PERFORMANCES OF LIMESTONE MODIFIED PORTLAND CEMENT AND CONCRETE

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1. Introduction

Fine limestone has been added to Portland cement for decades. This is normally achieved by “intergrinding” it with Portland cement clinker in the cement mill. Under normal operating conditions this will result in a surface area of the limestone fraction of between 800 and 1100 m^2/kg (depending on the *grindability* of the limestone) for a surface area of the clinker fraction of in the region of 400 m^2/kg. Less often the limestone is ground separately and blended with Portland cement. Separate addition of limestone to concrete as a clinker replacement is not widely practiced in conventional concrete, but is used as filler for modifying the rheology of self-compacting concrete.

In the early literature limestone was generally regarded as “inert filler”. For this reason it has e.g. become the main constituent in most masonry cements where high levels of replacement of the Portland cement are needed to reproduce the properties of traditional lime mortars. However, for its application in concrete, which is the primary focus of this report, the limestone’s contribution to the hydration reactions can be significant when it is co-ground with the clinker, albeit in relatively small amounts. So much so that it can arguably be classified as an SCM alongside GBFS and fly ash.

The first significant use of limestone in general purpose Portland cement took place during WWII when it was used in several European countries to cut costs and increase output (Lea, 1970). Its widespread use today can be traced back to the 1973 oil crisis, with France, which had low production of fly ash and blast furnace slag, leading the way. The Portland limestone cements in the European cement standard EN 197-1 (2001), were adopted more or less un-changed from the French standard NF P 15-301 (1981).

A systematic review of all standards and specifications for limestone and Portland limestone cements is beyond the scope of this report. The most recent and comprehensive review of this can be found in (Tennis *et al.*, 2011). Many countries allow minor clinker replacement in cement of 5 or 10% limestone, including China (10%), India (5%), Brazil (10%), and the US (5% in ASTM C150). Higher amounts are allowed in the cement standards in Europe (35%), Mexico (35%), Argentina (20%), the US (15% in ASTM C595) and Canada (15%).

Taking Europe as an example (Figures 1 and 2), where the volume of limestone used is greatest, in 2010, Portland limestone cements accounted for 27% of all cements produced, or even 46% if the CEM II M composite cements which allows mixtures of limestone and other SCMs to be considered. This amount to 4-fold increases in the relative amount of Portland cement containing limestone as a major constituent since 1990 (Hertfort, 2008).

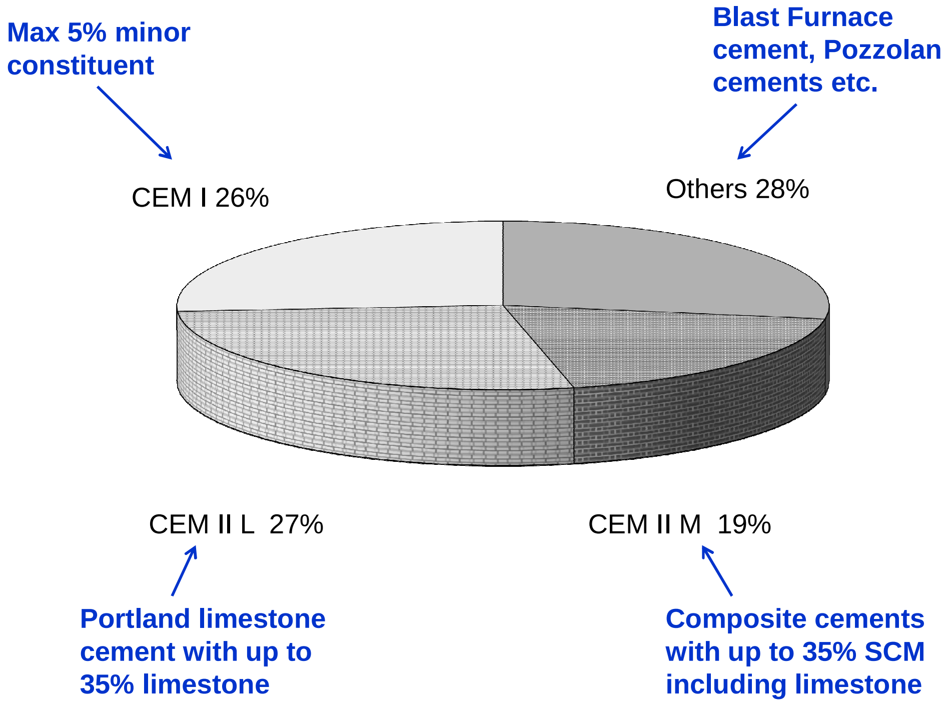


Fig. 1 Cement types produced in Europe in 2010 (reproduced from CEMBUREAU, 2008). Others include CEM II, IV, V and CEM II not containing limestone as a major constituent (i.e Portland-slag, silica, pozzolana, fly ash, & burned shale cements containing up to 35% clinker replacement)

As shown in figure 2 most of the Portland limestone and composite cements conform to the 32.5 and 42.5 strength classes, although “*very high strength*” 52.5 Portland limestone cements are also produced.

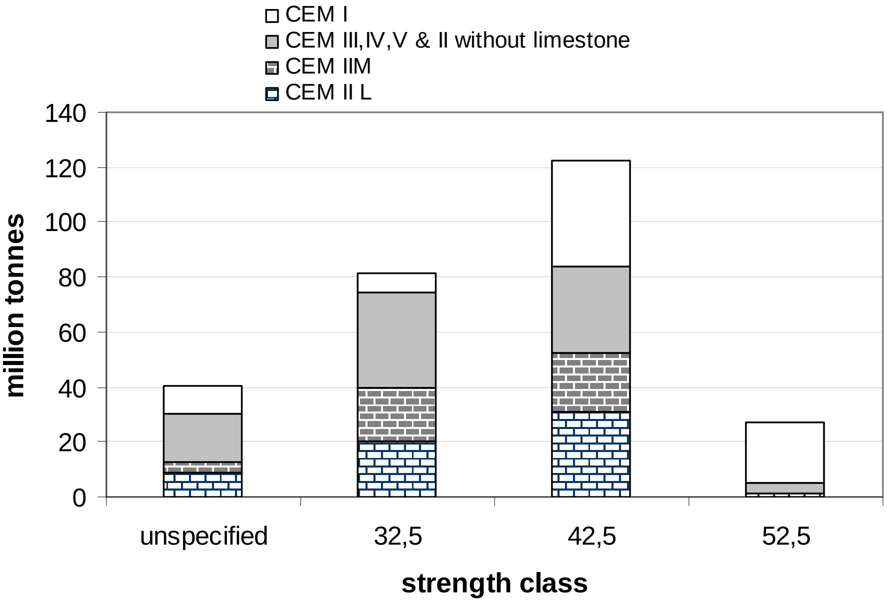
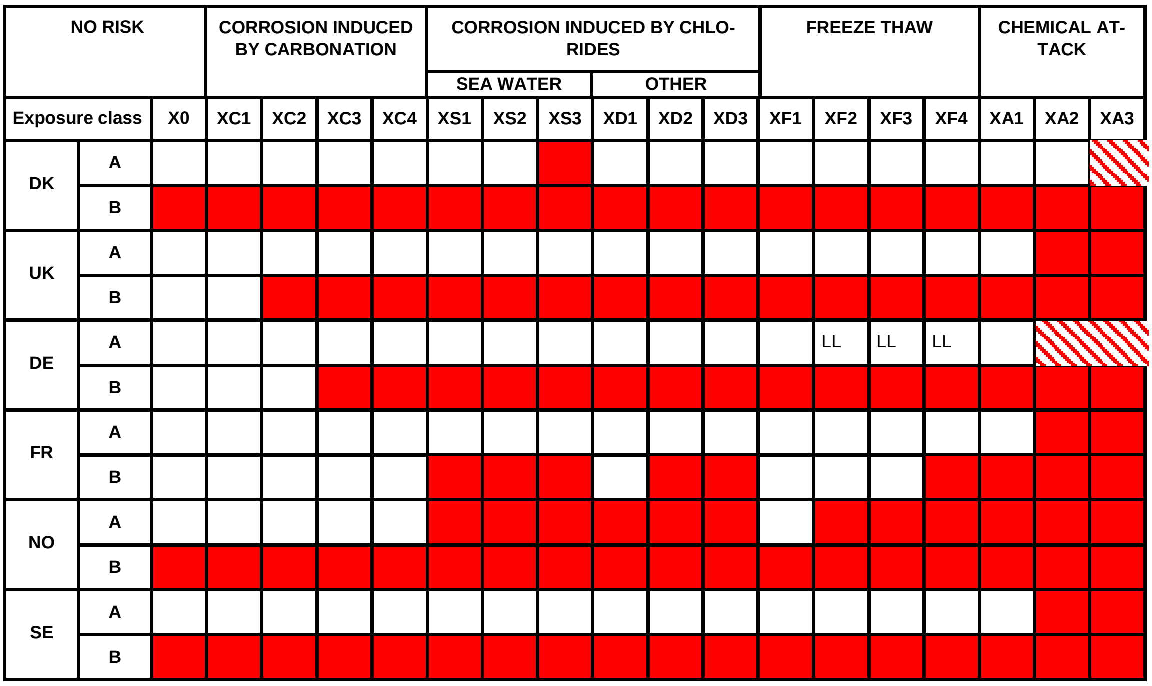


Fig. 2 Breakdown of cement types into strength classes (reproduced from CEMBUREAU, 2008)

Most countries around the world specify similar chemical and physical requirements for the limestone that can be used, including a minimum $CaCO_3$ content of 70 or 75%, and maximum contents of clay and TOC (total organic carbon).

