Construction and Building Materials 188 (2018) 599–606

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Does phosphorus affect the industrial Portland cement reactivity?

Sonia Boughanmi [a,*], Islem Labidi [a], Adel Megriche [a], Houssine Tiss [b], André Nonat [c]

[a] Université de Tunis El Manar, Faculté des Sciences de Tunis, UR11ES18 Chimie Minérale Appliquée, Campus Universitaire Farhat Hached, 2092 Tunis, Tunisia
[b] Laboratoire de Production, les Ciments de Bizerte, 7000 Bizerte, Tunisia
[c] Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS-Université de Bourgogne Franche, Comté, BP 47870, 21078 Dijon Cedex, France

HIGHLIGHTS

- Study of properties of industrial clinkers with $0.5 < P_2O_5 < 1.1\%$
- No direct relation between reactivity and mineralogy.
- Compressive strength is not affected in the range $0.5 < P_2O_5 < 1.1\%$

ARTICLE INFO

Article history:
Received 28 September 2017
Received in revised form 15 July 2018
Accepted 11 August 2018

Keywords:
Industrial clinkers
Phosphorous
Mineralogy
Reactivity

ABSTRACT

The effect of phosphorous on the mineralogy and reactivity of Portland cement has been investigated through an industrial clinkers series. The samples were collected from the same Tunisian cement plant and classified according to the content of P_2O_5 from 0.5% to 1.1%. All samples were manufactured at the same thermal and cooling conditions as well as possible. The specimens were characterized by X-ray fluorescence spectrometry and optical microscopy techniques and their mineralogy was determined by X-ray powder diffraction coupled to the Rietveld analysis. The cements reactivity prepared from the clinkers was followed by means of isothermalcalorimetry. The compressive strength of the cement pastes was measured.

The results revealed that the content of phosphorous in this range has not a significant influence on the clinkers mineralogy cement reactivity and concrete performance.

1. Introduction

Hydration of Portland cement remains a subject of a lot of researches because of its complexity, the needs to improve its environmental footprint and the properties of the final materials. For example, the presence of minor elements coming from both raw materials and fuels in the clinkering process, may introduce some modifications in the main constituents and modify the kinetics of the hydration reactions. The effects of the impurities on the clinker mineralogy and hydraulic cement reactivity are often complex because many variables are involved which are difficult or impossible to control independently. These include chemical composition and polymorphic changes but also inclusion of defects, morphologic and textural modifications such as particle size distribution, presence of microcracks etc… [1]. Among these foreign elements, the phosphorous coming from raw materials (marls and limestone) or alternative fuels (meat and bone meals) has been identified as having important effects on the distribution of the main phases in Portland clinker and on the cement reactivity [2–8]. In fact Portland clinker typically contain around 0.2 wt% of P_2O_5. Most of the studies agree to show that higher phosphorus contents in clinker favors the formation of belite (C_2S) and free lime to the expense of alite (C_3S) [1]. As alite is the main hydraulic compound of Portland cement and the most reactive phase, its decrease causes the decrease of the amount of its hydration product, calcium silicate hydrate (C-S-H) at early age, which leads to the decrease of the development of strength in concrete in the first 28 days.

The stabilization of C_2S by phosphorous is well documented; during the clinkering process phosphorus is firstly fixed by calcium in forms of apatite C_3P which becomes unstable at higher temperatures leading to α'-C_2S, a stable solid solution of C_3P in C_2S. As a result the C_3S formation becomes more and more impeded with the P_2O_5 addition and it results an increase of free lime [9–11]. The decomposition of alite is generally observed above 0.5 wt% P_2O_5 [4] but in the case of the pure CaO-SiO_2 system, Noirefontaine found that the addition of 0.1 wt% P_2O_5 is enough to cause a partial

---

[*] Corresponding author.
E-mail address: ingenieursonia@gmail.com (S. Boughanmi).

https://doi.org/10.1016/j.conbuildmat.2018.08.060

decomposition of triclinic C_3S into α'_H-C_2S and CaO. If P_2O_5 content increases, the α'-C_2S phase appears as a layer covering more and more C_3S grains [12].

As far as the mechanical properties are concerned, the presence of phosphorus in the range of 1–2% in Portland cement clinkers slows the rate of hardening of the cement [13]. Nurse [14] found that the early strength falls as phosphorous content in the clinker increases. When the P_2O_5 reaches 2.25 wt% the cement fails to meet the British standard requirements. So a threshold limit for P_2O_5 (wt.% $P_2O_5 = 0.5$) on clinker has been fixed. It would correspond to the maximum amount of P_2O_5 that could be incorporated into clinker before the detection of α'-C_2S [4]. However most of the above studies relate to materials prepared under laboratory conditions from raw materials and sometimes pure phases. To the best of our knowledge there is no published systematic study investigating the effect of phosphorus in the range 0.5–1 wt% of P_2O_5 on the mineralogy and reactivity of industrial clinkers. Indeed ordinary Portland cement generally contains phosphorus in the range 0.2 to 0.3 wt% P_2O_5 [1], also the effect of larger amounts of P_2O_5 on the quality of industrial clinkers remains until now an open question. Therefore we have chosen to investigate the effect of this impurity on a series of 8 industrial clinkers containing phosphorous in the range 0.5–1.1 wt% P_2O_5 coming from a same Tunisian cement factory. Here, phosphorus comes from the raw materials especially limestone, mostly in the form of calcium phosphate ($Ca_3(PO_4)_2$), extracted from the cement plant quarries. The 8 clinkers were elaborated in the same kiln with the same heat treatment and underwent the same cooling conditions. The chemical composition of the samples was determined by X-ray fluorescence, their mineralogical compositions by X-ray diffraction/Rietveld analysis, and the cement reactivity was controlled by isothermal calorimetry and compressive strength.

