INTERNATIONAL CONGRESS on DURABILITY of CONCRETE

NATURAL LIMESTONE FILLER: PHYSICAL AND CHEMICAL PROPERTIES WITH REGARD TO CEMENT BASED MATERIALS PROPERTIES

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ABSTRACT

Natural limestone fillers are available on the market and supplied by limestone aggregates industry but also ornamental stone suppliers. The use of limestone fillers in cement based concrete requires a thorough characterization of the materials. Physical and chemical properties will influence behaviour of the fresh and hardened concrete. Impurities may affect cement hydration process, delay the setting time and decrease the compressive strength.
Six types of limestone fillers, in the form of finely ground limestone powders, have been collected in Belgium (more precisely in Wallonia Region). They differ from each other through their physical properties (Blaine fineness, particle size distribution, water demand) but also chemical and mineralogical properties (presence of impurities such as sulphate, clay, quartz and dolomite). Special attention has been focused on clay content and type influences; limestone fillers have been artificially polluted with clays in order to investigate their behaviour in cement based mortars.
The effect of the nature and the substitution rate of the fillers on the properties of mortars are investigated. Relationships between physico-chemical properties of the fillers and the properties of mortars clearly indicate a harder influence of the limestone composition on the fresh than the hardened properties.

Key-words: limestone fillers, size, shape, specific surface, water demand, mineralogy

INTRODUCTION

Limestone fillers are notably used as cement replacement materials (cement additions) [1, 2]. As the behaviour of fresh and hardened concrete depends on the intrinsic properties of fines, notably the so-called “filler effect” [3, 4, 5], the use of these by-products requires a thorough characterization [6]. Rheological problems may be solved usually by means of admixtures and viscosity agents [7, 8].
In Belgium, typical additions for concrete like fly ashes and blast furnace slags are becoming rare. Limestone fillers are quite abundant and already used in several applications: they are actually cheaper and less polluting than cement. These are the reasons why limestone fillers in

cement based composites were investigated, specifically for Self Compacting Repair Mortars [9] and Self Compacting Concrete [10]. The effects of this material on fresh concrete properties and the low influence on hardened concrete properties have been already pointed out [11, 12]. When analysing and optimizing mixes, very particular behaviour of cement based composites has been observed with specific fillers; chemical analysis revealed higher clay material content [13, 14]. Clay materials generally present high specific surface and contribute to an increase in water demand of cement based materials [15]: that is the reason why clay content is usually limited for sands and aggregates [16, 17] in order to maintain good consistency without increasing water content. Moreover, interactions may exist between cement paste and clay: when clay particles are covering sand grains instead of being well dispersed into cement matrix, mechanical performances as well as durability of concrete may be affected. Other authors however consider that clay is inert and could induce higher density of the interfacial transition zone (ITZ) due to fine granulometry [16, 17]. Finally, specific clay materials like montmorillonite type may swell – 5 times initial volume for some materials – and produce swelling and/or shrinkage into concrete, leading to potential cracking [16].

The suitability of these limestone fillers for production of cement based composites, specifically SCM, has been consequently more deeply investigated [6, 9]. In the present research, investigations are focused on clay materials in limestone fillers and their influence on the design of mortars and the behaviour of fresh and hardened mortars. Natural limestone fillers collected in Belgium as well as modified limestone fillers with fixed clay content have been used.

MATERIALS

Table 1 shows specific characteristics of six limestone fillers used in this study. Drying and subsequent desagglomeration operations for materials with high level of moisture (wet process) were necessary; they didn't induce any significant grain size reduction because of the use of a dry mill equipment working in semi-autogenous conditions [1].
Ordinary Portland Cement (OPC) CEM I 42.5 R HES (EN 197-1 [19]), with a clinker mineralogical composition (Bogue method) of C_3S=69%, C_2S=7%, C_3A=8% and C_4AF=7%, was used for mortar preparation.

