

## Limestone and fly ash blended cements: correlation between durability, performances and particle size distribution

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### INTRODUCTION

Nowadays, considering the stringent requirements for greenhouse gas reduction, use of blended cements with low clinker content is mandatory and there is a general tendency to increase as much as possible the supplementary cementitious materials (SCMs) in cement composition or in concrete mix design. Although positive in the light of clinker reduction, high substitution levels have several side-effects such as reduced mechanical performances and, in some cases, reduced durability (e.g. lower resistance to carbonation [1]). There is a strong drive for innovation with the purpose to improve performance of highly substituted cements and to allow extremely low clinker factors. Two technologies (that can be used in combination) are available for improvement of blended cements performances:

1. Control of particle size distribution (PSD) through clinker/SCMs grinding. For pozzolanic-type additions (blast furnace slag, fly ash, pozzolan), the fineness increase promotes a faster and more complete formation of secondary C-S-H after reaction with portlandite released during C3S hydration. Ideally, using separate grinding of clinker/gypsum and SCMs, it would be possible to optimize the manufacturing process selecting the most suitable PSD for a specific strength development.
2. Use of chemical additives to accelerate hydration. Grinding aids/performance enhancers are regularly used during modern cement manufacturing, with the purpose to reduce energy consumption related to grinding process and to improve cement quality. Hydration in presence of selected chemical additives proceeds in a different way with respect to cement produced without additives, and this may remarkably improve cement properties.

In this paper we describe both approaches, with reference to highly substituted limestone and fly ash blended cements. Microscopy techniques give a relevant contribution to the study of these cement-based systems.

## EXPERIMENTAL

Two samples of highly substituted fly ash blended cements (30% FA content, CEM II/B-V according to European Standard EN 197-1) were reproduced by blending a commercially available CEM I (95% clinker + 5% gypsum) and two samples of the same fly ash: sample 1 was used as received, without any further grinding; sample 2 was previously ground in a lab mill. The two samples (CEM II/B-V -1- and CEM II/B-V -2-) hence have the same PSD of the clinker/gypsum part, but different PSD of the fly ash part. Fineness was measured using air-jet residuals (Hosokawa Alpine 200-LS model, pressure drop:  $4750 \pm 250$  Pa, sieving time: 6 minutes). Limestone blended cements (CEM II/B-L type, 30% limestone content) were reproduced through separate grinding and blending of CEM I and limestone. FA cement samples were hydrated without additives, while limestone cements were hydrated also with the addition (directly in mixing water during mortar or cement paste preparation) of some typical cement additives: 1) a blend of alkanolamines, dosage 300 ppm with respect to cement and 2) a combination of alkanolamine blend (dosage 300 ppm) and an inorganic accelerator (dosage: 4600 ppm with respect to cement). Mortar compressive strengths were tested according to European Standard EN 196-1 (water to cement ratio 1:2, cement to sand ratio 1:3, fresh mortar is casted in 4x4x16 cm moulds, demoulded after 24 h and cured in water for the required time). The reproducibility of compressive strengths test (expressed as% standard deviation over average) can be considered  $\pm 3\%$ . Hydration was studied through preparation of cement pastes ( $w/cm = 0.5$ ), ground after required curing time and analyzed with X-Ray Diffraction (PANalytical X'pertPro MPD diffractometer with theta-theta geometry equipped with an X'Celerator detector working with the CuK radiation in the 2theta range 5-80 degrees). Quantitative analyses have been obtained by Rietveld method using the Bruker AXS software package TOPAS 6. Samples morphology was observed by Philips XL30 ESEM-FEG (Environmental Scanning Electron Microscope, equipped with a Field Emission Gun) on fresh fractured samples in HI-VAC mode after Pd-Au Sputtering. Total water bound in hydrates and calcium hydroxide after selected curing time were determined through TGA - Thermo Gravimetric Analysis (Simultaneous Thermal Analysis Netzsch STA Jupiter F1). For FA cements, an accelerated carbonation test was used to check carbonation resistance: mortar prisms (with  $w/cm = 0.55$ ) were cast, wrapped in polyethylene after demoulding and stored for 13 days. Polyethylene was removed and specimens stored for three weeks at 20°C/50% humidity and natural CO<sub>2</sub> (below 400 ppm). After this, specimens were exposed to accelerated carbonation (1% CO<sub>2</sub>, 20 °C and 60% relative humidity) for 8 weeks. CO<sub>2</sub> diffuses in the mortars from the edge to the core [1] and the penetration depth can be checked by cutting the prisms and treating the internal surface with phenolphthalein (1% in ethanol). On the external border (fully carbonated, where pH is lower than 8) no colour change is noticed. The penetration depth can be quantified by measuring the border thickness with a ruler. Usually an accuracy  $\pm 0.5$  mm can be assumed.

