INVESTIGATION OF FLY ASH ACTIVATION WITH CHEMICAL ADDITIVES: INTERACTIONS WITH PORTLAND CEMENT HYDRATION

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ABSTRACT

The reduction of greenhouse gases emission is the main issue the cement industry is facing now and will be facing in the near future. In the light of this, the use of the so-called secondary cementitous materials is mandatory for all modern cements. Among other types of mineral additions, fly ashes represent one of the most promising, due to availability and hydraulic behavior. In this paper we discuss the reactivity of several fly ash sources in a typical blended cement system, with particular reference to chemical additive used as performance enhancer. Physico-mechanical parameters such as compressive strengths and physico-chemical measurement are discussed and commented, with the aid of microscopy techniques for microstructure evaluation.

INTRODUCTION

As it is well known and reported in many occasions, one of the most effective ways to lower the manufacturing cost of cement is by lowering the clinker factor. Clinker is the single most expensive component of cement, due to the high-energy process required to obtain it in the kiln. Many standards all over the world allow for the manufacturing of blended cements, where part of the clinker is substituted by supplementary materials as limestone, fly ash, or blastfurnace slag. These secondary materials are directly ground together with clinker and gypsum, or milled in a separate stage, followed by blending with ordinary Portland cement. Each of them provides advantages and disadvantages (related to cost, grindability, chemical reactivity, availability) that can drive their specific application.

Fly ash is one of the most widely available supplementary cementitious materials, being the byproduct of coal burning in power plants. During the burning, fused fine particles are carried away by the flue gas and solidify by cooling to glassy amorphous ash particles with a glass content of approximately 60-85% in weight (Lutze and vom Berg, 2004). Composition in terms of crystalline phases and chemical elements has been investigated by many authors (e.g. in Prause, 1991, Richartz, 1984 and Kautz and Prause, 1986). Hydration reaction in alkaline conditions is the phenomenon that allows their extensive use as a clinker replacement: overly simplifying, this consists in the reaction of amorphous silica contained in the ashes with the calcium hydroxide produced by the hydration of cement clinker. This means that the effectiveness of the ashes in providing strength through the formation of C-S-H gel is mainly focused at later ages, since some time is needed to thoroughly spread the presence of $Ca(OH)_2$ in the matrix of cement to get it reacting with the fly ash particles. Hence, blended cements based on the substitution of clinker with fly ashes usually suffer from lower early strengths (Fraay, 1990, Huettl, 2000, Lee C. Y. *et al.*, 2003, Mueller *et al.*). Several studies have been published regarding the activation of fly ash through chemical compounds, both inorganic (e.g. alkali sulphates) and organic (e.g. alkanolamines) (Gartner and Myers, 1993, Sandberg, 2008, Scholze, 1977). In particular, triethanolamine (TEA) has been the subject of several investigations regarding the activation of blended cements containing fly ashes or other secondary components (e.g. in Lee C. Y. *et al.*, 2003). Additional work has been done to try and correlate the chemical composition of fly ashes with their reactivity (Schulze and Rickert, 2011). This study was carried out by preparing artificial cement pore solutions and varying different parameters.

PURPOSE OF THE WORK

In the present work, we try to take a move towards the field application, by trying to investigate the possible correlations between the fly ash composition and its reactivity in blended cements, with and without the presence of chemical activators normally used in the cement industry. The chosen approach is on purpose very practical: two industrial clinkers were selected, together with four different fly ashes, analysed for their composition, ground and mixed to yield blended cements with 20% fly ash content. These cements were used to prepare EN-196/1 mortars and determine compressive strengths. Strengths were measured on blank cements and by adding chemicals in the mixing water. The strengths results were then analysed to assess any correlation.

Data obtained through this work are not conclusive: additional investigation should and will be carried out to confirm the findings and better understand the mechanism of hydration of fly ashes in their practical application as a clinker substitute.