A comprehensive review of the application standards for Portland limestone in concrete is beyond the scope in this report, and practices differ widely from country to country. In the US for example cement types for a given application are specified at state level. In Europe, although the cement standard EN 197-1 is harmonized, the cement types that can be used in a given exposure class (defined in the European concrete standard, EN 206) are specified in the national application standards. This is shown for selected countries in figure 3. Germany and Denmark, for example, allow the CEM II/A L, LL cements, with up to 20% limestone, in all exposure classes except where high sulphate concentrations are involved in classes XA2 and XA3. The CEM II/B cements allowing up to 35% limestone have more limited application, and where they are allowed, are restricted to the exposure classes where carbonation is the sole source of attack.



NO RISK			CORROSION INDUCED BY CARBONATION				CORROSION INDUCED BY CHLORIDES						FREEZE THAW				CHEMICAL ATTACK		
							SEA WATER			OTHER									
Exposure class		X0	XC1	XC2	XC3	XC4	XS1	XS2	XS3	XD1	XD2	XD3	XF1	XF2	XF3	XF4	XA1	XA2	XA3
DK	A								🟥										▨
	B	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥
UK	A																	🟥	🟥
	B			🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥
DE	A													LL	LL	LL		▨	▨
	B				🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥
FR	A																	🟥	🟥
	B						🟥	🟥	🟥		🟥	🟥				🟥	🟥	🟥	🟥
NO	A						🟥	🟥	🟥	🟥	🟥	🟥		🟥	🟥	🟥	🟥	🟥	🟥
	B	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥
SE	A																	🟥	🟥
	B	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥

Fig. 3 National application standards allowing Portland limestone cements in selected European countries (Herfort, 2008)
🟥 not allowed ☐ allowed ▨ allowed except for highly aggressive sulphate environments
LL LL refers to a maximum of 0.20%

2. Hydration reactions and strength of Portland limestone cements

Although it has not been widely accepted until fairly recently that limestone additions are not inert, reports in the literature date back at least 30 years (Bensted, 1980) showing that calcium carbonate reacts with the AFm phases to form carbo-aluminate analogues, i.e. the so-called hemi- and mono carbo-aluminate hydrates. Probably the most comprehensive work on these reactions to date has been performed by Nanocem network partners over recent years (Matchei *et al.*, 2007; Lothenbach *et al.*, 2008; De Weerdt *et al.*, 2010). The results from this work are adapted in this report to show the compatibility of relevant phase assemblages on the sub-ternary phase diagram shown in figure 4 (a detailed account of ternary phase diagrams applied to hydrated cement can be found in Herfort *et al.*, 2015). This makes it clear that the addition of limestone to a typical Portland cement will result in the following sequence of reactions:

1. where ettringite forms via consumption of monosulphate,
2. when monosulphate is exhausted, monocarbonate forms via consumption of hemicarbonate,

3. when the hemicarbonate phase is used up additional calcium carbonate does not react but persists as a stable phase.

Reactions 1 and 2 are space filling resulting in a reduction in porosity, whilst the further addition of carbonates in reaction 3 results in increased porosity. This type of diagram shows the relative contents of phases that form within the sub-system. Of course, higher absolute contents of aluminate (or C_3A defined here as a “component”) result in more monocarbonate formation and therefore higher amounts of reacted calcium carbonate before further additions result in an increase in porosity.

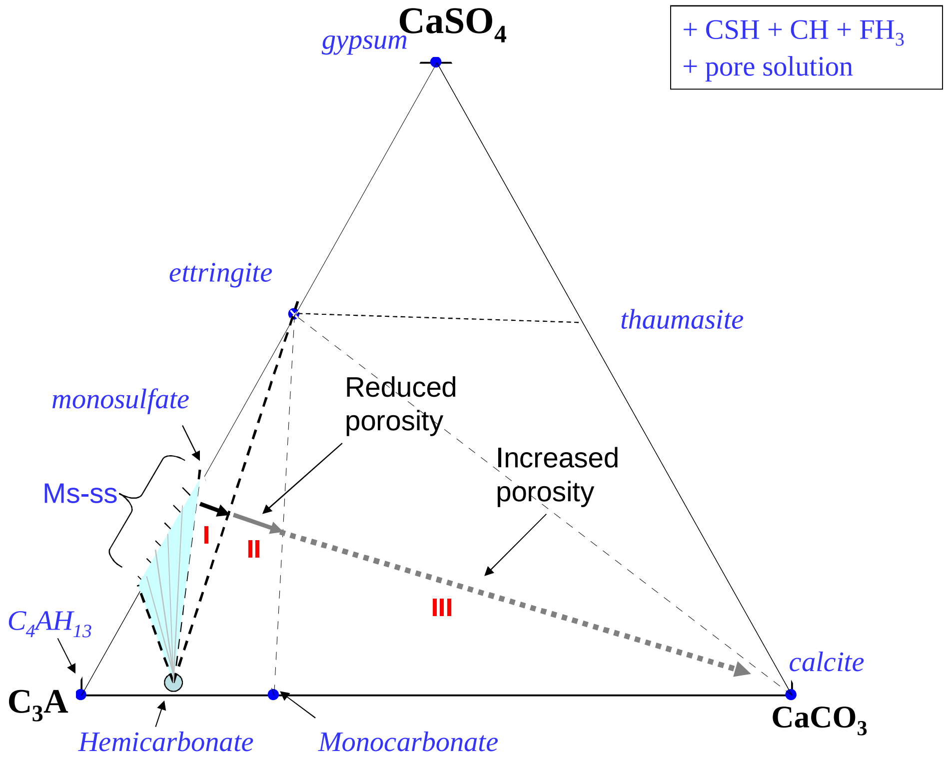


Fig. 4 Hydrate phase assemblages in the ternary sub-system for $CaSO_4$-C_3A-$CaCO_3$ within the multicomponent system for Portland limestone cement. Phases in this subsystem are given in italics, and regions of stability are indicated by the 3-phase regions in which the composition of any given system (e.g. CEM II L + additional $CaSO_4$) plots onto the diagram. Excess phases are shown in the top right inset of the diagram

By calculating the contents of phases in volume % (by assigning realistic densities to the phases), it is possible to calculate the theoretical porosities and then using an empirical relationship between strength and porosity the theoretical strength can also be predicted. This is illustrated in figure 5 (from Lothenbach *et al.*, 2008). What is important is the point at which additional calcite ceases to result in increased strength (reduced porosity) and the extent that this correlates with real strength data (in this case EN 196 strengths). In the example used here there is indeed good agreement with real data for the increased strengths achieved by the addition of limestone to mineralised cement (Borgholm *et al.*, 1995). Several other workers have confirmed the reactions shown in figure 4, and the associated reduction in porosity (Lothenbach *et al.*, 2008; De Weerdt *et al.*, 2010).