## RESULTS AND DISCUSSION

Table 1 summarizes the fineness, carbonation and mortar strengths results of fly ash blended cements.

Table 1: Fly ash fineness, strengths and carbonation of CEM II/B-V samples.

Cement	Fly ash% res. 32 mm	Mortar prism weight (g)	28 days compressive strength (MPa)	Carbonation depth (mm)
CEM II/B-V -1-	54.10%	569 g	43.9 MPa	10.1
CEM II/B-V -2-	4.30%	581 g	56.5 MPa	7.6

As expected, the higher fly ash reactivity (due to increased fineness) in cement 2 promotes much higher strengths (+29% after 28 days curing with respect to cement 1). The different particle size distribution seems to allow also a better compacting of the cement/sand/water mix in the mold, resulting in a higher mortar density and this may also be relevant for strength development. Carbonation depth is reduced: the increased reactivity of fly ash has probably consumed more portlandite for secondary C-S-H formation (as evidenced with XRD, where the sample with unground fly ash contains 25% portlandite while in the sample with ground fly ash portlandite goes down to 21%), leaving less calcium hydroxide for CO<sub>2</sub> fixation. In addition, the higher mortar density has probably promoted a more compact microstructure, reducing the diffusion of CO<sub>2</sub> in the mortar core. SEM images show the presence of smaller and broken fly ash particles in the sample prepared with ground fly ash, as well as surface etching of fly ash and hydration products (Figure 1). The effect of chemical additives on limestone blended cements is summarized in Table 2.

Table 2: details on limestone blended cements composition, chemical additives and early strengths.

Cement	Details	Additive	24 h strengths	2 d strengths
CEM II/B-L -A-	3.5%	-	7.1 MPa	12.6 MPa
	gypsum, 30%	300 ppm Alkanolamine blend	7.2 MPa	13.2 MPa
	limestone	300 ppm alkanolamine blend + 4600 ppm accelerator	10.0 MPa	16.4 MPa
CEM II/B-L -C-	4.9%	-	6.8 MPa	11.7 MPa
	gypsum, 30%	300 ppm Alkanolamine blend	8.1 MPa	13.4 MPa
	limestone	300 ppm alkanolamine blend + 4600 ppm accelerator	8.3 MPa	15.9 MPa