EXPERIMENTAL

The following materials were selected for the investigation:

- two Portland cement clinkers (coded C4564 and C4705)
- one natural gypsum
- four fly ashes (coded C4672, C4736, C4737 and C4738).

Criteria followed in choosing were to avoid very particular material, trying to focus on "typical" characteristics that could have the widest interest. The two clinkers come from different geographical areas, the fly ashes were the byproduct of different coals burned in different power plants.

Each clinker and gypsum were ground together in a laboratory mill for a standard time, in the ratio 95:5. Enough of these Ordinary Portland Cements (OPCs) was ground for all the tests, and thoroughly mixed and homogenized to avoid any effect of fineness variation between grinding batches.

Fly ashes were used as they were received: all of them were provided "ready to use", i.e. dry and already at a fineness compatible with direct use in cement.

Blended fly ash cements were prepared by dry blending the OPCs with each of the ashes in the ratio of 80:20, yielding 8 different cements (4 for each clinker).

For each of these 8 cements, compressive strengths were measured according to EN-196/1, so with standard water/cement ratio of 0.5 and standard sand/cement ratio of 3:1.

For the determination of strengths in the presence of chemicals, the latter were added directly in the mixing water by weighing the appropriate amount of each.

For the assessment of chemical and mineralogical composition of OPCs and fly ashes, X-Ray fluorescence (Bruker AXS S8 Tiger), thermogravimetric analysis (TGA Netzsch TG209F1 Iris) and quantitative X-Ray diffraction with Rietveld method were used. Powder diffraction data were collected with a PANalytical X'pertPro MPD diffractometer with theta–theta geometry, equipped with an X'Celerator detector working with the CuKα radiation (1.54184 Å) in the 2theta range 5–80, a step size of 0.017° 2 theta and a scan step time (s) of 102,1. All data collections were performed at room temperature with back-loading sample holders to avoid preferred orientation of crystallites. Data were analysed by the Rietveld method (Rietveld, 1969) using the Bruker AXS software package TOPAS 4.2 operated in the fundamental parameters mode (Cheary et al, 1992, Coelho, 2000, BRUKER AXS, 2003).

As for chemical additions, on each cement and fly ash combinations the following were added (dosages refer to total cementitious):

- triethanolamine (TEA) at a dosage of 250 ppm
- triethanolamine (TEA) at a dosage of 250 ppm and sodium chloride at a dosage of 500 ppm
- triethanolamine (TEA) at a dosage of 250 ppm and sodium thiocyanate at a dosage of 1000 ppm

Choice of dosages was dictated by actual use of these chemicals in practical use.

For the SEM analysis, cement pastes were prepared by mixing 50 g of fly ash cement and 50 g of water; chemicals were added directly in the mixing water. Samples were left in closed plastic containers at constant temperature of 20°C for 28 days. After 28 days, containers were open and the hardened paste was sampled for microscopy analysis.

Microscopic examination of pastes was performed with FEI QuantaFEG-250 SEM. Samples were prepared for standard high vacuum SEM, with sputter coating with Pd/Au.

RESULTS

Results of clinker XRD-Rietveld and calculated OPC composition are reported in table 1. All values are expressed in %.
Composition of fly ashes (XRF data) are reported in table 2. All values are expressed in %.
Table 3a and 3b report all the strengths data at 1, 2 and 28 days. In addition to the absolute values in MPa, % increase over the blank are reported.

