

Investigation on the reactivity of cement additives in blended cements

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Abstract

Due to the stringent requirements for the reduction of greenhouse gases emissions in the cement industry, the production of blended cements is rapidly increasing. The use of limestone as mineral addition, established in some countries since many decades and recognized in technical standards, has only recently been subject of scientific attention. Wrongly considered as an inert filler, limestone can influence cement hydration leading to the formation of Aft and Afm phases based on carbonate ion. A thermodynamic approach allowed to study the equilibrium between carbonate, sulfate and aluminate phases and to predict the effect of limestone addition on cement performances. Considering that several chemical additives have a strong influence on aluminate hydration, it is expected that the aforementioned equilibrium is modified by their presence. In this paper the effect of some selected cement chemical additives (widely used in the formulations of grinding aids and performance enhancer) on the hydration and physico-mechanical behavior of limestone blended cements is deeply investigated. Thanks to the combination of quantitative X-Ray diffraction and calorimetric techniques with the measurement of mortar properties, some hypothesis on the mechanism of action of cement additives are proposed.

Originality

The originality of this work lies in the detailed study of the relations between limestone, sulphate and aluminate content and the performances of cement additives in terms of compressive strength increase. As far as we know there are no papers dealing with this particular concept with specific reference to alkanolamine-based chemical additives.

Keywords: Limestone blended cement, grinding aids, chemical additives.

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1. Introduction

Manufacturing process of Portland cement is standardised and widely described in several publications (Alsop, P., 2001). Raw materials (usually limestone and clays) are quarried, then properly blended and ground in order to prepare the so-called raw mix. This is used as feeding for the pre-heater tower and kiln, where silica and lime (with alumina/iron oxides used as flux) react in a high temperature process to form the calcium silicates that compose the Portland clinker.

Clinker is then finely ground together with gypsum and secondary mineral additions (such as limestone, fly ash, granulated blast furnace slag, natural or artificial pozzolans) in order to obtain the well-known grey powder usually referred to as Portland cement, used by millions of construction workers as hydraulic binder in concrete, mortars, screeds, grouts and many others masonry applications.

Since the beginning of Portland cement manufacturing, the use of mineral additions that could reduce production costs has always been an important issue. Nowadays, considering the stringent requirements in greenhouses gases reduction, blended cements with low clinker content are mandatory. Starting from the ancient Roman Empire (that made use of Central Italy pozzolan blended with lime in order to produce high durability hydraulic binder) to modern world, natural or local availability of secondary cementitious materials has always been the main driving force for their use. Blast furnace slag is widely used in countries with a developed steel industry. Coal power plants are often surrounded by fly ash cement production and limestone cements are widespread where good quality limestone quarries are present.

Limestone blended cements in particular are widely used in all countries following (directly or indirectly) the European Standard EN 197-1, that allows limestone addition up to 35%. In this paper we concentrate on the reactivity of limestone blended cements, with particular reference to the interaction between calcium carbonate, clinker hydration and presence of chemical additive. Indeed, for good quality blended cements the use of a suitable cement additive that can control and improve performances is mandatory. In our opinion, the investigation of the mutual interactions of clinker and limestone when chemical additives are present has received less attention that what it would deserve.

1.1 Hydration of limestone blended cements

Good reviews on several physico-mechanical parameters related to limestone blended cements, in comparison to traditional cements, can be found in several publications (Hawkins P., *et al.*, 2003 – Caldarone M., 2006 – Caldarone M., *et al.*, 2008). Results show that long and short term macroscopic performances (including compressive strengths, drying shrinkage, durability) are not significantly affected by limestone additions up to 10-15%. Above this level, the decrease in clinker content can hardly be counterbalanced.

A deep investigation on the hydration details of limestone blended cements can be found in several high-level publications by Matschei, Lothenbach and Glasser (Matschei T., *et al.*, 2007a, 2007b, 2007c – Lothenbach B., *et al.*, 2008). After the evaluation of solubility and thermodynamic data for several hydrated cement phases (including Aft and carbonate-based AFm), it had been possible to conclude that the presence of carbonate stabilise monocarbonate, thus reducing the stability of monosulphate. The excess of sulphate is bound in ettringite that, thanks to high crystallisation water content, contributes to increase the solid mass of cement paste. This is a further reason for the increase (or not decreased) compressive strengths found when part of clinker is substituted with limestone, in addition to the well-known filler effect related to fine particle size distribution of limestone.