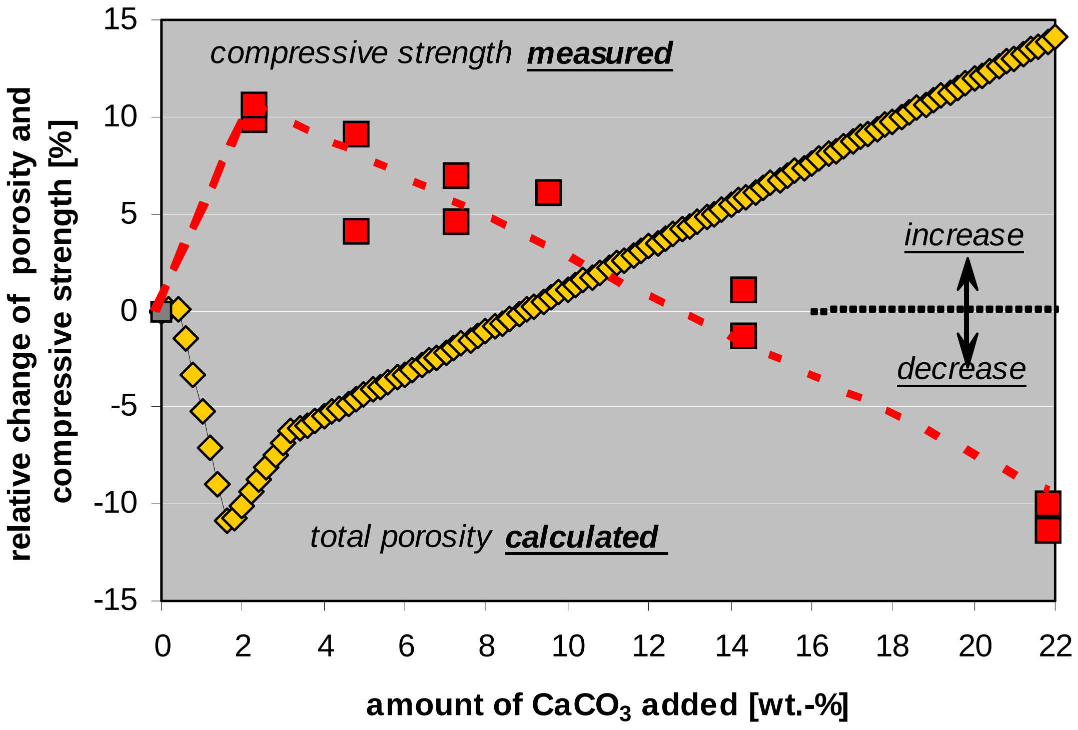


Fig. 5 The effect on 28 day cement (EN 196 mortar) strengths with additions of fine limestone (c. 1100 m^2/kg) to mineralised cement (c. 400 m^2/kg) (reproduced from Borgholm *et al.*, 1995)

The optimum 28 day strength occurs at c. 2% addition corresponding to the point where all of the available alumina from the clinker has reacted with the calcium carbonate and sulphate to form AFm and AFt phases. The theoretical porosity is calculated by the method described e.g. in (Bensted, 1980).

In addition to the hydration reactions described above, fine limestone has also been shown to result in an accelerated hydration of the C_3S phase in Portland cement without directly taking part in the reactions: this is resulting in early strengths being, either unaffected, or increased with up to 10% fine limestone replacement (Borgholm *et al.*, 1995; Kristensen, 2008).

3. Effect of limestone fillers on fresh properties of mortar and concrete

3.1. Influence on water requirement

Usually, the main physical characteristics of limestone powder that are highlighted regarding water requirement are fineness, particle size distribution (PSD), and particle morphology (Arvaniti *et al.*, 2014). From the comparison of different studies in the literature on limestone powder use in concrete, Diederich *et al.* (2012) concludes that water demand of concrete is affected by the limestone powder content depending on its physical properties. However, a warning should be made as only focusing on the physical properties of limestone powder may lead to contradictory outcome due to the potential influence of certain minor components of limestone on its water requirement (Diederich *et al.*, 2012).

Michel *et al.* (2007) studied the relation between the properties of several limestone powders and their water requirements. These limestone powders were different from each other with regard to fineness and clay content. Differences between Blaine and BET specific surface areas (Arvaniti *et al.*, 2015) were pointed out and linked to the clay content of limestone. A clear connection between BET specific surface area and clay content determined by methylene blue adsorption (EN 933-9) can be seen in Figure 6. This is reflected in the water requirement (Figure 7), which did not show a good correlation with the Blaine specific surface area or the particle size distribution (Figures 7 and 8), even if these results changing for the different methods at the same time (Figure 8).

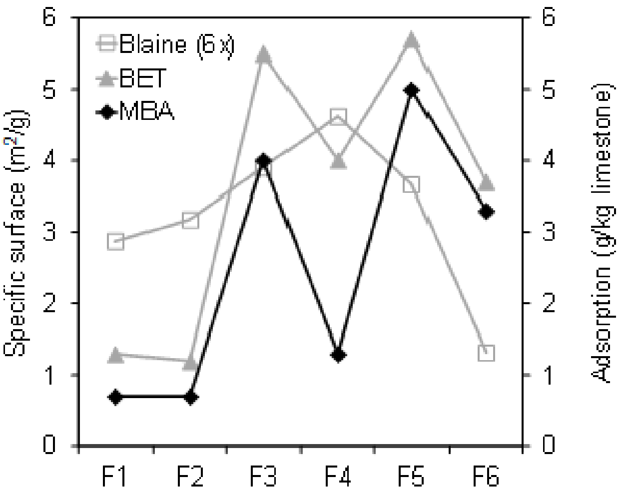


Fig. 6 Comparison between Blaine specific surface area, BET specific surface area, and methylene blue adsorption (MBA) of limestone powders (F1 to F6) (from data in Michel *et al.*, 2007).

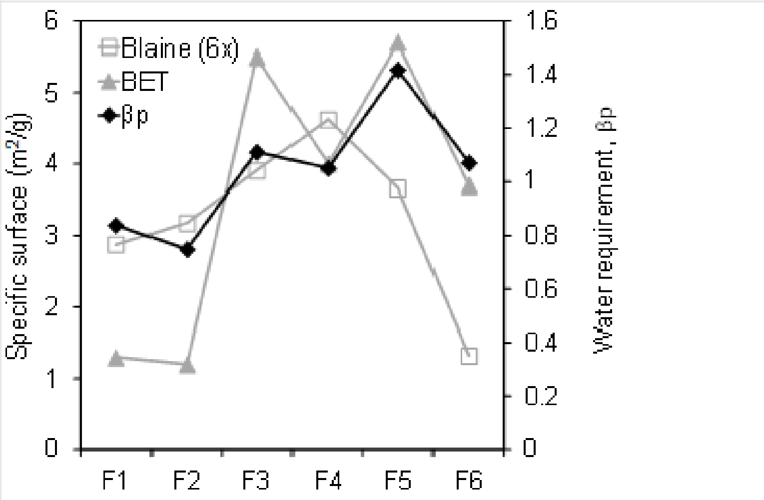


Fig. 7 Comparison between Blaine specific surface area, BET specific surface area, and water requirement (βp) of limestone powders (F1 to F6) (from data in Michel *et al.*, 2007)

Clay content and type are changing dramatically changing the percentage of fine particles in the mix.

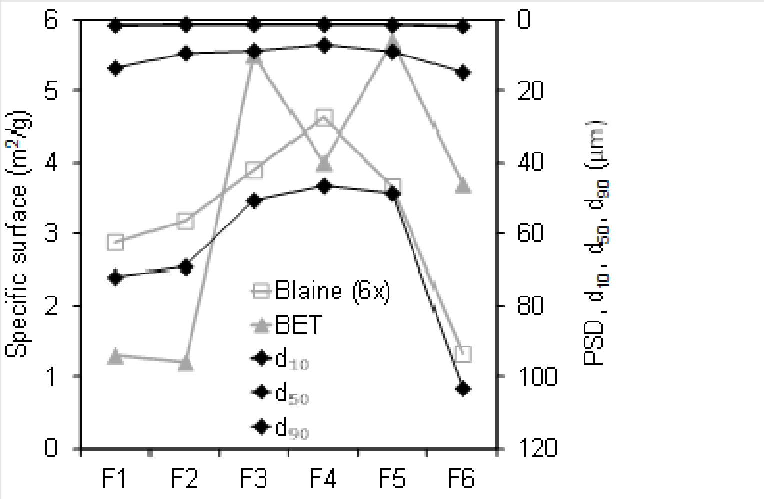


Fig. 8 Comparison between Blaine specific surface area, BET specific surface area, and particle size distribution (PSD – laser granulometry) of limestone powders (F1 to F6) (from data in Michel *et al.*, 2007)

Equation 1 can be empirically derived (Michel *et al.*, 2007) for estimating the water requirement of limestone powder on the basis of its Blaine specific surface area and clay content, where MBA is the methylene blue adsorption in g/kg of limestone and Blaine is the Blaine specific surface area in m^2/g. The coefficients in Equation 1 were obtained by multiple linear regression of data (Michel et al., 2007), with $R^2 = 0.86$ (Figure 9).

$$\beta p = 0.6 + 0.12 \cdot MBA + 0.28 \cdot Blaine \qquad \text{(Equation 1)}$$

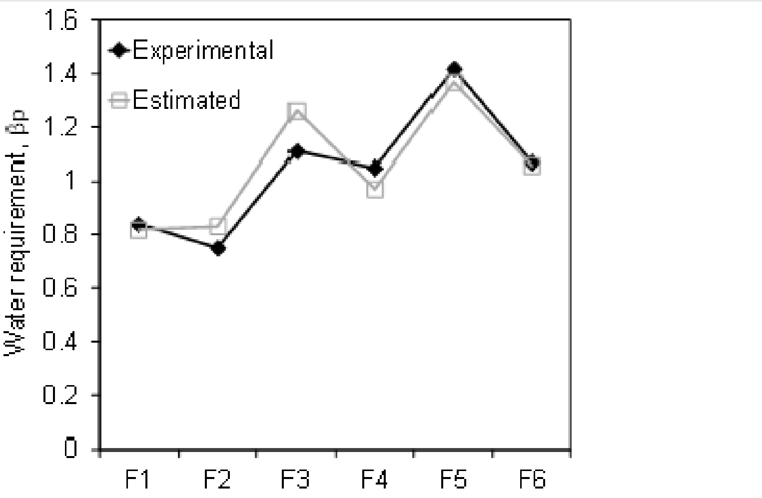


Fig. 9 Correlation between the estimated water requirement with the experimental water requirement of limestone powders (F1 to F6) (from data in Michel *et al.*, 2007)

The clay content of limestone powder is definitely a key parameter to appreciate its influence on water demand. Good correlations (Michel *et al.*, 2007) have been found between mortar consistence and water requirement of limestone powder, i.e. fineness and clay content. It should be noted that Michel *et al.* (2007) obtained lower values for βp than those obtained for the ordinary Portland cement (OPC) when they used in mortar manufacture only limestones F1 and F2. Then, these two limestone powders would have been capable of reducing water requirement, whereas the rest would have increased it. F1 and F2 were characterized by a Blaine specific surface area lower than 0.55 m^2/g and a methylene blue adsorption lower than 1 g/kg of limestone. This implies that the maximum limit established in EN 197 (EN 197-1: 2011) of 1.2g/100g is about ten times higher than the value for which water requirement seems to be affected by the inclusion of limestone.