Sample	OPC C4564	OPC C4705
C_3S M3	30.5	34.6
C_3S M1	29.0	28.2
C_2S	20.2	17.2
C_3A, cubic	4.4	4.3
C_3A, orthorombic	1.5	-
C_4AF	6.4	6.9
CaO	0.5	1.0
MgO	2.1	1.1
Gypsum	2.2	2.3
Bassanite	-	0.5
Anhydrite	0.2	-
Calcite	-	0.9
Portlandite	1.0	1.2
Arcanite	1.1	0.8
Ca-Langbeinite	-	0.9
Aphtitalite	0.6	-

Table 1 - Composition of OPCs (XRD), %

Sample	Fly ash C4672	Fly ash C4736	Fly ash C4737	Fly ash C4738
MgO	1.06	1.54	1.18	1.61
K_2O	0.62	1.76	1.74	1.45
Al_2O_3	29.61	24.29	19.32	27.72
SiO_2	51.43	57.51	60.60	50.74
CaO	5.49	3.36	1.73	5.32
Na_2O	0.00	1.33	0.60	0.44
SO_3	0.27	0.00	0.00	0.28
TiO_2	1.64	1.35	0.84	1.75
P_2O_5	1.22	0.31	0.23	0.62
Fe_2O_3	3.34	6.03	8.71	3.93

Table 2 – Composition of fly ashes (XRF), %

Sample		1d str	%	2d str	%	28 str	%
FA C4672	**blank**	12.7		24.0		52.4	
FA C4672	**TEA**	13.7	7.9	23.9	-0.4	51.6	-1.5
FA C4672	**TEA NaCl**	14.7	15.7	25.4	5.8	49.6	-5.3
FA C4672	**TEA NaSCN**	16.0	26.0	26.5	10.4	51.6	-1.5
FA C4736	**blank**	13.1		23.0		53.3	
FA C4736	**TEA**	12.8	-2.3	23.8	3.5	53.7	0.8
FA C4736	**TEA NaCl**	15.0	14.5	24.8	7.8	51.4	-3.6
FA C4736	**TEA NaSCN**	15.9	21.4	25.1	9.1	50.8	-4.7
FA C4737	**blank**	11.9		22.2		47.9	
FA C4737	**TEA**	12.8	7.6	22.9	3.2	48.2	0.6
FA C4737	**TEA NaCl**	14.2	19.3	23.8	7.2	49.7	3.8
FA C4737	**TEA NaSCN**	14.5	21.8	24.3	9.5	48.7	1.7
FA C4738	**blank**	10.6		23.6		53.6	
FA C4738	**TEA**	13.4	26.4	25.3	7.2	56.8	6.0
FA C4738	**TEA NaCl**	15.0	41.5	26.4	11.9	54.4	1.5
FA C4738	**TEA NaSCN**	15.3	44.3	26.2	11.0	53.3	-0.6

Table 3a – Clinker C4564 Compressive strengths (EN-196/1), MPa

Sample		1d str	%	2d str	%	28 str	%
FA C4672	**blank**	13.4		23.2		49.5	
FA C4672	**TEA**	13.6	1.5	24.3	4.7	49.2	-0.6
FA C4672	**TEA NaCl**	15.1	12.7	24.0	3.4	48.7	-1.6
FA C4672	**TEA NaSCN**	16.2	20.9	24.8	6.9	50.6	2.2
FA C4736	**blank**	13.4		22.2		45.9	
FA C4736	**TEA**	14.3	6.7	23.4	5.4	45.2	-1.5
FA C4736	**TEA NaCl**	14.4	7.5	23.6	6.3	48.9	6.5
FA C4736	**TEA NaSCN**	15.4	14.9	23.8	7.2	48.0	4.6
FA C4737	**blank**	12.8		22.6		46.0	
FA C4737	**TEA**	13.7	7.0	22.9	1.3	48.0	4.3
FA C4737	**TEA NaCl**	14.4	12.5	22.8	0.9	46.8	1.7
FA C4737	**TEA NaSCN**	15.1	18.0	24.5	8.4	47.1	2.4
FA C4738	**blank**	13.9		22.7		50.6	
FA C4738	**TEA**	14.6	5.0	23.7	4.4	50.6	0.0
FA C4738	**TEA NaCl**	15.4	10.8	24.2	6.6	49.8	-1.6
FA C4738	**TEA NaSCN**	15.8	13.7	25.1	10.6	49.8	-1.6