1.2 Target of the present investigation

Modern cement production could not be performed without the use of specific organic process additives. Grinding aids as well as performance enhancers based on alkanolamines are used worldwide in the cement industry. Triethanolamine (TEA) is probably today's most widely used alkanolamine for the formulation of cement additives. While the addition of TEA-based additives during cement grinding process (usually in very low dosages: only 0,01 to 0,05%) positively affects the resulting cement's particle size distribution, TEA exhibits in most cases a different behaviour as performance

enhancers. TEA is reported to accelerate the hydration of C_3A (Ramachandran, 1976). In literature there are some discrepancies about the influence on setting time and compressive strengths, probably due to the fact that the effect of TEA on cement hydration is strongly related to dosage (Dodson, 1990), but in the end TEA can be considered as an early compressive strength enhancer, particularly at dosages commonly used during cement production.

The accelerating effect of TEA on the hydration of C_3A highlighted by several authors (Ramachandran, 1976, Dodson, 1990) may be explained considering that TEA is an effective chelating agent in alkaline media for Al^{3+} ion. This has been also demonstrated through the use of ^{13}C NMR spectroscopy (Scott et al., 1990). Complexation of Al^{3+} may increase the dissolution rate of C_3A and may accelerate all the reactions involving Al^{3+} .

Purpose of the present paper is the investigation of the effect of TEA on the equilibrium among aluminates, AFm and Aft during the hydration of limestone blended cements and deeply described in the aforementioned publications.

2. Experimental

2.1. Cements preparation and analysis

OPC (CEM I according to European Standard EN 197-1) was reproduced by grinding clinker and gypsum in a lab ball mill. Two samples of limestone blended cements were reproduced by mixing CEM I and ground limestone (first sample: 90% CEM I + 10% limestone, second sample: 80% CEM I + 20% limestone, on a mass basis – both cements can be considered CEM II/A-L type according to EN 197-1). Separate grinding and interblending of CEM I and limestone allows maintaining the same clinker particle size distribution and the same sulphate/clinker ratio in all cement samples.

In table 1 the chemical and mineralogical composition of CEM I is reported, while in table 2 details of limestone composition are summarized. For the assessment of chemical and mineralogical composition of CEM I respectively X-Ray fluorescence (Bruker AXS S8 Tiger), thermogravimetric analysis (TGA Netzsch TG209F1 Iris) and quantitative X-Ray diffraction (QXRD) 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 $CuK\alpha$ 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).

CEM I contains some calcite and portlandite (calcium hydroxide), originated from carbonation and hydration of free lime. Mineralogical data are in good agreement with chemical composition as evaluated with XRF/TGA.

Composition of limestone was determined using qualitative XRD and TGA. Calcite is the main carbonate, while dolomite is present only in traces.

Tab. 1 Chemical and mineralogical composition of CEM I /mass %

Chemical composition	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	Ca(OH) ₂	CaCO ₃	K ₂ O	SO ₃	Minor
Content	20.51	3.37	5.14	64.45	2.11	0.25	0.41	0.65	2.85	0.92
Mineralogical composition	C ₃ S	C ₂ S	C ₃ A cubic	C ₃ A ortho	C ₄ AF	CaSO ₄ ·2H ₂ O (Gypsum)	CaSO ₄ ·0.5H ₂ O (Bassanite)	CaSO ₄ (Anhydrite)	K ₂ SO ₄	Minor
Content	62.2	14.6	5.5	1.5	10.2	1.1	1.3	2.3	0.6	0.7

Tab. 2 Composition of limestone /mass %

Chemical composition	CO ₂ content	CaCO ₃ (Calcite)	Other phases
Content	39.89	90.7	Dolomite, quartz

Table 3 summarizes several data referring to the cements reproduced:

- Fineness in terms of 32 and 40 μm sieve air-jet residuals (Hosokawa Alpine LS200 N, sieving time: 6 minutes, pressure drop: 4750 ± 250 Pa, reproducibility: $\pm 1.0\%$).
- Composition in terms of mass % clinker, calcium sulphate blend, limestone, as ground in the lab mill or interblended.
- Molar bulk ratio $\text{SO}_3/\text{Al}_2\text{O}_3$ and $\text{CO}_2/\text{Al}_2\text{O}_3$, calculated on the basis of chemical analysis reported in Tables 1 and 2. The importance of the aforementioned molar bulk ratios is described in previously cited publications (Matschei T. *et al.*, 2007b).

