Fly ash blended cements: process and hydration improvement through the use of cement additives

Davide Padovani, Paolo Forni, Awadalkarim Fakhraldin, MAPEI SpA

1 Fly ashes in cement

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 6085%- 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: 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). In particular, triethanolamine 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).

2 Fly ash cements enhancement with additives

The first approach to improving strengths of fly ash cements, and hence the amount of fly ash substituting clinker, is through the use of a chemical activator. Cement additives can be added in the grinding stage to gain the simultaneous benefit of decreasing the energy needed to reach a given fineness and enhancing the hydration process of cement. For the purpose of demonstrating the effect of the additives, a laboratory programme was set up. Two laboratory cements were selected (ground using clinkers internally coded C4564 and C4705 and a natural gypsum), together with four different fly ashes (coded C4672, C4736, C4737 and C4738). All materials were analysed for their composition with a combination of analytical techniques (XRD-Rietveld, TGA, XRF). Results are collected in the following tables.

Table 1 - Composition of OPCs (XRD, TGA), %

Sample	OPC C4564	OPC C4705
C_3S	59.7	62.8
C_2S	20.3	17.3
C_3A, cubic	4.4	4.3
C_3A, orthorombic	1.5	-
C4AF	6.4	6.9
CaO	0.5	1.0
MgO	2.1	1.1
Gypsum (dihydrate)	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 2 – Composition of fly ashes (XRF), %

Sample	Fly ash C4672	Fly ash C4736	Fly ash C4737	Fly ash C4738
MgO	1.06	1.54	1.18	1.61
K2O	0.62	1.76	1.74	1.45
Al2O3	29.61	24.29	19.32	27.72
SiO2	51.43	57.51	60.60	50.74
CaO	5.49	3.36	1.73	5.32
Na2O	0.00	1.33	0.60	0.44
SO3	0.27	0.00	0.00	0.28
TiO2	1.64	1.35	0.84	1.75
P2O5	1.22	0.31	0.23	0.62
Fe2O3	3.34	6.03	8.71	3.93
LOI and not determined	5.32	2.52	5.05	6.14

OPCs and fly ashes described above were dry mixed to yield blended cements with 20% fly ash content. These blended cements were used to prepare EN-1961/ mortars and determine compressive strengths. Strengths were measured on blank cements and by adding chemicals in the mixing water. On each cement and fly ash combination, the following chemical activators were added (dosage refers to total cementitious):

- MA.G.A. activator at a dosage of 250 ppm
- MA.P.E. activator, type A at a dosage of 2000 ppm
- MA.P.E. activator, type B at a dosage of 2000 ppm

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

Strength values are reported in the following tables. The first table refers to the first clinker mixed with the different fly ashes, the second table refers to the second clinker. Each cement was coded according to the codenumber of the fly ash used.

In all cases the additives give good/very good strength enhancement at early ages, with less pronounced effect at 28 days. This is what is normally desired with fly ash cement for the reasons detailed above.

Table 3a – Clinker C4564 Compressive strengths (EN-1961/), MPa

Sample		1d str	%	2d str	%	28 str	%
FA C4672	blank	12.7		24.0		52.4	
FA C4672	MA.G.A. activator	13.7	7.9	23.9	0.4	52.6	0.5
FA C4672	MA.P.E. activator, type A	14.7	15.7	25.4	5.8	52.5	0.3
FA C4672	MA.P.E. activator, type B	16.0	26.0	26.5	10.4	52.6	0.5
FA C4736	blank	13.1		23.0		53.3	
FA C4736	MA.G.A. activator	13.4	2.3	23.8	3.5	53.7	0.8
FA C4736	MA.P.E. activator, type A	15.0	14.5	24.8	7.8	53.6	0.6
FA C4736	MA.P.E. activator, type B	15.9	21.4	25.1	9.1	53.6	0.7
FA C4737	blank	11.9		22.2		47.9	
FA C4737	MA.G.A. activator	12.8	7.6	22.9	3.2	48.2	0.6
FA C4737	MA.P.E. activator,	14.2	19.3	23.8	7.2	49.7	3.8
FA C4737	MA.P.E. activator, type B	14.5	21.8	24.3	9.5	48.7	1.7
FA C4738	blank	10.6		23.6		53.6	
FA C4738	MA.G.A. activator	13.4	26.4	25.3	7.2	56.8	6.0
FA C4738	MA.P.E. activator, type A	15.0	41.5	26.4	11.9	54.4	1.5
FA C4738	MA.P.E. activator, type B	15.3	44.3	26.2	11.0	53.7	0.2