Table 1 - Origin and production process of limestone fillers

Limestone filler reference	Production process		Industrial sector
F1	Dry process	Crushing	Lime
F2			
F3		Drying / crushing	Aggregates
F4	Wet process	Sawing	Ornamental stones
F5		Washing	Aggregates
F6			

EXPERIMENTAL PROCEDURE

A quantitative mineralogical characterization and a chemical analysis of the limestone fillers were done by means of X-Ray Diffraction (XRD) and Inductively Coupled Plasma (ICP) spectroscopy, respectively. Methylene Blue Adsorption (MBA) was conducted in accordance with EN 933-9 [20].

Particle Size Distributions (PSD) of limestone fillers and cement were performed by means of laser diffraction. Specific surface area was measured according to Blaine and B.E.T. methods. The flow spread test was used to determine the water requirement β_P [6].
Modified Blended Mortars (MBM) were prepared on the basis of a reference mortar in which cement has been successively substituted by 15, 25 and 35% in mass of limestone fillers, respectively. The Water-to-Binder (W/B) ratio was kept to 0.5. No superplasticizer was added. Preparation of mortars and measurement of the compressive strength were carried out according to EN 196-1 [21]. The consistency and the initial setting time of mortars were determined according to EN 1015-3 [22] and EN 480-2 [23], respectively.

NATURAL LIMESTONE: RESULTS AND DISCUSSIONS

Physico-chemical characterization

Table 2 shows the main results of mineralogical and chemical characterizations. Fillers coming from lime production (F1, F2) and ornamental stones sawing (F4) present a very high $CaCO_3$ content whereas large amounts of impurities are observed in the case of fillers produced in limestone quarries (15% of quartz for F3 and 23% of dolomite for F6). Moreover, Al_2O_3 and alkalis (Na_2O and K_2O) contents indicate a contamination by clay for fillers coming from aggregate production industry [18]. This is confirmed by Methylene Blue Adsorption results.

Table 2 - Mineralogical and chemical characterization of limestone fillers

Limestone filler reference	F1	F2	F3	F4	F5	F6
Mineralogical analysis (main phases)						
Calcite $CaCO_3$ [%]	99.5	99.5	82.0	94.5	86.0	75.0
Quartz SiO_2 [%]	0.0	0.0	<u>15.5</u>	1.8	6.5	2.0
Dolomite $Ca(Mg,Fe)(CO_3)_2$ [%]	0.5	0.5	2.5	3.7	7.5	<u>23.0</u>
Chemical analysis (minor components)						
Al_2O_3 [%]	0.15	0.07	<u>2.38</u>	0.63	<u>4.45</u>	<u>1.38</u>
Na_2O [%]	0.07	0.03	0.33	0.27	0.10	0.06
K_2O [%]	0.03	0.02	0.61	0.11	1.02	0.28
Fe_2O_3 [%]	0.15	0.04	0.90	0.33	1.71	0.82
Methylene Blue Adsorption [g/kg filler]	0.7	0.7	4.0	1.3	5.0	3.3

Physical properties of limestone fillers and OPC are listed in Table 3. The characteristic percentile diameters d_{10}, d_{50} and d_{90} and the uniformity coefficient C_u (d_{60}/d_{10}) are reported. Limestone fillers are very fine products with d_{50} between 7.1 µm (F4) and 14.8 µm (F6). The OPC is well graded with the smallest amount of fine particles (around 19% of particles smaller than 5 µm).
Blaine specific surface areas $S_{S,Blaine}$ of samples are ranged from about 0.22 to 0.77 m^2/g. In comparison, B.E.T. specific surface areas $S_{S,BET}$ are very high with values between 1.2 and 5.7 m^2/g. Figure 1 shows good correlation between MBA and $S_{S,BET}$, except for F4, i.e. the finest filler. It points out the high influence of clay fine particles in the measurement of $S_{S,BET}$. The presence of clay fine particles could also partially explain the lack of correlation between specific surface areas measured with the two methods. Indeed, Blaine permeability method considers neither the entire external surface of small clayey particles physically adsorbed on bigger calcite particles, nor the internal surface of clay [3]. On the other hand, B.E.T method is much more influenced by the particle shapes than the Blaine method.