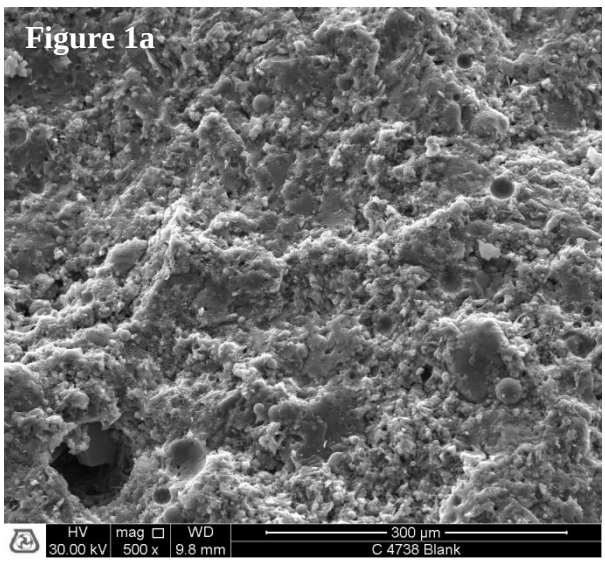
Table 3b – Clinker C4705 Compressive strengths (EN-196/1), MPa

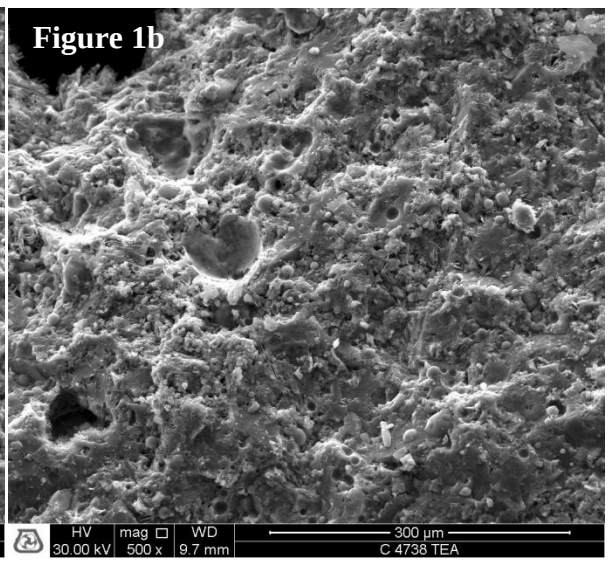
SEM ANALYSIS

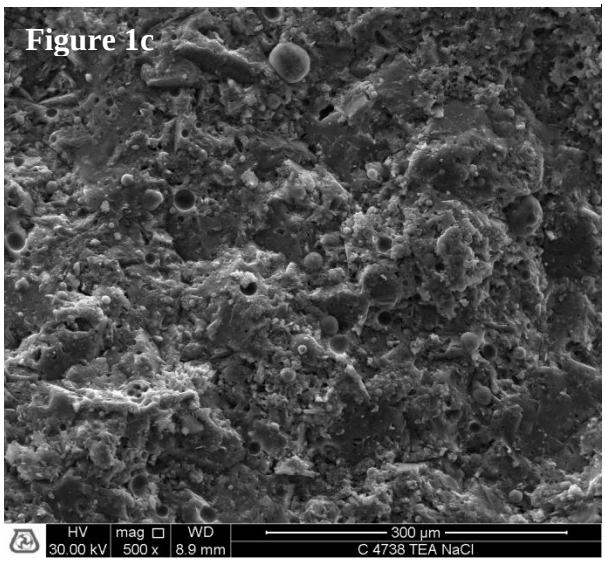
For the purpose of this study, we focused on the microscopical analysis of the structure of the hydrated cement after 28 days. At this later age, differences in strengths between the blank and the added cements are less pronounced, and in some cases even not present (see for example clinker C4564 with fly ash C4737, and clinker C4705 with fly ash C4737). However, early strengths are quite different: hence, we tried to assess if it was possible to detect differences in structure when the strength were at the same level or, in other words, if the different speed of reaction was leaving traces even after 28 days.
Micrographs of the pastes prepared as described above were taken at several magnitudes. We report here some images, with the most representative findings (Figure 1 and Figure 2). In particular, we selected the series of samples corresponding to the blended cement composed of clinker C4705, gypsum and fly ash C4738. This cement gave significant strength increases at early ages with the additives, but very similar 28 days values between blank and treated samples. In all pictures, fly ash spherical shapes are visible as enveloped by the hydration products. As can be seen in the pictures, increasing density of the hydrated structure is quite evident in the scale