Table 3b – Clinker C4705 Compressive strengths (EN-1961/), MPa

Sample		1d str	%	2d str	%	28 str	%
FA C4672	blank	13.4		23.2		49.5	
FA C4672	MA.G.A. activator	13.6	1.5	24.3	4.7	49.8	0.6
FA C4672	MA.P.E. activator, type A	15.1	12.7	24.0	3.4	49.8	0.6
FA C4672	MA.P.E. activator, type B	16.2	20.9	24.8	6.9	50.6	2.2
FA C4736	blank	13.4		22.2		45.9	
FA C4736	MA.G.A. activator	14.3	6.7	23.4	5.4	46.1	0.5
FA C4736	MA.P.E. activator, type A	14.4	7.5	23.6	6.3	48.9	6.5
FA C4736	MA.P.E. activator, type B	15.4	14.9	23.8	7.2	48.0	4.6
FA C4737	blank	12.8		22.6		46.0	
FA C4737	MA.G.A. activator	13.7	7.0	22.9	1.3	48.0	
FA C4737	MA.P.E. activator, type A	14.4	12.5	22.8	0.9	46.8	4.3
FA C4737	MA.P.E. activator, type B	15.1	18.0	24.5	8.4	47.1	2.4
FA C4738	blank	13.9		22.7		50.6	
FA C4738	MA.G.A. activator	14.6	5.0	23.7	4.4	50.6	0.0
FA C4738	MA.P.E. activator, type A	15.4	10.8	24.2	6.6	50.9	0.6
FA C4738	MA.P.E. activator, type B	15.8	13.7	25.1	10.6	50.9	0.6

Despite the fact that after 28 days the strengths tend to reach the same values between the blank and the added samples, microscopic investigation with ESEM shows that the hydration products structure is different. This means that the additives are able to modify the structure due to the different speed of reaction in the first days of hydration. In fact, the higher is the strength increasing effect at early ages, the higher is the density of the hydration products. Images (figure 1a-d) clearly show this trend in the scale
blank < MA.G.A. activator < MA.P.E. activator, type A < MA.P.E. activator, type B.
Less voids are present going from blank to MA.P.E. activator, type B.