The water requirement β_P of limestone fillers varies between 0.75 and 1.42 and is related to MBA and $S_{S, BET}$ values.

Table 3 - Physical characterization of limestone fillers and OPC

Limestone filler reference	F1	F2	F3	F4	F5	F6	OPC
Particle size distribution							
d_{10} [µm]	1.5	1.2	1.2	1.2	1.4	1.7	2.4
d_{50} [µm]	13.6	9.4	8.8	7.1	9.0	14.8	16.6
d_{90} [µm]	72.0	69.2	50.6	46.5	48.6	103.3	48.1
C_u [---]	14.1	12.0	11.5	9.1	9.1	12.9	8.8
Specific surface area							
$S_{S,Blaine}$ [m^2/g]	0.48	0.53	0.65	0.77	0.61	0.22	0.31
$S_{S,BET}$ [m^2/g]	1.3	1.2	5.5	4.0	5.7	3.7	---
Water requirement							
β_P [---]	0.84	0.75	1.11	1.05	1.42	1.07	0.99
Setting time (25% substitution in mass)							
Time (min)	282	280	286	254	309	306	302
Hardening time (25% substitution in mass)							
Time (min)	401	387	428	332	453	412	400

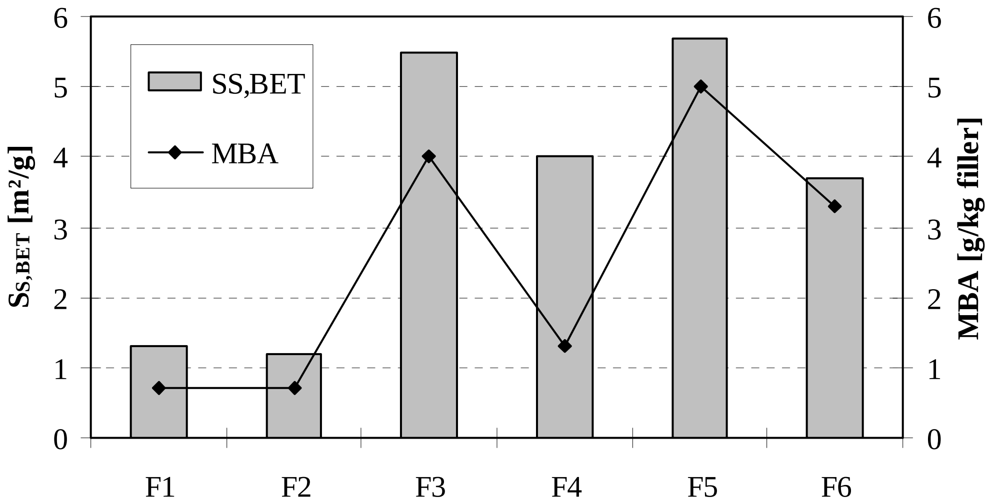

Figure 1 - Relationship between $S_{S,BET}$ and Methylene Blue Adsorption MBA

Mortar performances

Figure 2 shows the Relative Loss of Flow (RLF) of MBM as a function of the increasing proportion of limestone filler. The flow of the reference mortar is equal to 220 mm. It can be seen that a low substitution rate of 15% of OPC by limestone filler tends to reduce the mortar consistency by min. 5% (F2, F3) and up to 17% (F5). As explained before by Gallias for cement-blended pastes [8], this effect could mainly be attributed to a less good arrangement of the fine particles in the absence of superplasticizer. In case of filler F5, the RLF increases as the content of limestone filler increases from 15 to 35%; for F3 and F6, it seems to be constant above 15%. For the other fillers, the RLF tends to decrease. This difference in behaviour can be related to the presence or absence of swelling clay minerals in the fillers, as illustrated in figure 3 for mortars prepared with 65% OPC and 35% limestone filler by mass: an increase of flow rate is directly correlated to a decrease of MBA. Moreover, a good correlation (Fig. 3) between the mortar consistency and the water requirement of fillers has been found (β_P values).