Moreover, Courard *et al.* (2011) also analyzed differences between bentonite and kaolinite as minor components of limestone powder. They found a remarkable influence of bentonite on water demand, and a very little influence of kaolinite, which is explained by the much higher swelling property of bentonite. Therefore, they refer to the swelling clay content as the key property as regards water demand, instead of the total clay content.

Diederich *et al.* (2012) found no relationships between the flow properties of mortar including limestone powder and its morphology. They derived that it should not be considered that clay is included as grains, but as phases included in the grains of limestone particles. Therefore, under the effect of the grinding process, these phases would be exposed at the surface of grains and modify the surface properties that affect the flow.

In a comparison with other blended Portland cements (Voglis *et al.*, 2005) and despite a higher fineness of limestone cement (required to achieve a similar strength level than others), water demand of limestone cement was not higher than that of OPC, but it was lower than for pozzolanic and fly ash cements. Similar results are presented in (Courard and Michel, 2014) where they use limestone powder in partial substitution of cement to produce mortars. All these binary cements were produced by intergrinding of clinker, gypsum and supplementary cementitous materials (replacement percentage of 15%). The main reason given for this lower water demand of limestone cement is that its particles had a wider particle size distribution than the particles of the other blended cements. This may imply a better packing density of particles and a lower requirement of water.

When cement is blended with different limestone percentage replacements, the optimum dry packing density of fines is obtained for a certain powder content dependent on the particle size distribution of both cement and limestone powder. In this regard, Joudi-Bahri *et al.* (2012) reported optimum limestone powder contents in concrete between 100–120 kg/m^3. They argued that intergranular voids are not well filled with lower limestone powder contents, whereas excess of single-sized particles lead to a loose suspension that demands higher mixing water content for a specific consistence level. This is in partial agreement with results from (Jones *et al.*, 2003), where it is shown that the limestone powder content giving the lowest water demand is less than the powder content required to achieve a minimum voids ratio from theoretical dry packing computations. They argue that the agglomeration of limestone powder particles, which increases its particle size and voids ratio, is responsible for this difference. In concrete with a lower Portland cement content (< 350 kg/m^3), the voids ratio of the concrete decreases with an increase in limestone content up to a certain limit, after which further increases in limestone content only result in small changes in the voids ratio. The decrease of voids ratio with increasing limestone content is reduced with increasing Portland cement contents; for high cement contents, the addition of cement-sized powder will even increase the voids ratio and the water demand. Since the lowest water demand, for a given workability of a binary limestone powder-Portland cement, was obtained for a limestone powder content lower than the one corresponding to the highest packing density, Jones et al. (2003) suggested two criteria to determine the optimum powder content for minimum water demand in plasticized mixes: a voids ratio reduction of 0.02 (equivalent to a reduction of concrete water demand of 15 l/m^3) in comparison with cement paste without limestone powder and a voids ratio reduction rate larger than 0.02% m^3/kg (i.e., the voids ratio reduced by more than 0.02% per m^3 of concrete through the addition of 1 kg of powder).

In a different direction, Wong and Kwan (2008) asserted that the packing density of particles is not directly related to the solid concentration in the mix, which varies with the w/c ratio. Therefore, the water demand could not be deduced from dry packing density of particles. Here, it is noted that the mixing water content at standard consistence of the mix is quite different from the basic water content, which is just sufficient to fill up the voids in the granular skeleton, or the minimum voids ratio. Moreover, entrapped air in the mix causes a positive effect giving more mobility to the mix and indirectly affecting water demand (Wong and Kwan, 2008).

Using the method to determine the wet packing density (Wong and Kwan, 2008) for limestone and cement blends, Diederich *et al.* (2012) found that the multiple influences of the different limestone powder and cement characteristics can be accurately represented through the evaluation of the excess water volume ratio defined as the surplus over the minimum void volume ratio of the paste. Accordingly, they found a general relationship between excess water volume ratio and flow parameters (yield stress and viscosity) for several limestone powders and cement types (Diederich *et al.*, 2012).

3.2.Influence on bleeding

Soria and Rahhal (2003) obtained similar bleeding values for 19cm-slump at 20ºC for concrete with or without a limestone powder content near 20%. At higher temperatures, however, they found that limestone concrete reduced bleeding capacity. The main explanation comes from the increase in the hydration rate caused by the filler effect.

On the other hand, Joudi-Bahri *et al.* (2012) reported decreasing bleeding capacity with higher limestone powder content for 23cm-slump concrete. The influence reported for 15 and 7cm-slump concrete mixes analyzed in the same study was much lower. The Blaine specific surface area of limestone was 310 m^2/kg, and its PSD was d10/ d50/ d90=1.5/18/65µm, respectively; the same parameters for the OPC were 320 m^2/kg, and d10/d50/d90=0.8/7.5/35µm, respectively. The decreasing in bleeding is explained by the requirement of a high volume of powder for high-slump concrete in order to stabilize the suspension of particles: when high flow concrete with low powder content, an excess in mixing water content will increase bleeding.

It should be mentioned that, as finer limestone powder tends to give more cohesive mixes and stronger suspensions (Diederich *et al.*, 2012), an impact of the fineness of limestone powder on concrete bleeding may be expected, in accordance with the respective powder content. Three main physical phenomena acting on fresh cement paste are linked to bleeding (Perrot *et al.*, 2012): Brownian motion, colloidal attractive forces and gravity. For pure cement systems, if colloidal attractive forces prevail over gravity, a stable suspension of particles in which particles cannot rearrange their relative positions is obtained. Low bleeding is usually observed in stable mixes. Predominant colloidal attractive forces also result in the ability to withstand an external stress up to a critical value, called yield stress. Though there is no direct correlation between yield stress and bleeding (Perrot *et al.*, 2012), these two properties are strongly linked. On the other hand, gravity will dominate colloidal attractive forces in low viscosity mixes, and particles may settle with high bleeding capacity as a result. The phenomenon is of interest in the case of very fluid mixes such as self-consolidating ones. Several results on the influence of limestone powder on the yield stress and viscosity of cementitious systems can be found in the literature, especially for self-consolidating mixes. Forward, a section dealing with this topic can be found. It could be claimed that in the same way that limestone powder affects yield stress, and viscosity in the case of fluid mixes, it may also affect bleeding.

Joserrand *et al.* (2006) suggested that the influence of a limestone powder (BET s.s.a.=6081m^2/kg and PSD d10/d50/d90=1.7/10.5/52 µm) on cement hydration and particle flocculation can lead to more prolonged bleeding, and a consequent high bleeding capacity. This is in agreement with (Garcia *et al.*, 2008; Bentz and Garboczi, 1991), where initial setting time is reported as an indication of a percolation threshold that affects connectivity between solid particles and voids within the newly hardened cement paste.

3.3.Influence on setting

Fineness of limestone powder is a main characteristic as regards its influence on setting. Soria and Rahhal (2003) investigated the influence of ambient temperature of concrete made with limestone powder on slump, slump loss, setting time and bleeding. They found that, in hot weather conditions, concrete produced with limestone cement may result in a greater reduction in slump compared to OPC concrete. They also found shorter setting times for limestone concrete in comparison with pure cement concrete at 20, 30, and 40 ºC; they suggested that this is due to the increase in the hydration rate caused by nucleation effect. Similar results for the effect of the limestone powder content on setting time are presented in (Khaleel and Razak, 2012). On the other hand, limestone cement with replacement percentage of 15% showed similar setting times to ordinary, pozzolanic and fly ash cements, even when limestone cement had higher fineness (Voglis *et al.*, 2005). In this sense, Michel et al. (2007) noticed an influence of limestone powder on initial setting time only when it had a Blaine specific surface area of 770m^2/kg, whereas no influence was determined for limestone powder with Blaine fineness between 220 and 650m^2/kg. Courard *et al.* (2005) present results in agreement when they tested mortars with limestone powder with Blaine s.s.a.=305 m^2/kg in partial replacement of cement. Accordingly, Sato and Beaudoin (2011) proposed the addition of nano-$CaCO_3$ for accelerating the hydration of OPC when delayed by the presence of high volumes of supplementary cementitious materials, such as fly ash and slag. Based on this work, Bentz *et al.* (2012) added fine limestone powder to high volume fly ash concrete to compensate for the excessive retardation effect on hydration, delayed setting times, and low strengths at early age. They analyzed a nano-limestone powder and two other limestone powders of increasing median particle size (4.4 µm to 16.4 µm) for their propensity to reduce setting times in a Class C fly ash/cement blend. They obtained a measurable acceleration of hydration and compensation of setting times due to the fineness of the limestone, which they attributed to both physical and chemical action mechanisms of limestone particles.