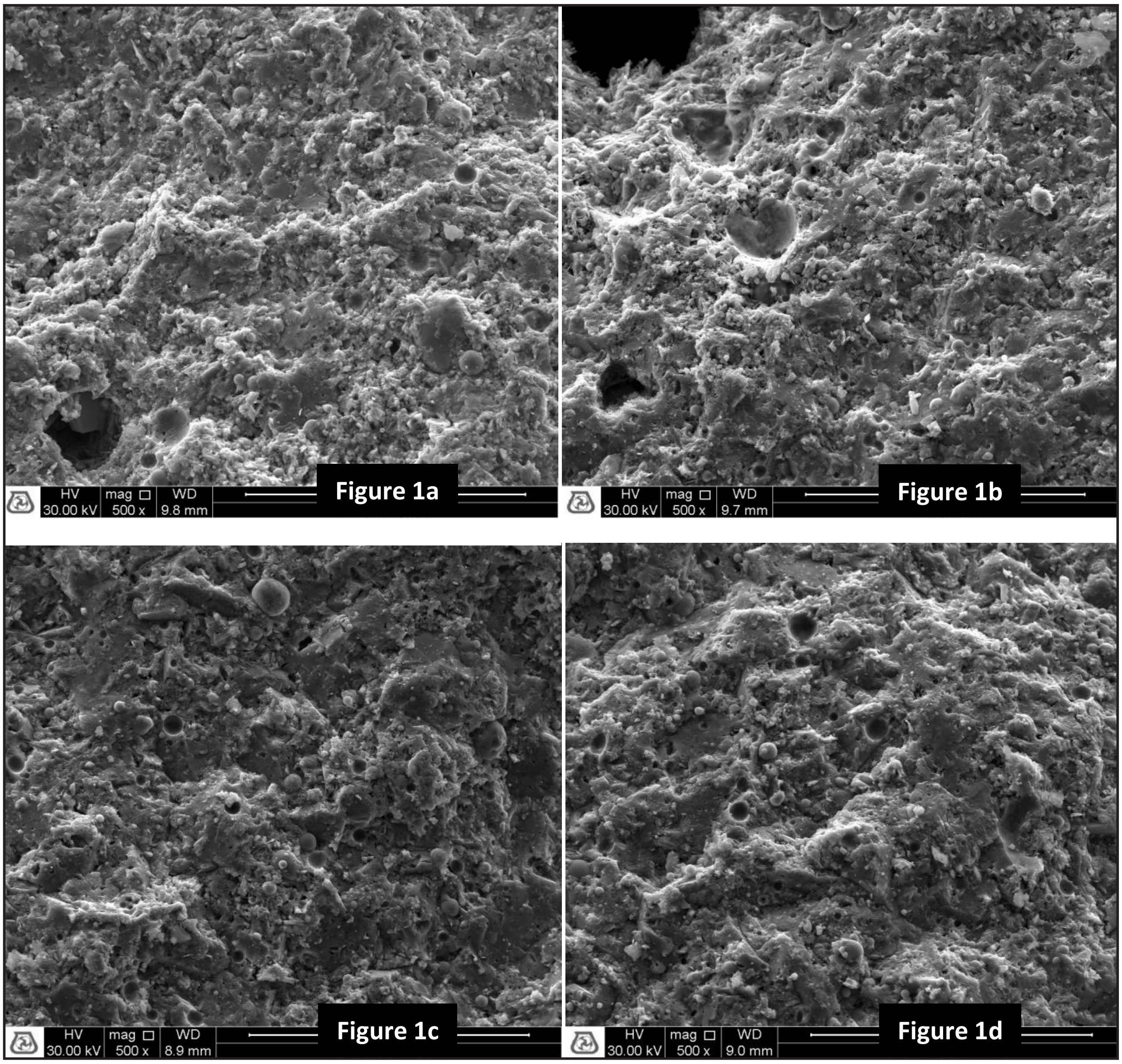


Figure 1: SEM images of hydrated cement pastes. 1a: blank sample – 1b: sample treated with MA.G.A. activator – 1c: sample treated with MA.P.E. activator, type A – 1d: sample treated with MA.P.E. activator, type B

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 2a-d).

