted. The lime saturation factor LSF and the C₃S and C₂S expected percentages calculated according to modified Bogue's equations, have been calculated according to two limit hypotheses (Table 4): first, all the phosphorous has been supposed to substitute silicon in the silicate phases, second, the fluorapatite does not react at all. In both cases LSF is smaller than 1. The alkalis and sulphate are only coming from the natural FAp, the other materials being pure analytical grade chemicals and remain low.

Table 1
Chemical composition of the natural fluorapatite (nFAp).

Components	CaO	P ₂ O ₅	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	F	K ₂ O	Na ₂ O	LOI
Content	48.5	28	5.6	0.65	0.35	3.5	0.6	3.3	0.1	1.3	8

Table 2
Raw meals composition.

% Fluorapatite	%CaCO ₃	%SiO ₂	%Al ₂ O ₃	%Fe ₂ O ₃
0	79.00	14	4.00	3.00
1	78.34	14	3.83	2.83
2	77.68	14	3.66	2.66
3	77.02	14	3.49	2.49
4	76.36	14	3.32	2.32
5	75.70	14	3.15	2.15
6	75.04	14	2.98	1.98
7	74.38	14	2.81	1.81
8	73.72	14	2.64	1.64
9	73.06	14	2.47	1.47
10	72.40	14	2.30	1.30
15	69.10	14	1.45	0.45

2.1.2. Clinkering process

The different mixtures are prepared in ethanol and shaped in nodules of 5 mm in diameter then dried in an oven for 24 h at 50 °C. The nodules were prepared and fired separately in platinum crucibles in an electric furnace at a heating rate of 10 °C/min and retained at a final temperature of 1450 °C for 1 h. Then the resulting clinkers were rapidly quenched in ambient air. The burning and cooling conditions were unchanged for the reference and the natural FAp clinkers. The samples were ground using a FRITSCH laboratory ball mill for 5 min, the material is ground and homogenized by impact and friction. The clinkers become easier to grind as the fluorapatite content increases probably because the interstitial phase volume decreases due to the diminution of Al₂O₃ and Fe₂O₃ content (see Table 3). Cements were prepared from these clinkers by mixing them with pure gypsum (arbitrary taken equal to 5% CaSO₄) from Prolabo.

2.2. Clinker mineralogy

2.2.1. X-ray diffraction and Reitveld analysis

The XRD patterns of all synthesized samples were recorded by using a Bruker D-8A25 Discover diffractometer operating at 40 kV and 30 mA. CuKα radiation of wavelength 1.5405 Å was used. The X-ray diffractometer is equipped with a LynxEye detector with a gap of 3°. With this configuration, XRD patterns were scanned from 10 to 90 2θ at the rate of 0.204 2θ per 3 s. The samples were prepared as pellets of 25 mm diameter.

Reitveld refinements of the XRD patterns were carried out in order to quantify the amounts of the various phases present in the samples. The crystallographic information was taken from crystallographic information files (CIF) of Inorganic Crystal Structure Database (ICSD) for all the samples; the references of the crystal structures are given in the Supplementary Information file associated to this paper. The fit quality was assessed by a visual examination of a difference profile plot to get a global idea but also by the Rietveld agreement factors Rp, Rwp and χ².

The refined parameters include scale factors, zero shift, background represented by a fifth order Chebyshev polynomial, unit cells, profile parameters and preferred orientations. The atomic positions as well as the temperature factors were kept constant for all the samples.

2.2.2. Optical microscopy

The microstructural evolution of the main clinker phases was studied on polished sections using an Axiovert 100 optical microscope at 20 magnification in reflected light. The clinker powders were

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