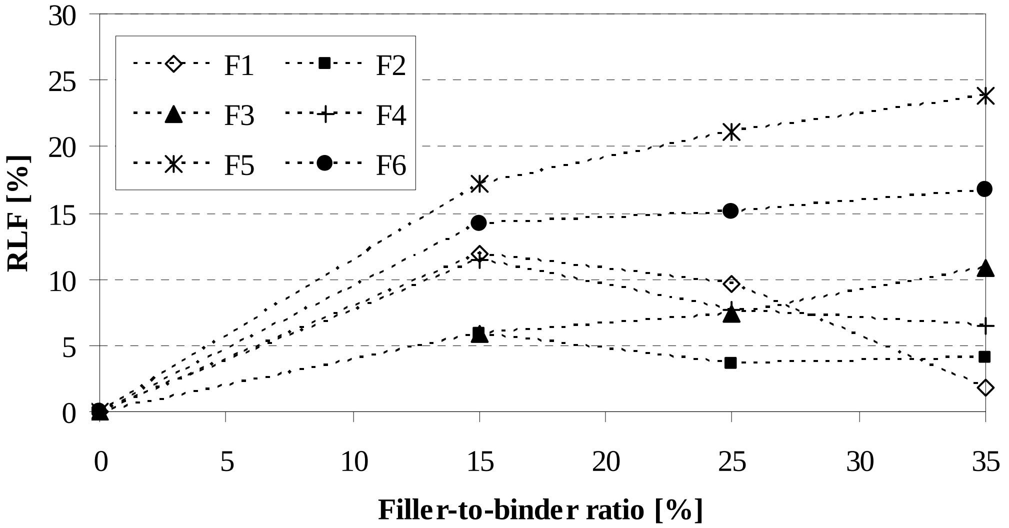

Figure 2 - Influence of limestone fillers on mortar consistency

These results indicate that the use of limestone filler containing a significant amount of clayey particles tends to decrease the mortar consistency. For practical applications, an increase in the W/B-ratio could be required, which could negatively affect the porosity of the microstructure, the mechanical properties and the durability of the mortar.

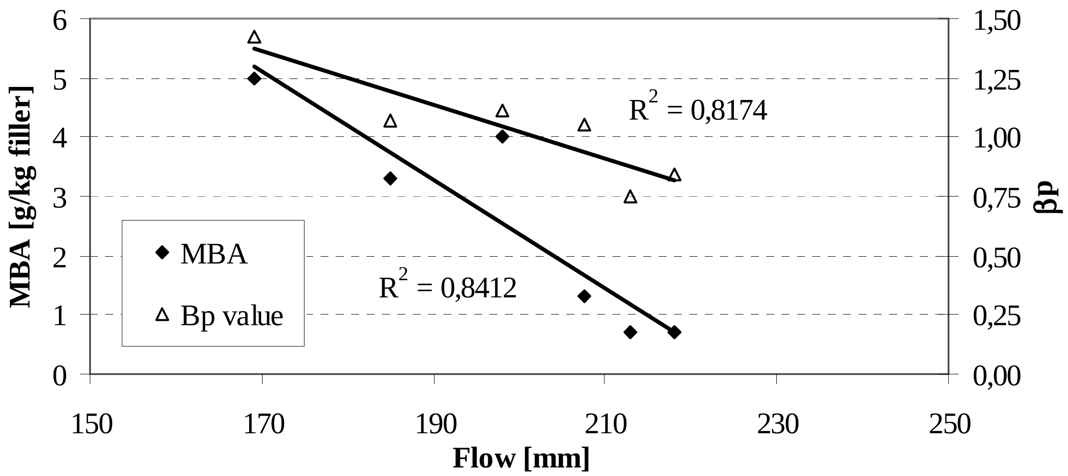

Figure 3 - Relationship between mortar consistency and MBA or β_P *of limestone fillers (substitution rate of 35% by mass)*