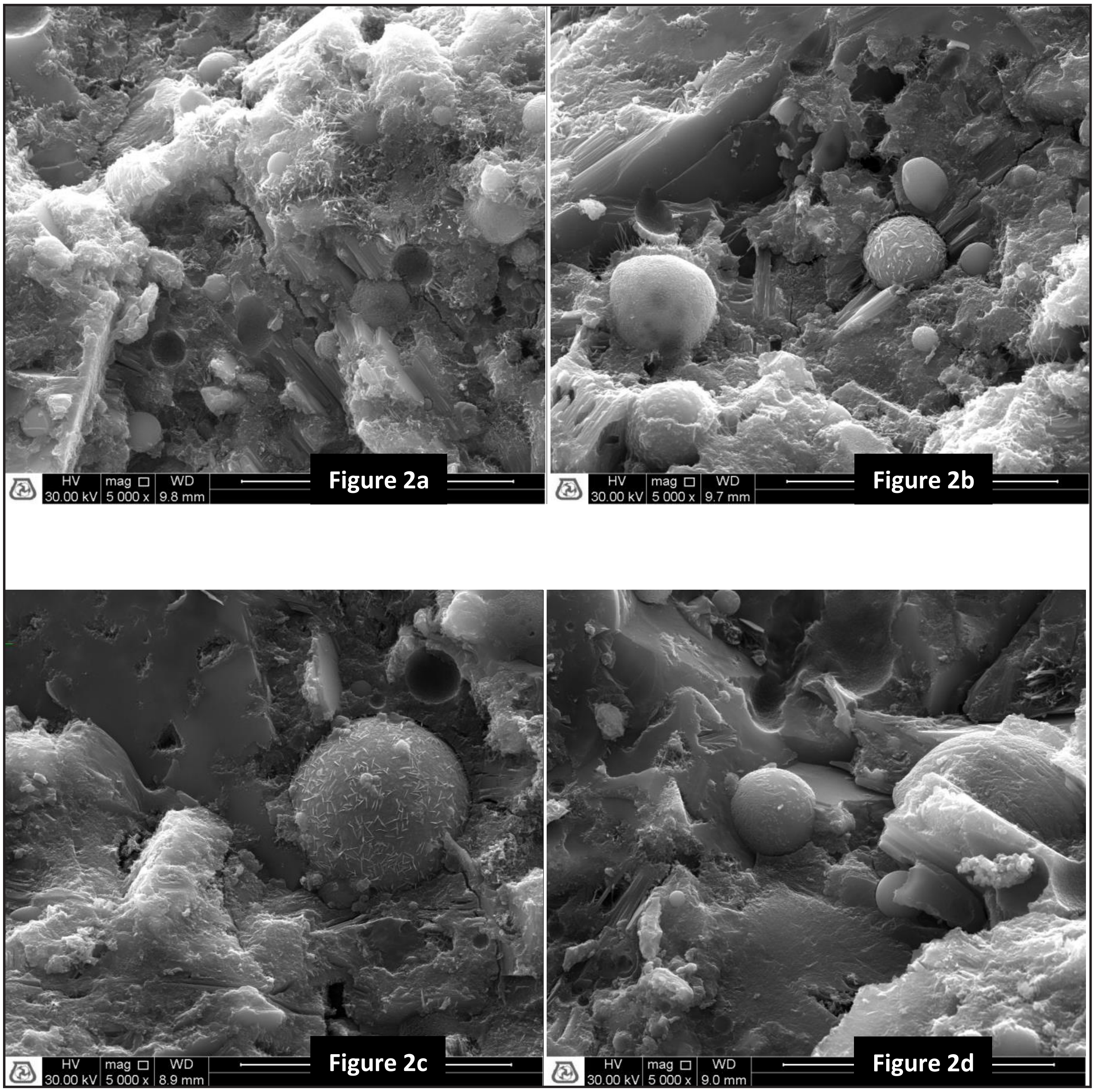


Figure 2- SEM images of hydrated cement pastes. 2a: blank sample – 2b: sample treated with MA.G.A. activator – 2c: sample treated with MA.P.E. activator, type A – 2d: sample treated with MA.P.E. activator, type B