On the other hand, Ezziane *et al.* (2010) found increasing setting times with limestone powder (Blaine s.s.a.=340m^2/kg) content when they tested superplasticized mortar. They attributed this delay to the higher effective relationship superplasticizer dosage/cement content. Thus, the increase in setting time should be attributed to the effect of the superplasticizer, in which the relative content to the cement weight is increased by the increase in the limestone powder content.

Courard *et al.* (2011) reported values for setting times of mortars including different limestone powders and without chemical admixtures. The influence of the mineral additions seems to be linked to their clay content and BET specific surface area. In most cases, however, this effect is very low and the overall effect on setting time is essentially neutral.

The effect of temperature on setting of limestone blended mixes has been also analyzed in (Ezziane *et al.*, 2010). They found consistent shortening of setting time with increasing temperature, but no influence of the limestone powder content on these decreases could be found, as the relative differences according to the limestone powder content remained similar for each series.

3.4.Influence on superplasticizer demand

Studies on interaction between limestone-blended cements and superplasticizers have primarily focused on polycarboxylic-ether (PCE) based admixtures (Magarotto *et al.*, 2003; Şahmaran *et al.*, 2006; Artelt and García, 2008; Plank *et al.*, 2010; Banfill, 2011), as they are commonly used in self-consolidating concrete.

Differences in superplasticizer demand between limestone-blended cement and ordinary cement would be mainly due to limestone-admixture interaction. According to Alonso et al. (2007), the effect of PCE admixtures on CEM II/B-L (Blaine s.s.a.=438m^2/kg) cement pastes is similar to the changes induced in cement pastes without mineral additions. The use of 30% limestone in cement pastes (Burgos-Montes *et al.*, 2012) raises the adsorption of both lignosulfonate- (LS) and melamine- (PMS) based superplasticizers, indicating that these admixtures had greater affinity to CEM II/B-L (Blaine s.s.a.=524m^2/kg, BET s.s.a.=2110m^2/kg) than to CEM I (Blaine s.s.a.=502m^2/kg, BET s.s.a.=1220m^2/kg), while naphthalene - (PNS) and PCE based superplasticizers behaved similarly with limestone blended and non-blended cements. The presence of supplementary cementitious materials changes the physical–chemical properties of the cement and its behavior in terms of superplasticizer adsorption. Results in (Burgos-Montes *et al.*, 2012) show that superplasticizer adsorption on limestone – or limestone and clayey material - was similar to its adsorption on limestone-blended cement because, although affinity was much smaller for limestone than for cement particles, the presence of limestone in the blend led to a higher total consumption of admixture as a result of its greater specific surface. Similarly, Mikanovic and Jolicoeur (2008) observed adsorption of PNS was twice as much as that of PCE, and that adsorption of both polymers was twice as high on CEM I cement as on pure $CaCO_3$ particles, both with the same BET s.s.a.=1200m^2/kg. Also Petit and Wirquin (2010) found increasing superplasticizer demand with limestone powder (of unknown fineness) content in self-consolidating mortar mixes with PNS admixture, but this increase was in connection with an increase in the content of fines in the mix.

Adsorption of PCE admixture on limestone particles is due to an enthalpic contribution resulting from the electrostatic attraction between the opposite charges of substrate and PCE molecules, and the entropic contribution originated in the release of numerous counter ions and water molecules into pore liquid. These contributions are influenced by the ionic composition of pore liquid. Plank *et al.* (2010) investigated the adsorption of different PCE admixtures on $CaCO_3$: whereas the electrostatic attraction between the substrate and the PCE molecules decreases in the presence of Ca^{2+} ions, PCE adsorption is connected with a high gain in entropy due to the same reason. The PCE molecule characteristics (structure, molecular weight, types of anchor groups), and the surface loading of the substrate with PCE are also important features in the adsorption process. These influences of the molecular weight and structure of the PCE have therefore a significant influence on the rheological behavior and water-reduction of the limestone cement (Magarotto *et al.*, 2003; Banfill, 2011). The anionic charge density of PCE molecules (Plank *et al.*, 2010) influences both enthalpy and entropy. With higher anionic charge density, the enthalpic contribution to adsorption increases, whereas the entropic contribution decreases. A higher anionic charge density results from decreasing the side chain length of the PCE macromolecule. In consequence, a gain in entropy is the major force driving PCE adsorption and a decisive parameter of its effectiveness as superplasticizer.

Mikanovic and Jolicoeur (2008) studied the relationship between particle–superplasticizer interactions, rheology and paste stability, and blending, sedimentation and consolidation. Their findings showed that the mechanisms involved in superplasticizer action on limestone and OPC cement varied depending on whether the admixture was PCE or PNS-based. They also observed that even if the dispersion effect of both admixtures was similar in water–limestone pastes, the presence of $Ca(OH)_2$ improved the effectiveness of PCE admixture. In this sense, Hallal *et al.* (2010) observed better compatibility of superplasticizers with limestone blended cement than with pozzolana blended cement.

Additionally, the BET is essential to describe the powder/superplasticizer interaction that controls particle dispersion (Diederich *et al.*, 2012). BET specific surface area allows the fineness of particles and their texture to be quantified as well (Arvaniti *et al.*, 2015). It is therefore more descriptive of the surface on which PCE molecules may be adsorbed than Blaine s.s.a., which is connected with particle size only. Therefore, the increase in specific surface area and packing density due to the partial replacement of OPC by limestone powder might affect concrete flowability (Esping, 2008), and the dosage of superplasticizer must therefore be modified to maintain it.

In this regard, Diederich *et al.* (2012) showed that the effectiveness of superplasticizer depends on the composition and surface charge of the limestone powder, specifically the effect of the presence of impurities such as clay. Limestone powder usually exhibits a rather low hydrophilic behavior (Diederich *et al.*, 2012). However, when a PCE admixture is included, different evolutions of the contact angle may be expected depending on the nature of the powders and in connection with their electrostatic charge. In this regard, negatively charged powders show a decrease in the contact angle, i.e. a higher affinity with the aqueous solution, whereas other powders show a lower affinity with the liquid phase (Diederich *et al.*, 2012). These dissimilar interactions between PCE admixture and limestone powder induce a modification of the rheological properties of suspensions: the yield stress (Figure 9) and the apparent viscosity of suspensions with limestone powder are reduced with the use of a PCE admixture to different extents depending on the nature of the limestone powder.

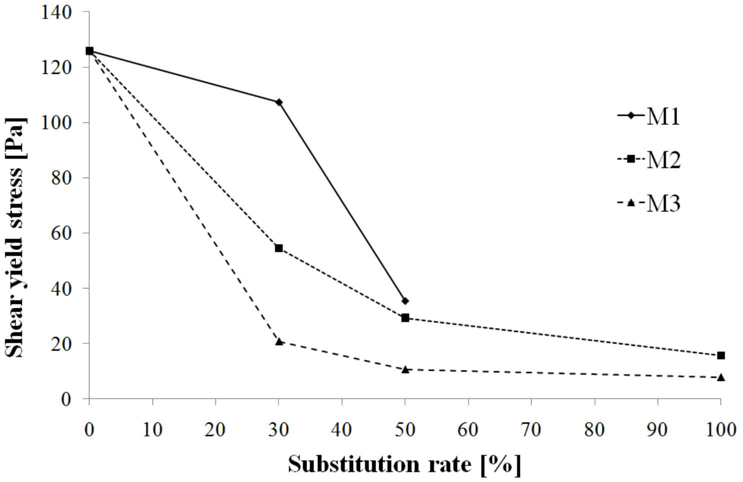


Fig. 9 Variation of the shear yield stress of slurries with constant spreading (ASTM C230) and with 0.5% polycarboxylate superplasticizer as a function of the filler amount (3 types of natural limestone fillers) (Courard *et al.*, under reviewing)

The obtained relative decreases in static yield stress and viscosity were significant only for limestone powders that showed a wettability decrease with the inclusion of PCE admixture. The lower wettability would allow a larger amount of free water available for the fluidification of the mix (Diederich *et al.*, 2012). In this analysis, it is important to note that the lower wettability may be in conjunction with a positive electrostatic charge of the powder, and, if so, limestone powder may be in competition with cement for the adsorption of PCE molecules. Therefore, this may result in a net negative influence on the flow properties of superplasticized mixes with limestone blended cement. On the other hand, Diederich *et al.* (2012) found no relationships between the flow properties of limestone suspensions incorporating PCE and those of limestone-blended cement-based suspensions. They accordingly conclude that the flow of the *cement+limestone+PCE+water* suspension is influenced by the properties of the individual components and also by their concentration and the interactions existing between them.