Tab. 3 Further details on cements reproduced

Cement sample	Clinker (%)	Gypsum (%)	Limestone (%)	32 μm air-jet residual (%)	40 μm air-jet residual (%)	Molar bulk ratio $\text{SO}_3/\text{Al}_2\text{O}_3$	Molar bulk ratio $\text{CO}_2/\text{Al}_2\text{O}_3$
CEM I	95.0	5.0	--	16.0	7.7	0.7	0.1
10% Limestone	85.5	4.5	10.0	15.1	8.9	0.7	2.1
20% Limestone	76.0	4.0	20.0	18.3	9.6	0.7	4.6

2.2. Physico-mechanical tests and hydration study

24 hours mortar compressive strengths of all cements reproduced were tested (fixed W/C=0.5, according to European Standard EN 196-1). Two different sets of strengths determination were run: first without any chemical additive, second with the addition of triethanolamine (TEA - analytical grade) in mixing water dosed at 300 ppm (300 mg/kg cement). Reproducibility of mortar compressive strengths determination can be considered close to $\pm 3\%$ (expressed as standard deviation/average ratio).

Following the same schema, several hydration studies were run on hydrated cement pastes (in all cases W/C=0,5), as described here below:

- Determination of hydration heat profile, using isothermal calorimetry (TAM-Air, 23°C).
- Determination of water bound in hydrated cement phases, using thermogravimetric analysis.
- Determination of phases using QXRD/Rietveld method.

Cement pastes for TGA and QXRD were prepared by mixing cement and water (or cement and a water solution of TEA) in a closed polyethylene cup and allowed to hydrate in a conditioned room at 23°C. After the required hydration times (6, 9, 18 and 24 hours), cement pastes were ground in acetone to stop hydration, filtered and dried in oven at 50°C. A detailed summary of all the hydration studies performed is reported in Table 4.

Tab. 4 Details of hydration studies

Run	Cement sample	Chemical additive	Analysis
A	CEM I	-	Isothermal calorimetry, TGA and QXRD on quenched cement pastes at 6, 9, 18 and 24 h)
B	CEM I	300 ppm TEA	
C	10% LS	-	
D	10% LS	300 ppm TEA	
E	20% LS	-	
F	20% LS	300 ppm TEA	

3. Results and Discussion

3.1. Physico-mechanical tests

Results of compressive strengths determination are summarized in Table 5. Main comments are as follows:

- Substitution of CEM I with limestone promotes a decrease in strengths, as expected due to clinker reduction. Strength reduction on the other hand is acceptable with 10% limestone addition, but really detrimental when 20% CEM I is substituted by limestone.
- The effect of strengths increase promoted by the addition of TEA in mixing water is progressively more evident as limestone addition is increased. Although in CEM I no effect are noticed (the increase falls within one standard deviation of the mean, thus it can also be referred to natural oscillation of results), with 10% limestone addition the use of TEA allows a 10% strength increase. With 20% addition, the improvement is close to 20%. This has a deep impact on commercial cements, allowing the production of blended cements (with limestone in this case) and reducing the performance loss due to clinker reduction.
- As reported in the table, the weight of mortar specimens decreases with limestone addition (obviously, considering the lower specific gravity of limestone in comparison to CEM I), but also with TEA addition in mixing water. This weight decrease (probably related to air entrainment) happens quite often when pure chemicals are used in mixing water. Commercial cement additives are accordingly formulated in order to avoid excessive air entrainment.

Tab. 5 Results of 24 h mortar compressive strengths

Run	Cement sample	Chemical additive	Mortar specimen weight (g)	24 h mortar compressive strengths (MPa)	% strengths increase with reference to blank
A	CEM I	-	576	13.2	-
B	CEM I	300 ppm TEA	572	13.5	+2.3% ¹
C	10% LS	-	573	11.7	-
D	10% LS	300 ppm TEA	565	13.1	+12.0%
E	20% LS	-	571	9.9	-
F	20% LS	300 ppm TEA	566	11.8	+19.2%