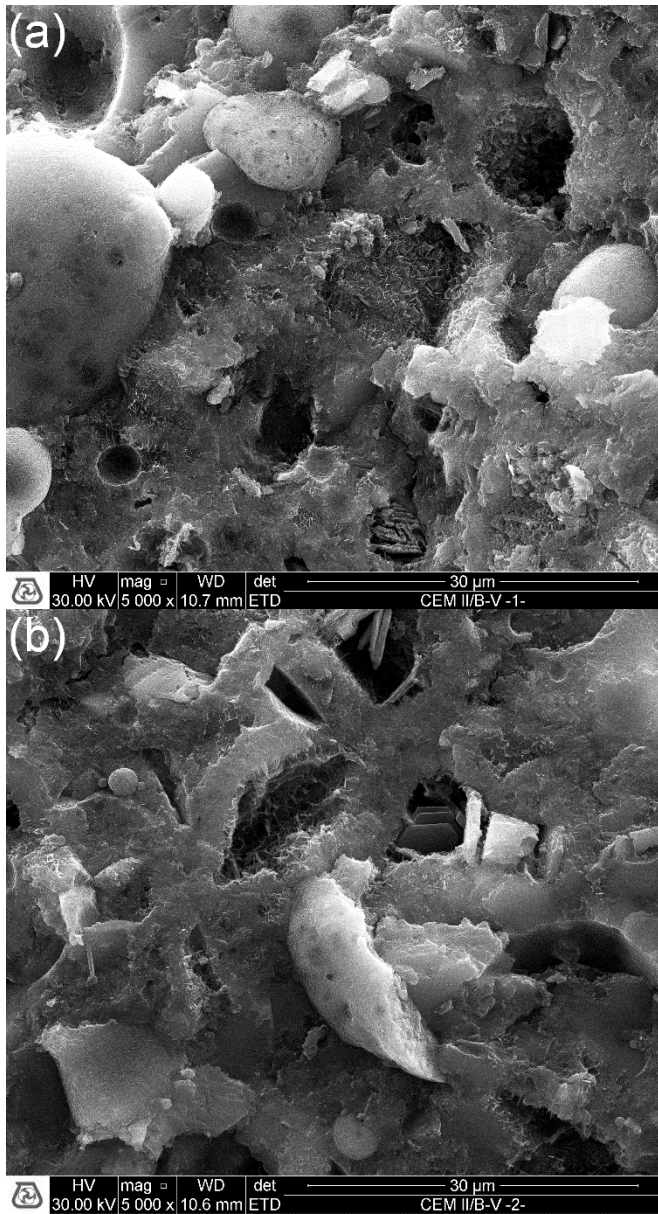


Figure 1: SEM micrographs: (a) hydrated CEM II/B-V pastes, unground and (b) ground FA.

There is a general improvement in mechanical performances, with the combination of alkanolamine blend and inorganic accelerator. Hydration analysis after 24 h of curing allows a better understanding of the chemical effect of additives and the reason behind strength increase (Table 3).

Table 3: XRD and TGA hydration data of limestone blended cements

Cement	Additive	C <sub>3</sub> S 24 h	C <sub>3</sub> A 24 h	Ca(OH) <sub>2</sub> XRD	Ca(OH) <sub>2</sub> TGA	Ettringite	Mono-carb.	Hemi-carb.
II/B-L -A-	-	11.8	3.2	11.5	9.8	4	0	0
	Alk	9.7	2.1	12.1	9.1	4.3	1.3	5.7
	Alk+Acc	8.8	1.6	13.2	9.3	5.6	3.2	4.2
II/B-L -C-	-	8.5	2.1	10.7	9.3	8.1	0.2	1
	Alk	8.3	1.7	10.4	8.4	7.9	2.4	6.7
	Alk+Acc	9	1.7	11.9	8.9	8	2.7	5

Basically, the presence of an additive promotes an acceleration of all the reactions involving aluminum: C<sub>3</sub>A consumption and the conversion of Aft to Afm phases. Considering the presence of high limestone substitution, the Afm phases are basically monocarboaluminate and hemicarboaluminate [2]. A correlation between early strengths and monocarboaluminate can be observed, while portlandite content developed because of C<sub>3</sub>S hydration looks similar in all samples. This suggests that mechanical performance after 24 h curing are mainly related to Afm phases, strongly affected by the presence of chemical additives. C-S-H and C<sub>3</sub>S hydration are expected to give relevant contribution to strengths at later ages. SEM images of 24 h hydrated CEM II/B-L are particularly interesting (Figures 2 and 3). In the bulk microstructure the original cement grains surrounded by needle-shaped ettringite and C-S-H are visible. In samples treated with additives, the presence of hexagonal plates (probably portlandite or mono- hemi-carboaluminate [3]) becomes more evident (Figure 2). Ettringite morphology in "blank" sample (Figure 3) shows longer needles (3-5  $\mu\text{m}$  length), while in samples treated with additives ettringite crystals look shorter and more distributed around cement grains (Figure 2). This is probably related to presence of alkanolamines, well known complexing agents for Al<sup>3+</sup>, that have an impact on nucleation and growth of Aft and its conversion to Afm, thus modifying the morphology of crystals [4].