Then, it seems very important to take into account the particle size distribution and the complementary effect with that of the cement in order to achieve minimum voids and allow lower superplasticizer demand.

4. Effect of limestone powder on fresh properties of Self-Consolidating Concrete

In a comprehensive study performed by the BRE (Building Research establishment) and BCA (British Cement Association) in the early 90s (Moir and Kehlman, 1993), Portland limestone cements were shown to "*have a largely neutral effect on slump, and are mostly beneficial particularly if the limestone is interground with the clinker and the fineness of* *the clinker fraction is less than c. 380 m^2/kg*" (Moir and Kelham, 1997). The same study showed clear benefits in reducing the tendency of bleeding for cements that without limestone addition had a narrow size distribution (which are more common nowadays with more efficient closed circuit cement mills), or in self compacting concrete (Moir and Kelham, 1997; Livesey, 1991). These conclusions were generally confirmed in a recent review of limestone cements by the PCA (Tennis *et al.*, 2011).

Much of the research that has been done on the influence of limestone powder on the fresh state concerns self-consolidating concrete. Self-consolidating Concrete (SCC) is stable highly flowable concrete that can spread readily into place and fill the formwork without any consolidation and without undergoing any significant segregation. The solid fraction of paste phase of concrete must be increased in order to obtain stable and flowable SCC. In this sense, non-pozzolanic powders are frequently used to optimize the particle packing and flow behavior of cementitious paste in SCC mixtures.

By using limestone powder with fineness and grading that can greatly improve the particle packing and deformability of the cementitious paste, the amount of mixing water can be considerably reduced for set values of rheological parameters (Ghezal and Khayat, 2002; Bokan Bosiljkov 2003; Yahia *et al.,* 2005b, Courard *et al.*, under revision). Alternatively, limestone powder may enable superplasticizer contents to be reduced in some cases (Nepomuceno *et al.*, 2012): this is conditioned by the fineness of limestone powder. Increased superplasticizer demand of SCC due to the inclusion of limestone powder has also been reported (El Hilali *et al.*, 2006; Gesoğlu *et al.*, 2012).

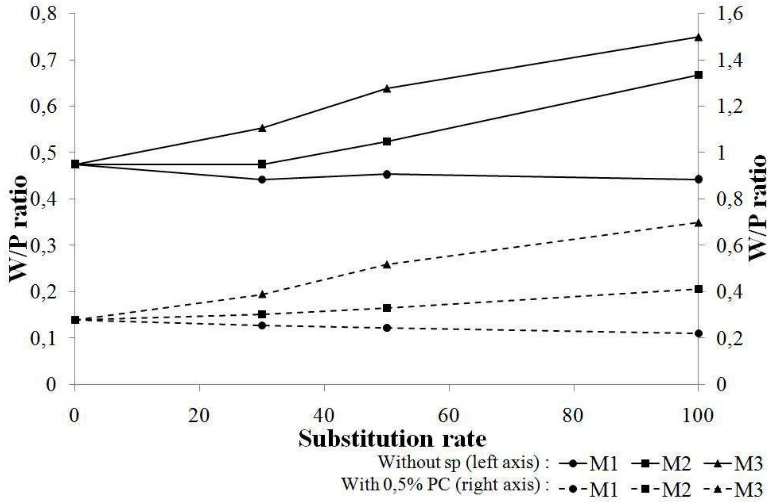


Fig. 10 Variation of W/P ratio for constant spread (ASTM C230) of 220mm, with and without PC superplasticizer (Courard *et al.*, under reviewing)

Limestone powder may play a significant role in the stability of self-consolidating concrete (Georgiadis *et al.*, 2010) by compensating poor gradation and enhancing mixture consistency. Yahia *et al.* (2005) investigated the effect of a limestone powder addition in superplasticized cement mortar rheology. Their results show that the physical effect of limestone powder is mainly affected by the W/C and the limestone powder content; for a given W/C, the addition of limestone powder within a certain range did not affect fluidity. However, beyond a critical dosage, the incorporation of some limestone powder resulted in a substantial increase of mortar viscosity. However, it must be taken into account that sand may be a substantial source of fines which may reduce the optimum limestone powder content to obtain a stable and flowable self-consolidating mix (Tobes *et al.*, 2007).

Similarly to conventional concrete, results for setting time of SCC with limestone powder are somewhat variable. Şahmaran *et al.* (2006) obtained increasing setting times when fly ash was included in SCC that could be reduced by using ternary mixtures including also limestone powder. In contrast, Gesoğlu et al. (2012) reported increased setting times for both binary and ternary self-consolidating mixes with limestone powder and fly ash. Again, the clear influence of limestone powder is a result of opposite effects of hydration stimulation and dilution of clinker. Limestone powder fineness might be the deciding factor on the predominance of one or the other.

Partial replacement of cement by limestone powder may reduce plastic viscosity and yield stress of highly-flowable mortars (Yahia *et al.*, 2005b). On the other hand, Gesoğlu *et al.* (2012) reported increased values for the viscosity of self-consolidating concrete due to the inclusion of limestone powder, including binary and ternary blended mixes with Portland cement and fly ash. The contradictory results on the effect of limestone powder on flow behavior may be explained by the fact that flow properties of the mix are highly influenced by the surface charges, wettability and fineness of limestone powder, which in turn may differ very much among different sources of raw material (Diederich *et al.*, 2012). In this sense, clay content of limestone powder, which affects its characteristics, is a key factor controlling the flow of limestone blended mixes.

Evidence on the influence of limestone powder on rheological parameters has also been presented by Vieira and Bettencourt (2007), in relation to the modification of particle packing. They reveal a higher influence of limestone powder content on the V-funnel time than the influence of superplasticizer content. In this sense, they explain that the V-funnel test is very dependent on the lubricant effect of particles, whereas the flow spread, which is less affected by the limestone powder content, depends on the characteristics of the paste as a whole. Similarly, slump flow was found to be more affected by the limestone powder content than by the superplasticizer content (Yahia *et al.*, 2005b). Diamantonis *et al.* (2010) also attributed the decreased values of plastic viscosity with limestone powder content for both binary and ternary pastes to a better packing density of fines provided by the inclusion of limestone powder. They also found lower values of yield shear stress when compared to other binary mixes, but not lower than that of the reference mix. In consequence, they suggest limestone powder as the most convenient mineral addition as regards SCC rheology.

Many authors (Heirman *et al.*, 2007) are suspecting that an excessive limestone powder content can considerably increase water demand of self-consolidating mixes if the specific surface area of the powder is increased (Yahia *et al*, 2005; Şahmaran *et al.*, 2006; Emdadi *et al.*, 2007; Uysal and Yilmaz, 2011; Petit and Wirquin, 2010). Though the specific surface area of limestone might not show a significant effect on slump flow and flow time responses (Yahia *et al.*, 2005b), it has a comparable opposite effect on plastic viscosity than the replacement percentage of limestone powder. Therefore, the use of powder with higher surface specific area increases the water and superplasticizer demands (Esping, 2008). Accordingly, Czarnecki *et al.* (2010) found decreased fluidity in mortar when they used limestone powder in comparison with coarser quartz powder, and Uysal and Yilmaz (2011) obtained increased fluidity in concrete when they used limestone powder in comparison with finer marble and basalt powders. On the contrary, Jones *et al.* (2003) showed that if limestone powder is included in replacement of sand instead of cement, it can lead to a reduction in the water demand as long as it reduced voids ratio of fines. This is more likely for ultrafine limestone powder than for coarser limestone powder. Diederich (Diederich *et al.*, 2012) contends that, to infer the influence of limestone powder on water demand of SCC, it is very important to characterize the BET specific surface area of limestone powder, as it is descriptive of its fineness, smoothness and particle shape, whereas the Blaine method only describes fineness.

Thixotropic characterization of cement pastes with different limestone powder contents has been pointed out (Rubio-Hernández *et al.*, 2013), where transitory flow was measured. Whereas the non-steady flow curve depends on the initial structural state of the material, flow after a pre-shear has been applied requires less work. Results from this study show that the required work per time and volume units necessary to break the microstructure that forms in the material decreases when the limestone powder proportion increases. Limestone powder develops a weaker structure than cement particles and its particles agglomerate without appreciable structural binding (Rubio-Hernández *et al.*, 2013): only cement particles develop a microstructure network, and, thus, the substitution of cement by limestone powder does not have substantial effect on the kinetic of microstructural development related with the thixotropy of cement paste.