¹Below usual reproducibility variation

3.2. Hydration studies

3.2.1 Isothermal calorimetry

Heat release in function of time as measured with isothermal calorimetry is summarized in figures 1, 2, 3 and 4. During cement hydration several thermic effects can be noticed, as recently summarized (Quennoz *et al.*, 2013). After the initial strong exothermic peak and the so-called “dormant” period, hydration of C₃S starts, followed by sulphate depletion (in properly sulphated cements this is noticed as a “shoulder” on the main silicate peak) and sometimes by a third peak, referred to further reactions of aluminates phases. In details:

- Figure 1 shows the effect of limestone substitution, that is particularly evident on the aluminates peak after main silicate peak, approximately after 14-17 hours after the beginning of the hydration. As limestone content increases, the appearance of this peak is brought forward and maximum of heat release is obtained after 14 hours in cement with 20%, while in CEM I this happens after 17 hours.
- Figure 2, 3 and 4 show the effect of TEA on CEM I, CEM I + 10% LS and CEM I + 20% LS. The organic additive accelerates the hydration, with particular reference, again, to the aluminates peak after main silicate peak.
- Total heat release (not showed) is slightly higher in all cements treated with TEA.

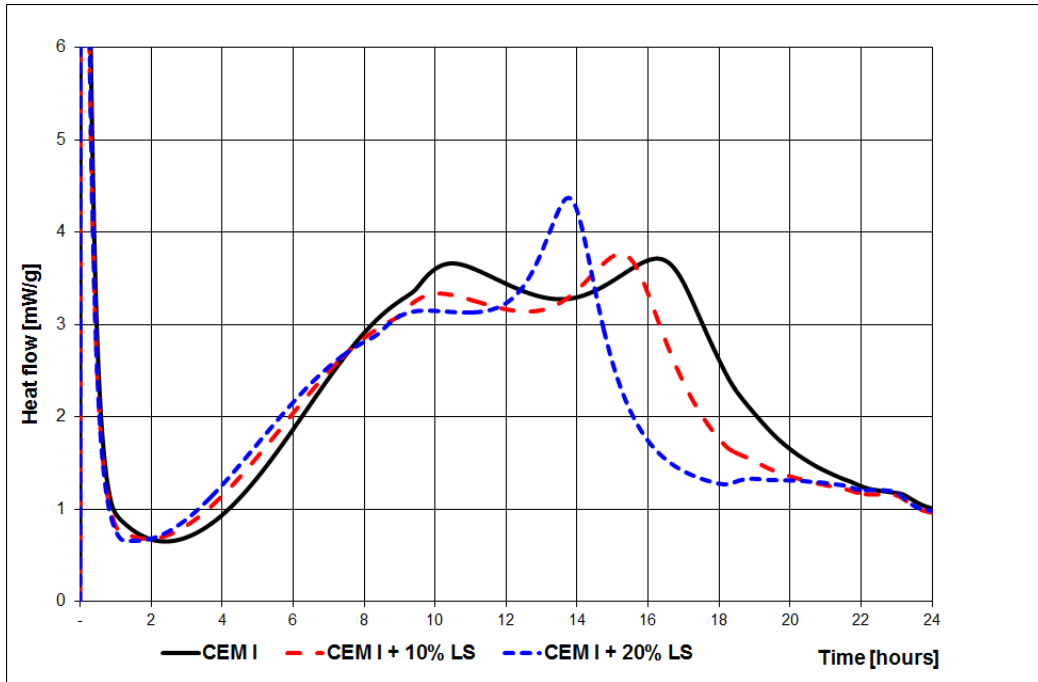


Figure 1 Isothermal calorimetry: effect of limestone addition

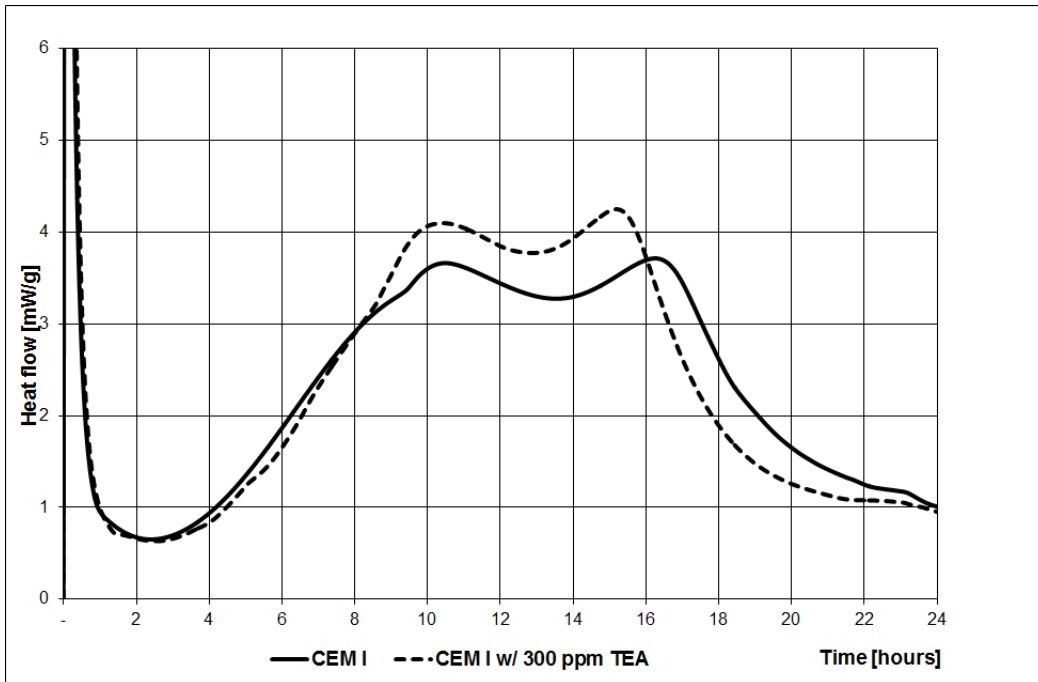


Figure 2 Isothermal calorimetry: effect of TEA on CEM I

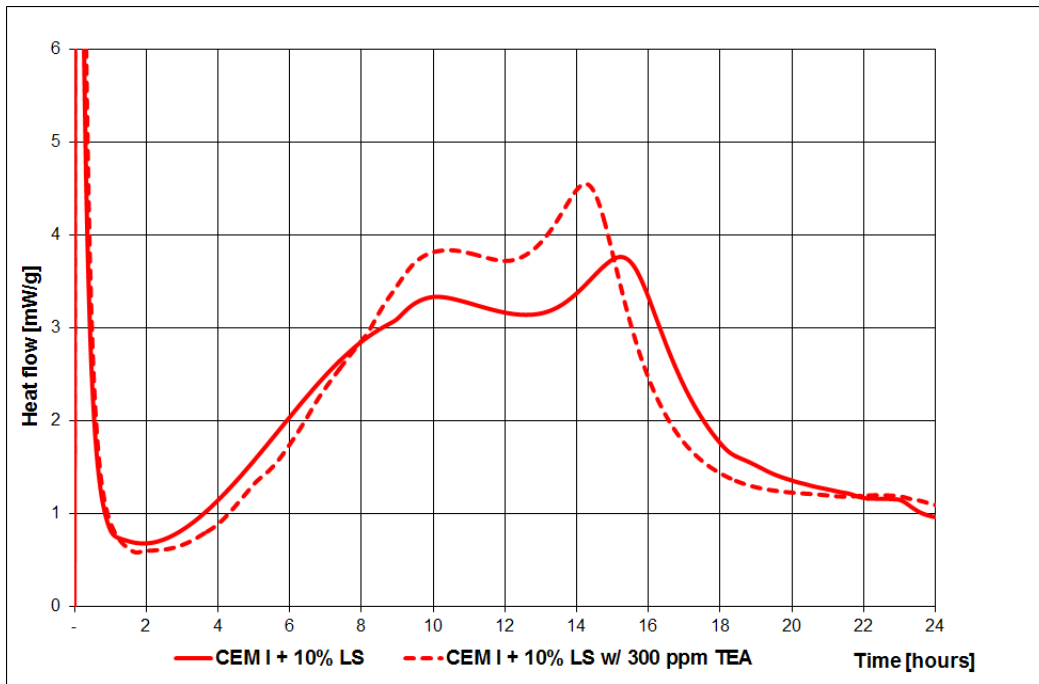


Figure 3 Isothermal calorimetry: effect of TEA on CEM I + 10% limestone

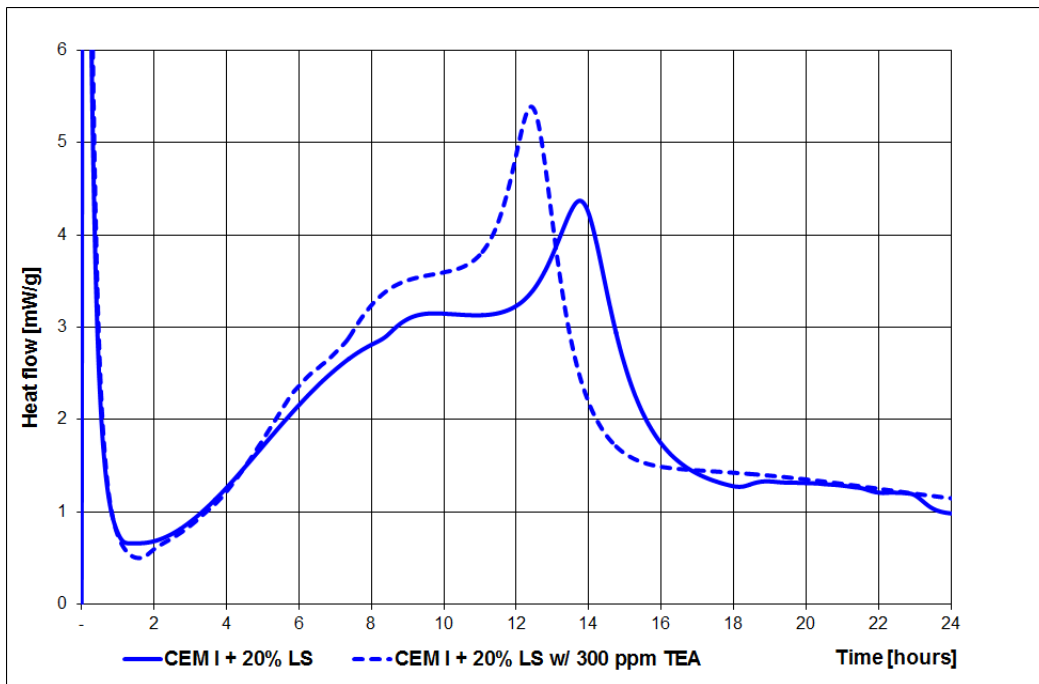


Figure 4 Isothermal calorimetry: effect of TEA on CEM I + 20% limestone

3.2.2 Thermogravimetric analysis and water bound in hydrated phases

Water bound in hydrated cement phases is lost after heating in some specific temperature intervals. It is then possible quantify up to some extent the content of some hydrated phases. Portlandite for example completely loses water in the range of 450-550°C. According to Lothenbach et al. (Lothenbach B. *et al.*, 2008), during first hours of hydration (thus when only little C-S-H is present), the weight decrease recorded between 50-110°C could be referred to ettringite, while the one at 110-140°C could be related to gypsum. On the other hand Perkins (Perkins, 2000) measured in details the TGA profile of synthesized ettringite concluding that, from a total water content close to 46%, around

33% of the mass is lost between 40-180°C. In the present paper, a cement with gypsum/bassanite blend – both phases lose water in the same range - has been used (as it happens quite often in industrial cements). It appears therefore difficult to estimate ettringite and gypsum and Aft/AFm content on the basis of the TGA profile.

Sulphate depletion is probably completed after 9 h, according to isothermal calorimetry and XRD data. We can thus consider that after 9 h from the beginning of hydration the water released in the range of 100-400°C is related to hydrated phases (AFm, Aft and C-S-H). Portlandite can be easily estimated considering the range of 450-550°C. Figures 5 and 6 show the weight decrease in the range of 100-400°C and the portlandite content calculated according to the weight decrease in the aforementioned temperature range, for samples hydrated 18 and 24 hours. In samples hydrated with TEA, there is a slight increase in the water bound in hydrated phases and a slight decrease in portlandite. In limestone blended cements, the decrease in portlandite content seems to be more evident.