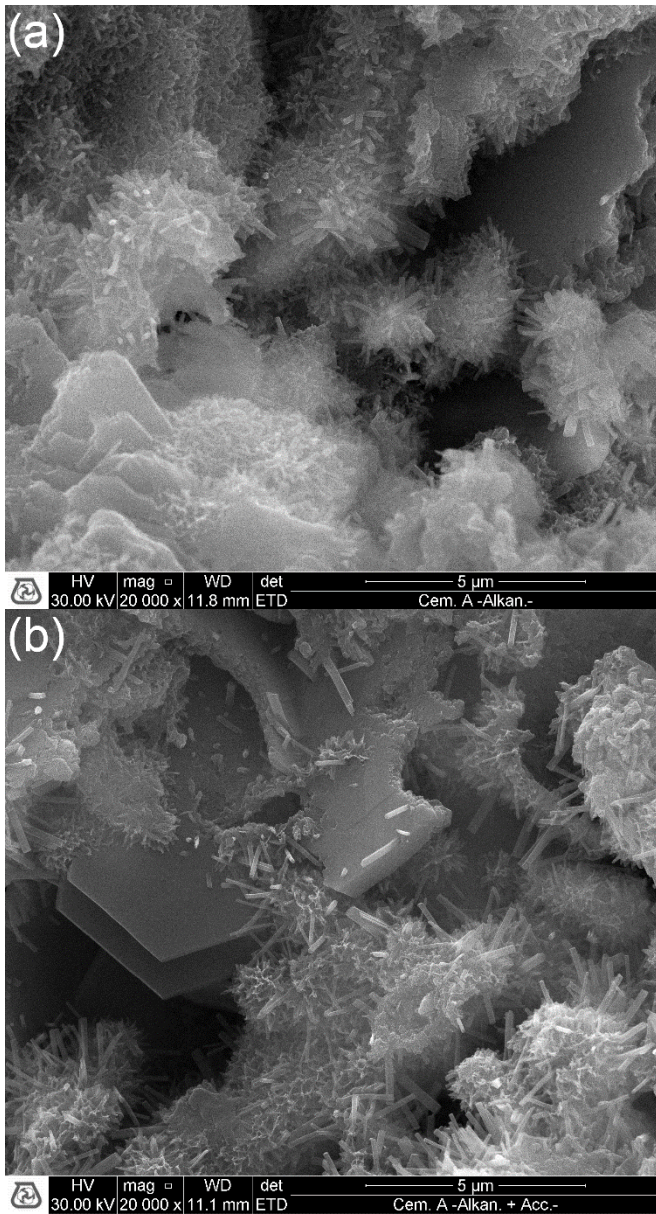


Figure 2: SEM micrographs of hydrated CEM II/B-L pastes (a) w/ alkanolamine blend, and (b) w/ alkanolamine blend + accelerator. Shorter and more distributed ettringite needles can be seen in samples treated with additives as compared to the blank paste of Figure 3. Hexagonal plates (not present in blank sample) may be identified as monocarbonate.

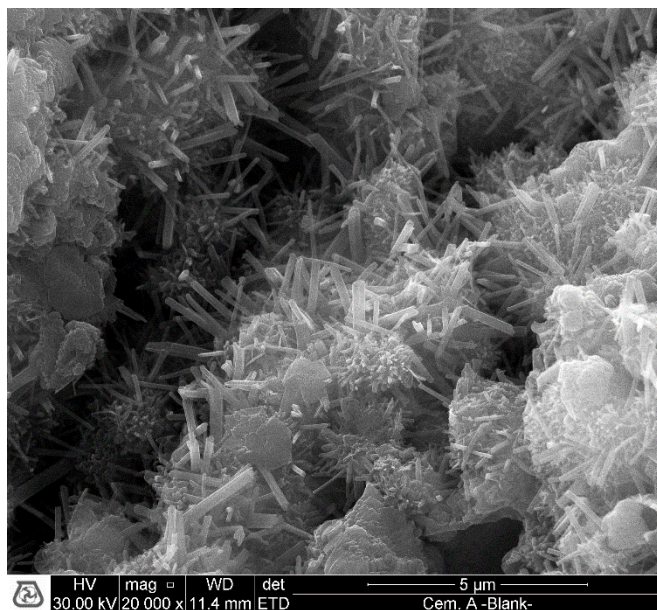


Figure 3: SEM micrograph of “blank” hydrated CEM II/B-L paste.

## CONCLUSION

Several technologies are available to improve performance of highly substituted blended cements. Through control of fineness of SCMs (e.g. manufacturing cements by separate grinding of clinker/gypsum and fly ash, followed by blending) and the use of suitable chemical additives, the mechanical and durability performances of blended cements can be remarkably enhanced, allowing higher substitution levels. This could be related to an increasing of the hydration degree and to a higher mortar density, as pointed out in fly ash cements. As far as limestone cements are concerned, the presence of chemical additives strongly affects their hydration behavior and strengths development, promoting a faster conversion Af<sub>t</sub> to Af<sub>m</sub>.

## REFERENCES

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