The air content in SCC does not seem to depend on the limestone powder content used in the mix, but on its rheological properties (Valcuende *et al.*, 2012). SCC usually shows lower volume of air than conventional concrete, but if its flowability is reduced or viscosity increased the air content increases and can far exceed the values recorded for normally vibrated concrete. In practical terms, air content can be directly linked to the parameters from the slump flow test: final diameter of the concrete mass and the time the mass takes to reach a diameter of 50 cm. Consequently, limestone powder content would affect air content to the extent that it also affects concrete rheology.

5. Hydration and strength of Portland composite cements containing limestone

As shown in figure 1, Portland composite cements (CEM II M), the bulk of which consist of combinations of limestone and slag or limestone and fly ash, account for close to 20% of cements produced in Europe. It has been shown that these combinations result in increased performance of the limestone constituent (Borgholm *et al.*, 1995). The same synergetic effect has also been shown for combinations of natural pozzolans and limestone (Torresan *et al.*, 2000; Steenberg *et al.*, 2011). This is illustrated in figure 11 (from Steenberg *et al.*, 2011) where the synergetic effect of the metakaolin-limestone reaction on strengths was shown to result from the increased formation of carboaluminate hydrates (Fig. 5) and the increased reaction of the limestone (Antoni *et al.*, 2012).

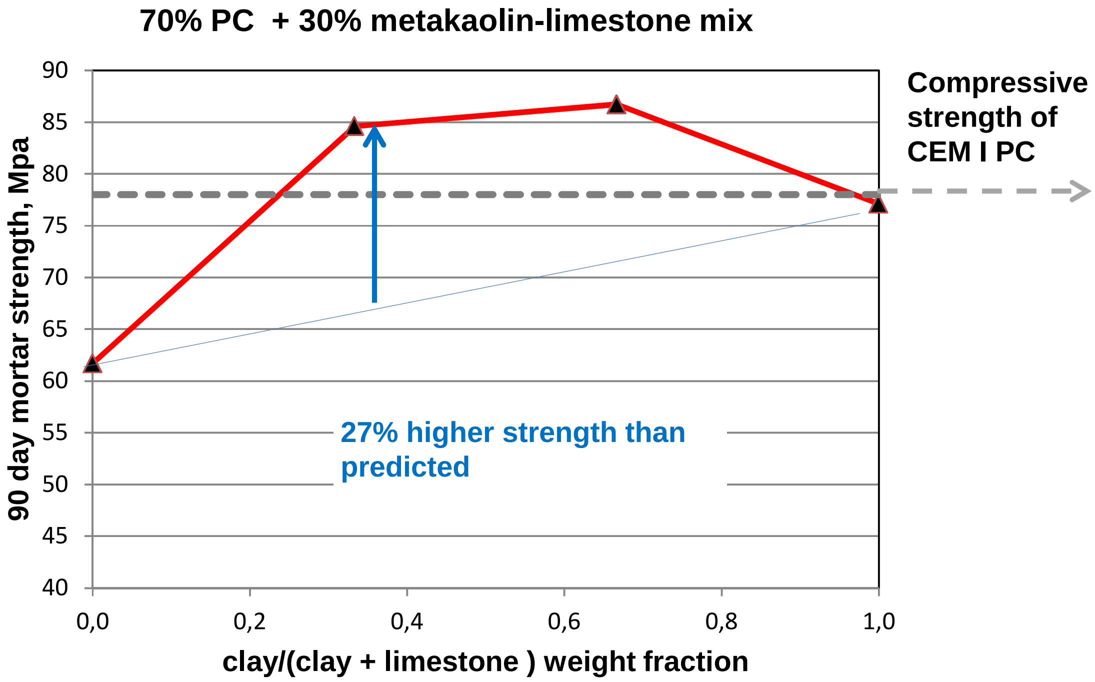


Fig. 11 Synergetic effect of metakaolin-limestone reaction on strengths (Steenberg *et al.*, 2011).

The impact of limestone on the hydration reactions described above, and the effect that this has on strength and porosity, is strongly dependent on the fineness of the limestone. In general, when the limestone is ground separately to a fineness comparable to the clinker fraction, e.g. in the region of 400 m^2/kg, performance resulting from either of the above reactions (early acceleration of the C_3S reaction, or later formation of carbo-AFm's) is limited. There seems to be a general agreement in the literature that the fineness of the limestone needs to be at least 600 m^2/g determined by the Blaine method, or with a median size of less than 5µm (Pera *et al.*, 1999; Berodier, 2013; Khanh, 1999; Hawkins *et al.*, 2013; BRE, 1993), with the best results achieved at a fineness of 1000 m^2/kg or more. This degree of fineness is only consistently achieved when the limestone is interground with the clinker, and in the majority of published reports where the limestone is blended with the clinker, the Blaine fineness of the limestone is less than 500 m^2/kg. That is not to say that blending cannot be achieved with a finer limestone, but in practice this is not normally the case.

In addition to the benefits of a high fineness of the limestone on the hydration reactions, the greater the difference between the fineness of the clinker fraction and the limestone fraction, the higher the packing density, resulting in a lower water content for the same concrete consistence. Evidence of this is clearest when the limestone and clinker is interground, or where the surface area of limestone is at least twice as high as the surface area of the clinker (Khanh, 1999; Moir and Kelham, 1993).

6. Evaluation of industrially produced Portland limestone cements

Even though industrially produced Portland limestone cements are overwhelmingly interground, performance, either regarding strength or durability, is not always in the limestone cement’s favor.

The most common reason for this is that, even though a Portland cement and comparable Portland limestone cement may be produced on the same mill from the same clinker with optimum gypsum addition, etc., the correct fineness needed to allow a meaningful comparison is not always targeted. For example, in normal closed circuit cement mill, a constant output and separator speed will achieve a significantly finer finished product for the limestone cement (c. 10 m^2/kg for each additional %point of limestone) at an essentially constant fineness of the clinker fraction (CemCalc, 2013). However, in some cases the target fineness of the limestone cement is relaxed, either to increase production output and reduce the specific power consumption, or due to bottlenecks elsewhere in the process such as insufficient capacity in the packing department for a finer product. Whatever the reason, direct comparison of the performance of Portland cement and Portland limestone cement is not possible if they are produced under different operating conditions of the mill because this will result in different finesses of the clinker fraction. Lower fineness of the clinker fraction will of course lead to poorer performance (i.e. slower rates of reaction and, higher porosity) other things equal. Despite this, for a given output and clinker fineness, optimum performance in terms of strengths, porosity and workability is ensured when the limestone is interground with the clinker.

7. Durability

With the possible exception of thaumasite formation discussed below, to the authors’ knowledge even if likely to be contentious, no investigations performed at equal strength have shown significantly inferior performance of Portland limestone cements compared to Portland cements. The conclusion of the BRE/BCA study mentioned above, (Moir and Kelham, 1993) was as follows: “*A relationship exists between the strength class of the cement, the cement content and the strength of the concrete. It demonstrates that the strength of the concrete is a better guide to carbonation than the type of cement used* *(which included a wide range of cements with different contents and sources of limestone); that the degree of air entrainment governs the performance in freeze/thaw conditions, and that the chemical composition of the base cement controls the resistance to sulphates and chlorides (i.e. regardless of the limestone content as long as the concrete is produced to the same strength)*".

In principle, dilution by limestone addition implies a reduction of chloride binding capacity in connection with lower content of aluminate and ferrite phases in cement, However some results indicate a contribution of the carbo-AFm phases to the chloride binding capacity owing to a continuous solid solution that forms between the chloride and carbo AFm phases, Friedel's salt and monocarbonate (Nielsen *et al.*, 2003). This is a different case from carbo-AFm phases formed during carbonation of concrete, where the associated reduction in pH decomposes Friedel's salt.

The increased use of Portland limestone cements is reflected by the national application standards where these cements are permitted in most European countries. Except for the exposure classes involving chemical attack (XA1,2 &3 defined in EN 206), most European national application standards permit the use of Portland limestone cements in the majority of exposure classes: this is particularly true for the CEM II/A-L,LL types, not so for the CEM II/B-L,LL (Fig. 3). In the UK for example they are permitted in all classes not involving chemical attack (BS 8500-1). In Denmark they are allowed in all classes except XS3 and XA3 (severest sea water and chemical attack) (DS/INF 158). The main reason for excluding Portland limestone cements from conditions involving sulphate attack is probably the perceived risk of thaumasite attack which is discussed in more detail below.

The general consensus after several years of research on the formation of thaumasite (Juel *et al.*, 2003; Schmidt *et al.*, 2008) is that:

1. although thaumasite may be thermodynamically stable at temperatures above 10ºC, reported field cases of thaumasite formation are virtually non-existent in warmer climates, even if not completely true (Torres *et al.*, 2011), and
2. where climatic conditions are conducive to thaumasite formation, an external source of sulphate is required, since there is invariably insufficient sulphate present in Portland cement to thermodynamically stabilise thaumasite regardless of the kinetic conditions.