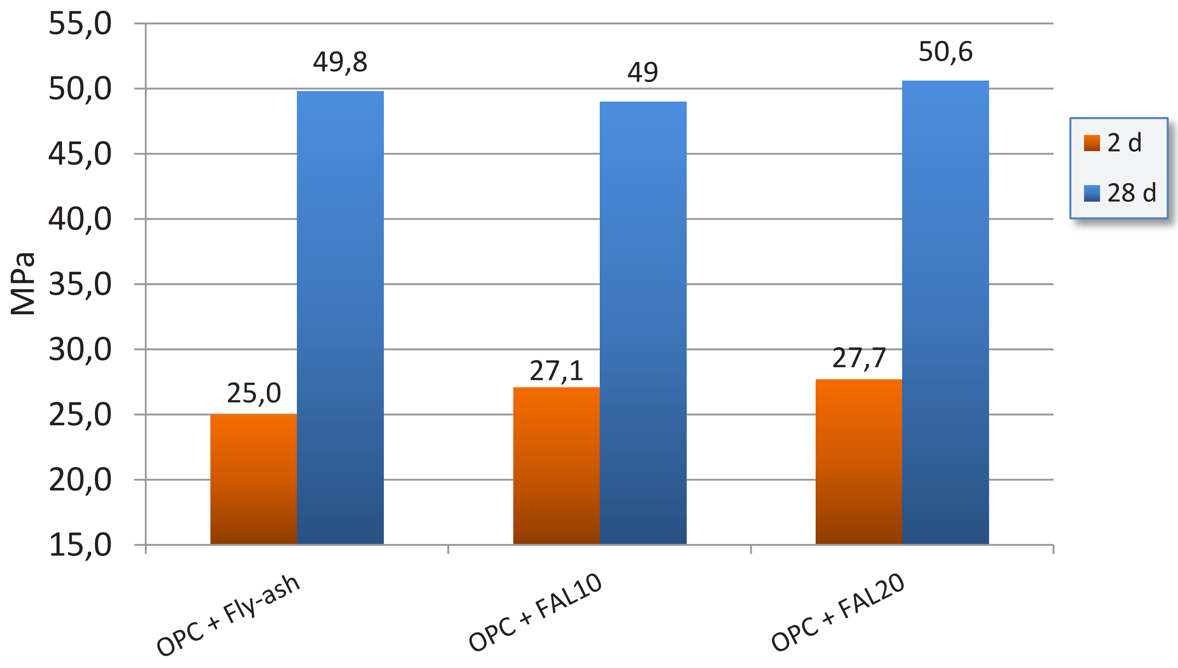
3 Fly ash cements optimisation with grinding and additives

An additional series of investigations has been carried out by grinding fly ash together with limestone, with the scope of enhancing its performance from the strength development point of view, so to allow for higher clinker substitution.

An OPC was ground in the lab (with only clinker and natural gypsum), and three different mineral additions were prepared:

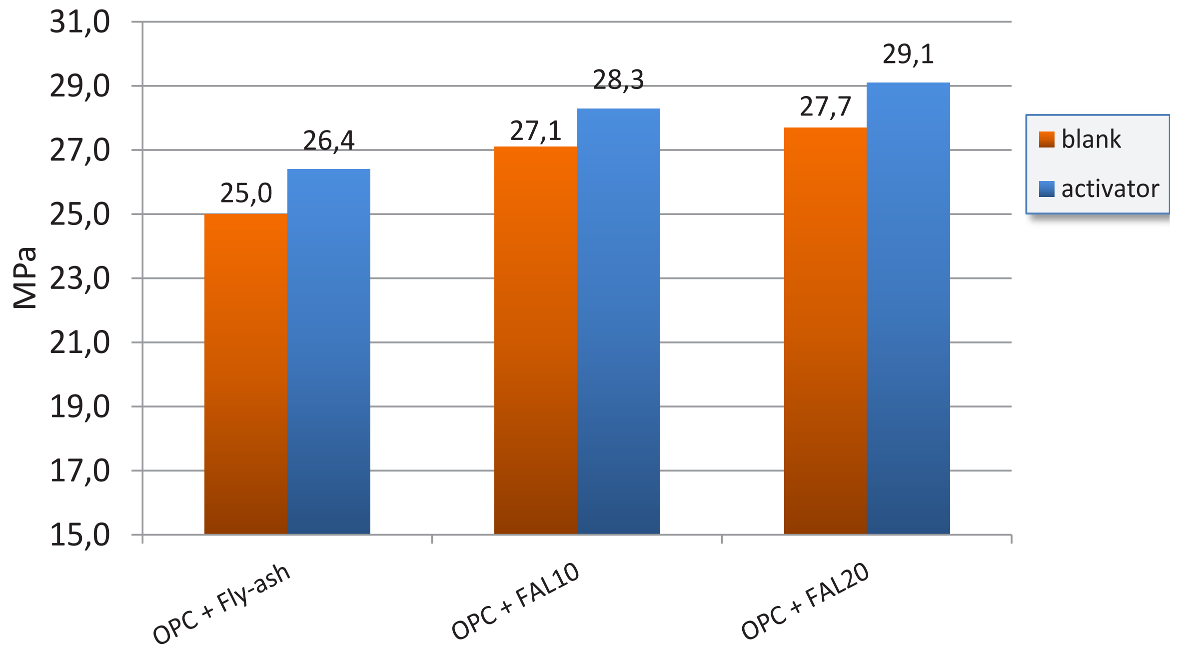
a) Standard fly ash (i.e. not treated or ground)
b) A mix of 90% fly ash and 10% limestone, ground in the lab (FAL10)
c) A mix of 80% fly ash and 20% limestone, ground in the lab (FAL20)