blank < TEA < TEA+NaCl <TEA+NaSCN.

Less voids are present going from blank to NaSCN .







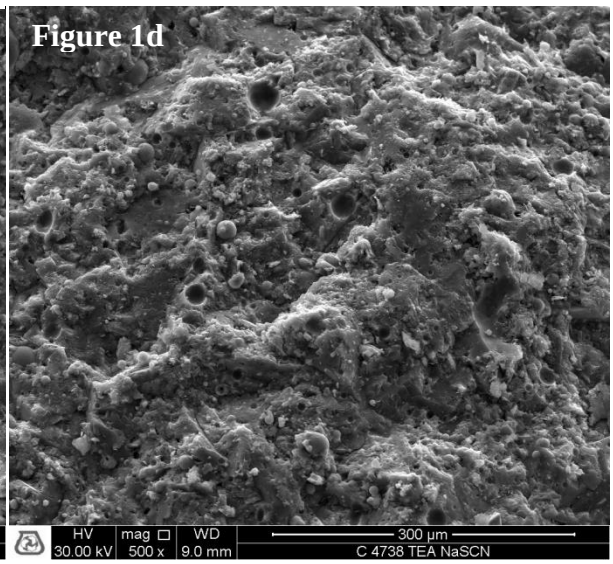
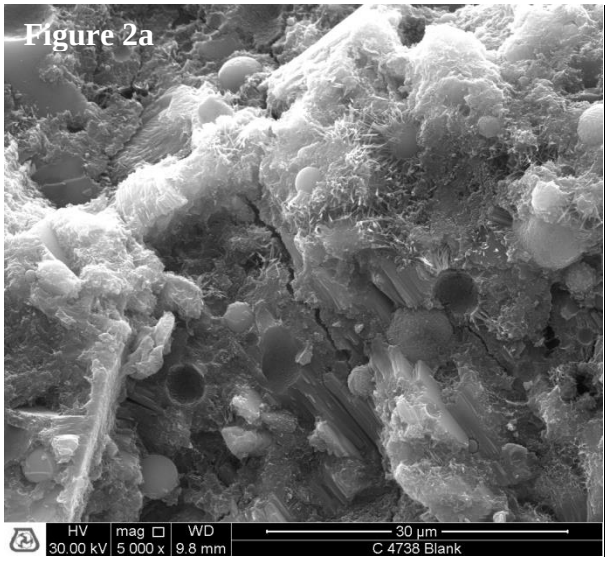
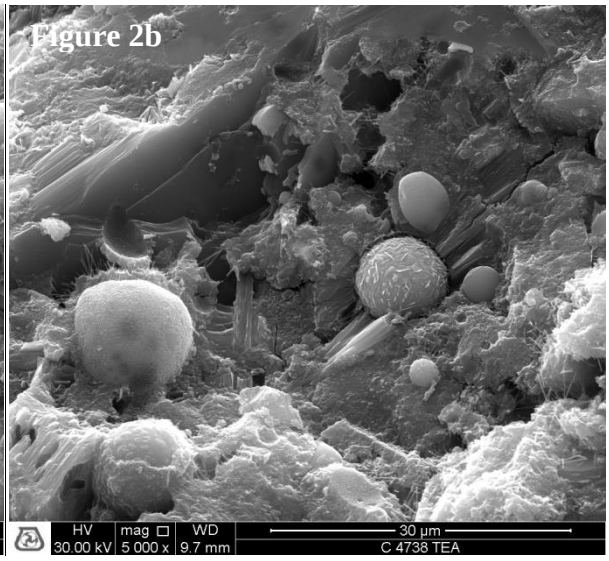


