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Characterization using thermomechanical and differential thermal analysis of the sinterization of Portland clinker doped with CaF_2

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ABSTRACT

In this work, the sintering process of Portland cement was studied by combining thermomechanical analysis (TMA) and differential thermal analysis (DTA), together with X-ray diffraction (XRD) and scanning electron microscopy (SEM). Thermal analysis results employing both techniques indicted that phase transformations appeared at lower temperatures when CaF_2 was incorporated in the raw materials. Besides, it was observed at high temperature that in some phase transformations TMA conducts to better resolution compared with the DTA measurements. Furthermore, mechanical properties and X-ray diffraction patterns corroborate the TMA and DTA results, corroborating that the final amount of alite (Ca_3SiO_5) is higher when a certain amount of CaF_2 was present during the clinkerization process.

1. Introduction

The use of industrial wastes and catalyzers as an alternative to fuel reduction in the cement industry is nowadays a reality in several countries because economical and environmental incomes are obtained. Since the average energy consumption by the cement industry is extremely high, a decrease in the burning temperature by the use of fluxes/mineralisers and other compounds should have economic and environmental advantages. There is evidence that CaF_2 has been added to the raw mix searching for reducing the clinkerization temperature without decreasing the clinker quality in this process [1–3]. The beneficial effect of fluoride upon combination is thought to be due to a reduction both in the temperature of initial melt formation and also to the formation of intermediate phases whose decomposition products readily form the clinker minerals [4–6]. Although there exists several works to characterize the effect of minor elements on the final properties of Portland cement [7–10], the same is not valid for the use of thermomechanical analysis (TMA) to study their impact on the clinkering process. In fact, almost all the work carried out to study the clinkerization process by thermal analysis have used only two techniques: differential thermal analysis (DTA) and thermogravimetric analysis (TGA) [2,11–16], and only recently other thermal techniques like dilatometry have been employed in belite clinkers [17].

The present work presents preliminary results indicating that TMA could be a supplementary technique to DTA, capable to give important information of the clinkerization process of conventional and new Portland cement formulations. In the

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Table 1 – Mean chemical composition of the cement raw mix and fluoride mineral.

wt.%	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	TiO_2	K_2O	Na_2O	P_2O_5	Total
Raw mix	65.9	20.9	6.5	3.7	1.2	1.1	0.3	0.2	<0.1	99.8
wt.%		CaF_2		$CaCO_3$		SiO_2		Fe_2O_3		Total
Fluorspar		96.9		1.1		1.5		0.5		100.0
			LSF			AR				SR
Clinker			0.97			1.80				2.05

present case, the effect of different amounts of CaF_2 on sintering and formation of different phases were employed to compare each thermal technique.

2. Experimental Procedure

2.1. *Instrumental Methods*

Interaction between CaF_2 and raw materials were tracked using a differential thermal analyser (DTA Model HT7, Perkin-Elmer) with a heating rates of 10 °C/min and sample chamber purged with N_2 (99.99%). The equipment was calibrated using the melting point of aluminium (99.98%) and nickel (99.99%) standards and all samples were heated from room temperature to 1450 °C.

Decomposition and/or volatilisation of compounds resulting from CaF_2 and raw materials interaction were tracked using the derivate of thermogravimetric data (DTGA) recollected by a thermogravimetric analyser (TGA Model HT7, Perkin-Elmer) with a heating rate of 10 °C/min and the sample chamber was purged with N_2 (99.99%). The equipment was calibrated using the Curie temperature of nickel (99.98%) and iron (99.95%) standards, and all samples were heated from room temperature to 1400 °C.

Samples change of volume, via shrinkage and expansion resulting from the interaction between CaF_2 and raw materials, were employed to corroborate the phase transformations occurring during the clinkerization process. Fluorspar effect on raw materials were tracked using the derivate of thermomechanical data (DTMA) recollected by a thermomechanical analyser (TMA Model Pyris-Diamond HT, Perkin-Elmer) with a constant load of 10 mN and a heating rate of 10 °C/min from room temperature to 1400 °C. The sample was purged with N_2 (99.999%) and the equipment was calibrated using the melting point of zinc (99.98%) and gold (99.99%) standards.

Phase identification was carried out using an X-ray diffractometer (XRD Model 2000, Rigaku Corp.) with Cu K_α radiation and a nickel monochromator using a scanning speed of 0.01°/min and an integration time of 2 s over the range 2θ from 20 to 75°. Microstructures were examined using a scanning microscope (SEM Model Philips XL30) attached to an energy-dispersive X-ray spectrometry (EDS, Model 350C, Edax Inst.).

Compressive strengths at room temperature were measured on samples cast in cylindrical plastic moulds having a diameter of 50 mm and a length of 100 mm. Compressive testing was performed under displacement control, using a universal testing machine (Model 10 T3, Shimadzu) with capacity of 10,000 kg and a crosshead speed of 0.76 mm/min was used. Five cylinders from each composition were tested for each measurement.

The chemical composition of all materials was determined by atomic absorption spectrometry (Analyst200, Perkin-Elmer) using Li_2CO_3 fusion followed by samples digestion in acidic aqueous solutions [18].

Cement clinker blends were obtained heating samples to 1350 °C and confined for 45 min. Immediately samples were cooled to room temperature using forced air blowers, basically to emulate as close as possible the industrial process.

2.2. *Materials' Chemical Composition*

The materials used were domestic commercial raw mix of clays, calcareous rocks and local fluorspar. Before samples were tested, the raw materials and the CaF_2 mineral were analysed, grounded, mixed and sieved to remove coarse particles and finally milled for blending. The mix proportions of the blends were made with 0.0, 0.2 and 0.4, wt.% of CaF_2. Table 1 shows the dosages, as oxides, used to prepare the clinker. It also shows the theoretical lime saturation factor (LSF), alumina ratio (AR) and silica ratio (SR). The clinker was adjusted to have typical values of modern industrial clinkers, where LSF ranges from 0.92 to 0.98, AR from 1.0 to 4.0 and SR ranges from 2.0 to 3.0 values [1,5].

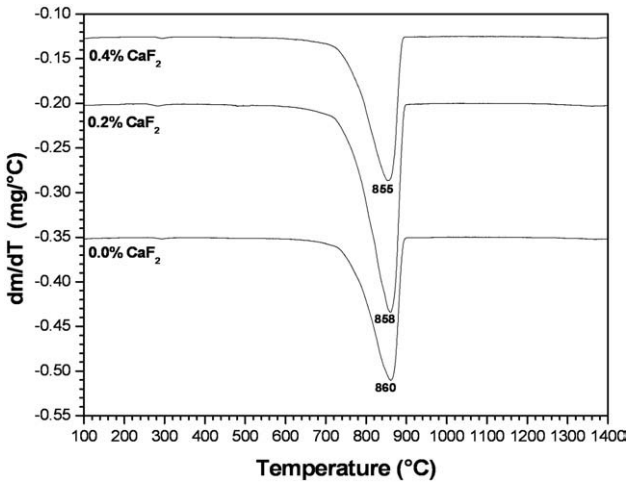

Fig. 1 – DTGA curves obtained from different cement clinker raw meals, using an atmosphere of N_2 and a heating rate of 10 °C/min.