As above, composite cements were prepared by dry mixing the OPC with each of the additions (80% OPC and 20% addition). Strengths of the mixes (according to EN-1961/) are reported in the following graph:



Graph 1 – Strengths of blended cements with different mineral additions

As can be seen, the modified additions enhance 2d strength significantly, while 28 days are not affected as much. The same mixes were treated with an activator (MA.P.E. activator, type B) added in mixing water: results show very clearly that combining chemical activation with the use of the modified mineral addition the effect is outstanding. Early strength data is shown in the following graph:



Graph 2 – Early strengths of blended cements with different mineral additions and MA.P.E. activator, type B

Strength increase at early ages is maximised, so that an even higher clinker substitution is possible.
The reason of the enhanced reactivity can be attributed to the grinding of the fly ash with limestone: the fly ash spheres are in fact broken during grinding, hence exposing more surface to hydration. This can clearly be seen in the following electronic microscope pictures.

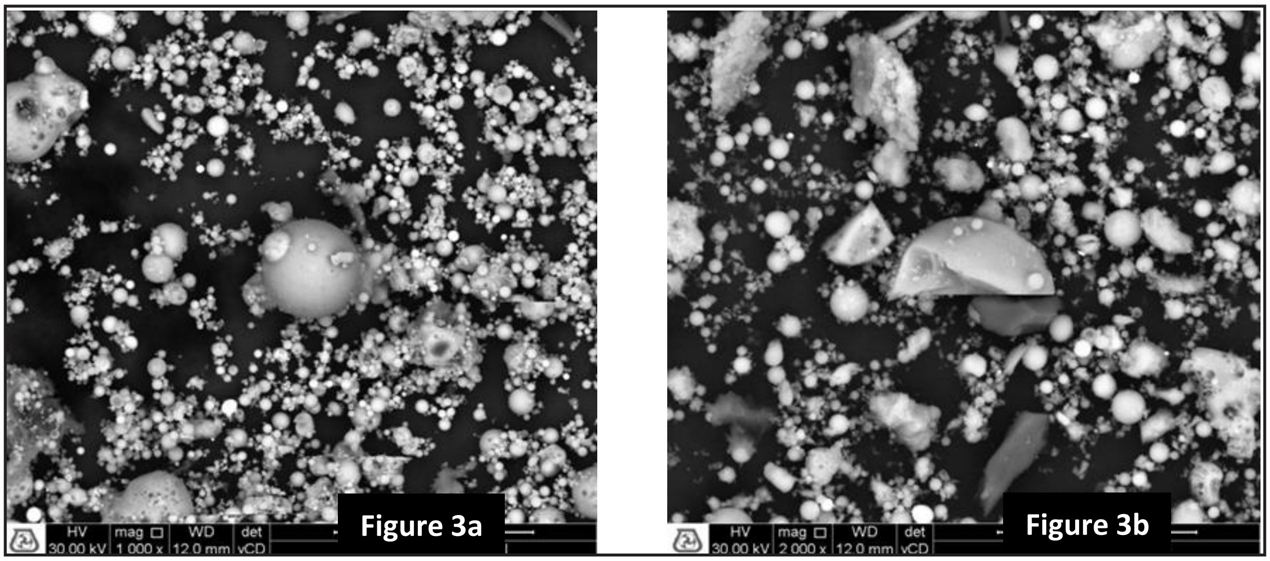


Figure 3- SEM images of mineral additions – a) fly ash, unground; b) Fal20, ground

In addition, the presence of the fine limestone provides nucleation surface for the hydration reaction, facilitating the development of the early strengths.

The process is additionally sped up by the presence of the chemical activator, resulting in the outstanding strength increase.

Further investigation on the ground additions seems to indicate that in ground fly ashes the amount of unburnt carbon is decreased. Loss on ignition data is reported in the following table:

Addition	Loss on ignition
Unground fly ash 2.48%	**2.48%**
Ground fly ash	**1.22%**

Of course, the less unburnt carbon is present, the higher is the reactivity of the fly ash, so this can provide an additional advantage to the strength development.

4 Conclusions