Figure 1: SEM images of hydrated cement pastes. 1a: blank sample – 1b: samples treated with TEA – 1c: sample treated with TEA/NaCl – 1d: sample treated with TEA/NaSCN

In the case of the blank, at higher magnification several areas rich in needle-shaped crystals are visible, as well as some Portlandite crystals. For samples treated with additives, needle crystals are no longer visible, and the overall structure looks much more compact. In general, the presence of additives enhances the envelopment of the fly ash spheres into the hydration gel matrix.





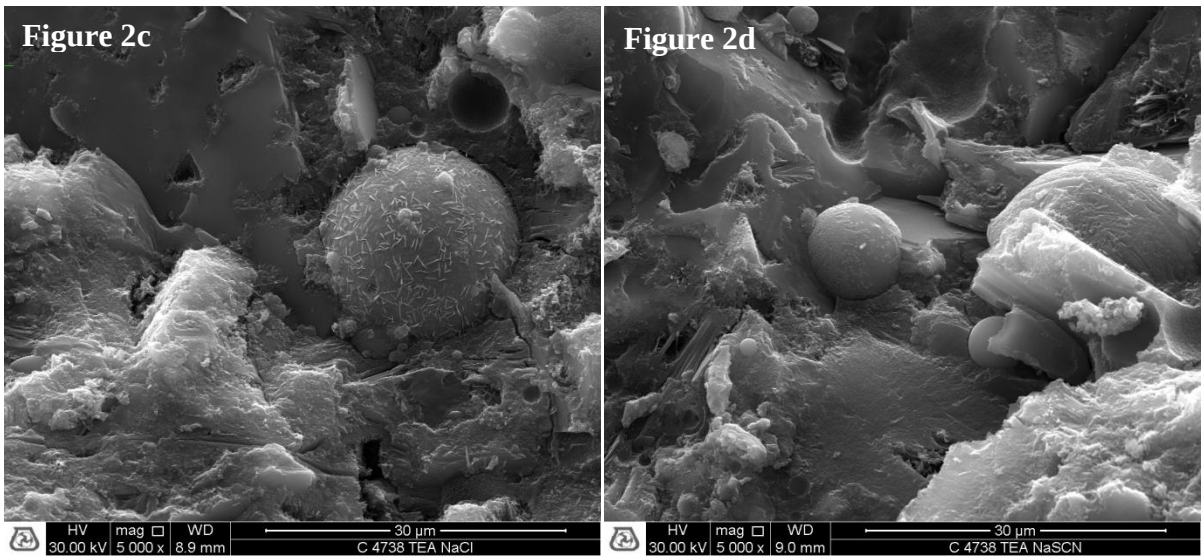


Figure 2- SEM images of hydrated cement pastes. 2a: blank sample – 2b: samples treated with TEA – 2c: sample treated with TEA/NaCl – 2d: sample treated with TEA/NaSCN

CONCLUSIONS

Micrographs collected show that the presence of early strength enhancing additives not only influences the structure of the hydrated cement at early ages, but that their effect extends up to later ages, showing very clearly also after 28 days. This is true even if the absolute strengths values are the same between the blank and the treated samples.

These results support the fact that hydration of cement in the presence of chemical additives follows different paths compared to the blank. Microscopy can be a useful technique to contribute to the better understanding of these reaction mechanisms.

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