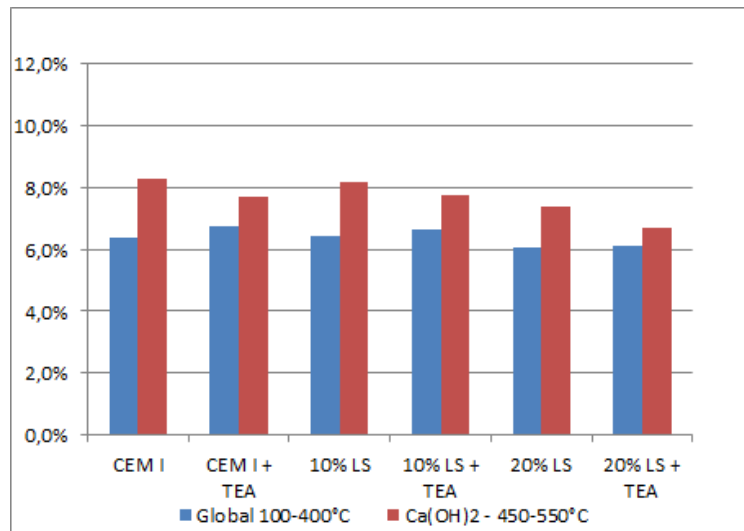


Figure 5 TGA – 18 h hydration: Portlandite and water bound in AFt/AFm/C-S-H

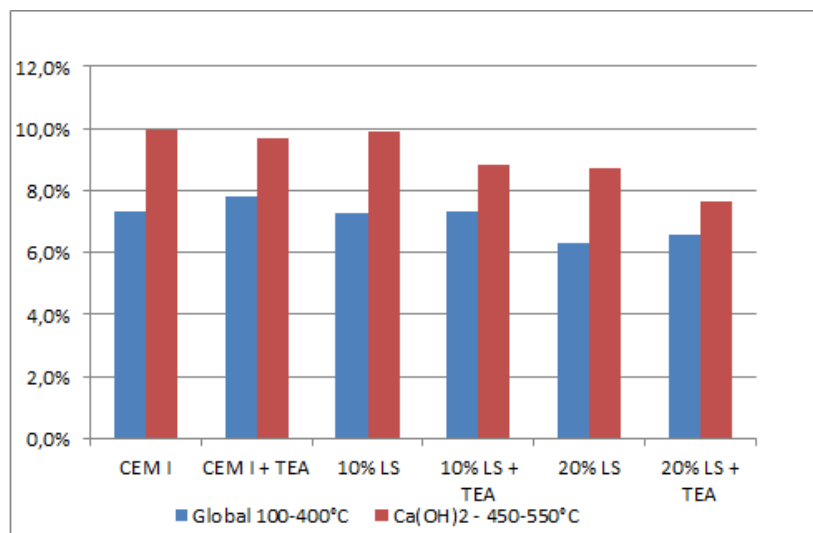


Figure 6 TGA – 24 h hydration: Portlandite and water bound in AFt/AFm/C-S-H

3.2.3 Determination of phases through QXRD

XRD analysis on hydrated cement pastes confirms the main findings of previous analytical techniques. Sulphate depletion is completed after around 9 hours from the beginning of hydration (when further peak on main silicate peak appears in isothermal calorimetry). The interval between 9 and 18 hours is

characterized by acceleration in C_3A disappearance (coherently with the strong exothermic peak in calorimetry). Ettringite is present in all samples and main AFm phases detected are monocarbonate and monosulphate, although in very low amount. It has to be pointed out that AFm phases, in particular at early hydration, have very low crystallinity, thus their quantification through Rietveld analysis is not reliable. A similar consideration can be made for ettringite. We can not exclude the presence of higher quantities of AFm and AFt, but characterized by lower crystallinity and hardly detectable with XRD.

4. Conclusion

Compressive strengths of the cement studied are clearly and positively affected by TEA when limestone content is progressively increased. The reason for these better mechanical performances is indeed hard to establish. Calorimetry data demonstrate that the presence of TEA accelerates the reactions of aluminate phases after main silicate peak, but due to intrinsic limits of the analytical methods it has not been possible to evidence whether the balance monocarbonate/monosulphate is affected by the presence of TEA. Also the ettringite level (at least the crystalline part) shows no remarkable differences. In presence of TEA, portlandite development is not affected (or is slightly reduced), thus strengths increase should not be related to higher degree of silicate hydration. Considering the hydration model proposed by Lothenbach et al., a possible reason for the strengths increase could be related to microstructural modification linked to the increase in the monocarbonate/ettringite and decrease of monosulphate when TEA is added to a limestone blended cement. Such microstructural modifications are probably related to the amorphous or low crystallinity part of AFm and AFt hydrated products.

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