A study on fly ash cement activation was carried out, focusing on early strength enhancement, so to allow for increase of clinker substitution in composite cements. Chemical activators provide a very good solution to the problem; however maximum effect can be obtained by using them and at the same time using fly ashes ground together with a small amount of limestone.

These results are given by the combination of three effects:

a) The chemical effect on cement hydration promoted by the cement additive (MA.G.A. or MA.P.E.)
b) The physical effect of the enhanced available surface of the fly ash
c) The physical effect of the presence of additional surface provided by the limestone

References

[1] Lutze D., vom Berg W. (ed.), 2004. Handbuch Flugasche in Beton, Duesseldorf: Verlag Bau + Technik.

[2] Prause B., 1991. Die Reaktion von Steinkohlen-Flugasche in hydraulisch und karbonatisch aushaertenden Bindemitteln. Kurzberichte aus der Bauforschung, 86, 629- 633.

[3] Richartz W., 1984. Zusammensetzung und Eigenschafen von Flugaschen. Zement-Kalk-Gips, 37, 62- 71.

[4] Kautz K., Prause B., 1986. Mineralogisch-chemische und technologische Eigenschaften von Steinkohlenflugaschen aus unterschiedlichen Feuerungen. VGB Kraftwerkstechnik, 66, 1194- 1199.

[5] Fraay A. L. A., 1990. Fly ash, a pozzolan in concrete, PhD thesis, TU Delft.

[6] Huettl, R., 2000. Der Wirkungsmechanismus von Steinkohlenflugasche als Betonzusatzstoff, PhD thesis, Bauingenieurwesen und Angewandte Geowissenschaften, TU Berlin.

[7] Lee C. Y., Lee H. K., Lee K. M., 2003. Strength and microstructural characteristics of chemically activated fly ash-cement systems, Cem. Concr. Res. 33 (3), 425- 431.

[8] Mueller H. S., Guse U., Schneider E., 2005. Leistungfaehigkeit von Betonen mit Flugasche, Beton- und Stahlbetonbau, 100, 693- 704.

[9] Gartner E., Myers D., 1993. Influence of tertiary alkanolamines on Portland cement hydration, J. Amer. Ceram. Soc., 76, 1521- 1530.

[10] Sandberg P., 2008. Effect of cement additives and chemical admixtures on cement hydration kinetics, Nanocem Articles, 1- 4.

[11] Schulze S. E., Rickert J., 2011. Influences of the chemical composition of fly ashes on their reactivity. In: Angel Palomo, Aniceto Zaragoza and Juan Carlos Lopez Aguì, ed. 13th International Congress on the Chemistry of Cement, Madrid 3- 8 July 2011.