2. Experimental details

2.1. Materials

All clinkers were ground and simultaneously homogenized using a horizontal vibration laboratory disc mill from HERZOG. To ensure homogeneity of the clinker samples, 250 g of crushed clinker of each sample were ground for 2 min to achieve a particle size distribution similar for all specimens. Finally the samples were selected after passed through a 90 µm sieve. The chemical composition of the 8 clinkers was determined by X-ray fluorescence using the ARL ADVANT'X series spectrometer, the measurements were made on pellets using the fusion technique. The samples chemical composition is reported in Table 1. The specimens present a similar chemical composition. Concerning the major components, SiO_2 content only varies from 20.8 to 22%, CaO from 64 to 65%, Al_2O_3 from 4.7 and 5.7% and Fe_2O_3 from 3.5 to 3.9%. The phosphorus content expressed in wt %P_2O_5 ranges from 0.57 to 1.06%. In the following the samples will be labeled in the increasing phosphorus way from CK01 to CK08. It is also noticeable that SO_3 content is close to 1% for all the clinkers except CK04 which only has 0.4% of SO_3 and CK08 which has more than 1.4% of SO_3.

2.2. Analytical techniques

2.2.1. Determination of the free lime

The free lime (f-CaO) content was determined according to the ethylene glycol extraction method [15]. The measurements were determined with ±0.1 precision.

2.2.1.1. X-ray diffraction. X-ray diffraction was performed using a Bruker D-8A25 Discover diffractometer operating at 40 kV and 30 mA equipped with a LynxEye detector with a gap of 3°. CuKα radiation (1.5405 Å) was used. With this configuration, XRD patterns were scanned from 10 to 90° 2θ at the rate of 0.0204 degree per 3 s. The samples were prepared as pellets of 25 mm diameter.

2.2.2. Rietveld method

The X-ray data were refined by Rietveld analysis [16–18] using X'Pert HighScore Plus from PANalytical. In all the refinements, a pseudo-Voigt profile shape function was chosen. Scale factors, instrumental values (zero, background) profile and cell parameters were refined but the atomic positions were fixed to their original values. In order to control the Rietveld refinement, the reverse Bogue calculation [19] giving the elemental oxide composition from phase content deduced by Rietveld analysis has been compared with the elemental oxide composition deduced by X-ray fluorescence.

2.2.3. Optical microscopy

The observation of the main clinker phases was done on polished sections using an Axiovert 100 optical microscope at 20 magnifications. The clinkers powders were impregnated in epoxy resin and encapsulated for 24 h. Finally the samples were polished with a polishing machine, using 1200 carborundum paper followed by a 4000 silicon carbide paper with petroleum as a lubricant.

2.2.4. Isothermal calorimetry

The rate of hydration of cements prepared with the clinker samples was estimated from their heat release measured by isothermal calorimetry. The experiments were carried out on a Tam air calorimeter (Thermometrics). All the experiments were conducted on 2 g of sample at a deionized water-to-cement weight ratio (W/C) of 0.5 and 23 °C. Cement and water were mixed outside the calorimeter with an electric mixer. The cements were obtained by adding pure gypsum from PROLABO to the studied clinkers. As the sulphate optima have not been determined, two series of

Table 1
Chemical composition of the 8 industrial clinkers.

	CK01	CK02	CK03	CK04	CK05	CK06	CK07	CK08
SiO_2	21.47	21.06	21.09	21.99	20.97	21.20	20.83	21.06
Al_2O_3	4.66	4.78	4.69	5.23	5.72	5.45	5.33	4.65
Fe_2O_3	3.61	3.93	3.78	3.63	3.75	3.51	3.49	3.59
CaO	64.57	64.68	65.04	64.40	64.83	64.30	64.69	63.96
MgO	1.55	1.52	1.53	1.53	1.44	1.23	1.15	1.83
SO_3	1.04	1.01	1.00	0.40	0.91	1.05	0.94	1.41
K_2O	0.36	0.42	0.42	0.36	0.33	0.39	0.36	0.39
TiO_2	0.26	0.24	0.24	0.26	0.27	0.26	0.26	0.17
MnO	0.02	0.05	0.04	0.08	0.04	0.07	0.07	0.05
Cr_2O_3	0.01	0.01	0.01	0.02	0.02	0.02	0.01	0.01
P_2O_5	0.57	0.72	0.73	0.74	0.75	0.82	0.97	1.06
LOI	0.56	0.33	0.32	0.23	0.47	0.54	0.66	0.63