This latter point is illustrated in figure 12. This diagram shows that thaumasite can only form at much higher sulphate contents than are present in normal Portland cements (between 6 and 8% SO_3 by weight of the anhydrous cement). Thaumasite can therefore only occur where external sulphate attack is involved, and to all extents and purposes, only where ambient temperatures are consistently below 10 to 15ºC. These phase relationships have been extensively tested and verified experimentally (Juel *et al.*, 2003; Schmidt *et al.*, 2008).

Where external sulphate attack is involved, it can be argued that resistance to ettringite related expansion is the main factor affecting performance, since as shown in figure 12, ettringite precedes thaumasite formation with increasing sulphate contents. In most cases the main cause of failure probably results from expansion due to ettringite formation, rather than thaumasite which is simply the final product to form. Maximum resistance is achieved at low C_3A contents and low porosity. In practice, the most workable means of achieving a low porosity is to target a high strength. For this reason specifying sufficiently high strengths for the concrete, and minimizing the water/cement ratio in the final application should offer the best protection against all types of attack, both chemical and physical. The situation is the same for Portland limestone cements regardless of the limestone content.

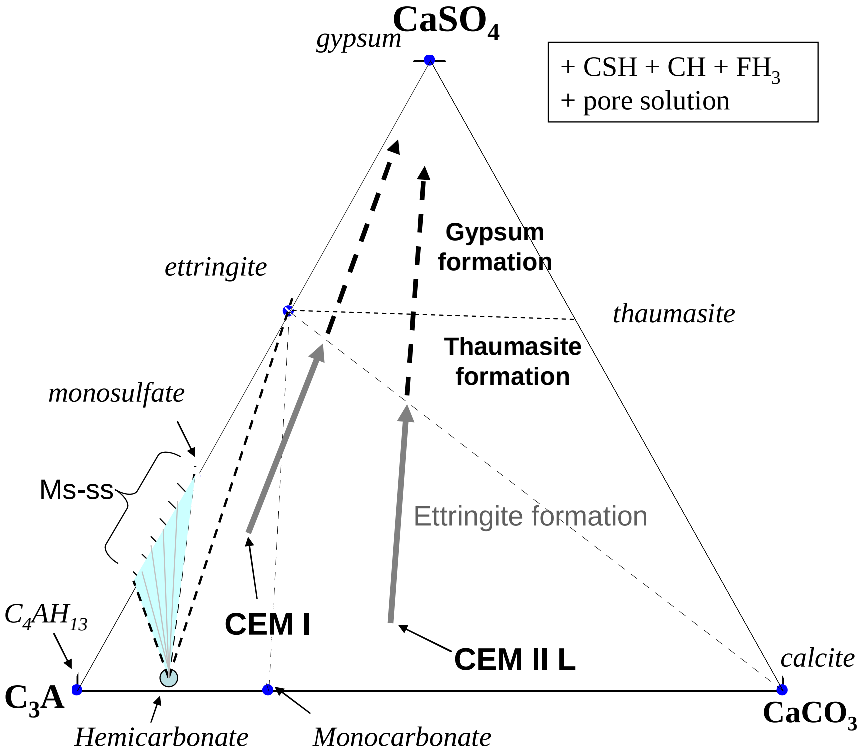


Fig. 12 Ternary sub-system for $CaSO_4$-C_3A-$CaCO_3$ from figure 4 showing the effect on the hydrate mineralogy of external sulphate attack of a typical CEM I and CEM II L

The relationships apply equally to attack by $MgSO_4$ or alkali sulphates which are of course much more soluble than the calcium sulphates and therefore more severe. In the case of $MgSO_4$, brucite forms as an excess phase, so that the composition plotted onto the sub-system follows the same path towards $CaSO_4$, and remains valid as long as calcium hydroxide (CH) remains in excess. This is also the case with alkali sulphates, but where the concentration of alkalis and hydroxyl ions (and therefore the pH) increases in the pore solution.

8. Environmental benefits

The 4-fold increase in the use of Portland limestone cement in Europe or as a substitute for cement since the early 1990s is a reflection of the limited supply of traditional supplementary cementiteous materials such as fly ash and granulated blast furnace slag and the relative cheapness of limestone fillers. Since further reductions in the clinker content of cement is a key element in reducing CO_2 emissions, this development is likely to continue with even higher contents of limestone. Moreover, limestone is one of the supplementary cementitious materials with the lowest transport-related CO_2 emission for cement production, as the source for the raw material is the same source for clinker production. This will no doubt lead to the increased use of CEM II/B Portland limestone cement and its acceptance in the concrete codes. Of course, this must take place at the same concrete performance in terms of strengths and durability, so the synergies outlined above between clinker, limestone and other SCMs must be fully exploited if levels of clinker replacement are to be maximised.

The current average clinker-to-cement ratio over all cement types in the EU27 is 73.7% (http://lowcarboneconomy.cembureau.eu). If all of the global production of hard coal fly ash and slag currently not utilized was used as a one to one clinker replacement for the same concrete performance, overall clinker contents in Portland cements could be reduced to current European level of about 0.76 (Herfort, 2008). It has been estimated that the theoretical limit for clinker replacement in Portland cement using combinations of limestone and traditional SCMs is about 40% before concrete performance is significantly affected. If this is to be achieved globally the level of replacement by limestone will probably need to be increased by c. 20% on average (Herfort, 2008).

9. Conclusions

As described above, when the limestone is ground to a Blaine fineness greater than c. 600 m^2/kg, its impact on the hydration reactions is usually significant. The acceleration of the C_3S reaction is significant within the first 24 hours, and formation of carbo-AFm phases is significant within 28 days, the latter having the biggest impact at higher aluminate contents, either from high C_3A contents in the clinker or from alumino-silicate pozzolans. The carbo-aluminate reaction involves the reaction of calcium carbonate with the alumina present in the pozzolan and $Ca(OH)_2$ supplied from the cement. To all intents and purposes limestone under these conditions should be regarded as an SCM with surface area being the primary determining factor. If it is sufficiently fine it will contribute to the space filling reactions which reduce porosity and increase strength within a period of around 28 days at normal temperature. If it is too coarse it will primarily function as inert filler. When ground separately to a comparable fineness of the clinker it will contribute to some (albeit limited) extent to the hydration reactions, but have little impact on reducing the water demand. Of course, when the limestone is ground to a lower fineness than the clinker this will improve workability, but it will have essentially no impact on the hydration reactions. In this case it should be solely characterized as filler.

Any attempt to define limestone as an SCM in a prescriptive standard or specification as a stand-alone material (i.e. not an integral constituent in a Portland cement) would require a dedicated systematic research program (http://www.astm.org/WorkItems/WK36906.htm), but the current literature does suggest a minimum fineness in the region of 600 m^2/kg as a working definition. At present, in order to ensure optimum workability and reactivity, the only effective solution at this stage is that the limestone is interground with the clinker. Intergrinding fulfills the requirements for both SMC reactivity and improved workability. There is no guarantee that similar performance can be achieved with a blended cement or direct concrete addition without specifying both the clinker and limestone fineness for a given application. Also, if a limestone of proven performance with a given source of clinker is used with another source of clinker, e.g. with a lower aluminate content or reactivity, or without optimizing the SO_3 content, its performance may be significantly affected. This is in contrast with other essentially pozzolanic SCMs such as fly ash and GBFS which are less dependent on the source of clinker, and makes it much more difficult to specify performance requirements such as the activity index or k-value for limestone additions to concrete.

Comparison of performance in concrete other than strength should also be made under realistic conditions. For example, ready mixed concrete is usually specified according to range of slump and minimum strength (e.g. S2 and C30 in EN 206). The amount of water needed to achieve the slump target may of course differ between a Portland and Portland limestone cement. In some cases the Portland limestone cement may require more water for the same concrete consistence, but in most cases when it is interground it will require less water (Tennis *et al.*, 2011). After adding the correct amount of water for the desired slump, the cement content is then adjusted to achieve the required w/c ratio for the desired strength. At low limestone contents, the W/C ratio (and cement content) will usually be comparable, or even higher (lower cement content) for the Portland limestone cement resulting in a direct saving and improved environmental performance. At higher limestone contents (e.g. higher than c. 10%), a lower W/C ratio (and higher cement content) will normally be required, but even here the overall clinker content would normally be lower compared to concrete produced from the Portland cement for the same concrete strength. i.e. also resulting in a net saving and improved environmental performance: but admixtures will also probably be needed.

Regarding the interaction with water reducers, limestone shows more extensive compatibility with these admixtures than other supplementary cementitious materials. Limestone cement usually exhibits lower superplaticizer demand than ordinary Portland cement due to less adsorption of the admixture on limestone than on clinker particles, but this reduction depends on the difference in the fineness and surface area. In this sense, limestone filler represents a key constituent for stable self-consolidating concrete, with some advantages over other types of filler.

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