The initial setting time of the reference mortar is about 300 minutes (Table 3). When testing mortars prepared with 25% limestone filler and 75% cement by mass, results are ranged between 280 and 310 minutes, except for F4 which is the finest filler: in this case, the initial setting time decreases to 254 minutes. Hardening time however is more variable, except once again for F4 which is smaller. Fillers act as nucleation sites, which promote chemical reactions and cement hydration process.

The 28-day compressive strength of mortars containing 0, 15, 25 and 35% of limestone filler (average of six samples for each filler/substitution rate) is given in Fig. 5.

The strength activity indexes at 28 days, determined in accordance with French standard NF P18-508 [24], are given in Table 4. Strength activity index is defined as the ratio between compressive strengths measured at the same age on specimens prepared with 75% reference cement and 25% limestone filler, by mass, and 100% reference cement, respectively [6].

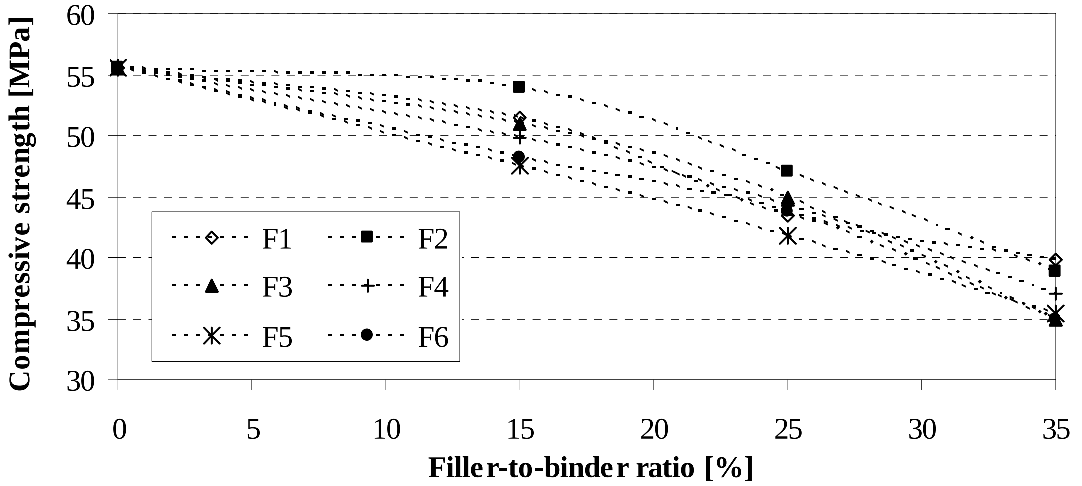

Figure 4 - Influence of limestone filler on 28-day compressive strength of mortars

Indexes vary from 0.75 to 0.85, which is quite good for such material: French standard NF P 18-508 [24] only covers limestone fillers with index higher than 0.71.

Table 4 - Strength activity index of the limestone fillers (W/B-ratio = 0.50)

Limestone filler reference	F1	F2	F3	F4	F5	F6
Activity index at 28 days	0.78	0.85	0.81	0.80	0.75	0.79
Activity index at 91 days	0.74	0.74	0.75	0.80	0.72	0.76

Clayey or organic material content that were here used don't seem to affect 28-day compressive strength results.

BEHAVIOUR OF MODIFIED LIMESTONE FILLERS

Physico-chemical characterization of modified limestone fillers

In order to clearly understand the mechanisms related to clayey materials, pure limestone filler F1 has been selected for clay substitution with 2.5, 5 and 7.5% in volume, respectively [25]. Two types of commercial clay materials were used: bentonite (B) and kaolinite (K). The influence of clay type and content on MBA is given in Fig. 5.

Table 5 - Size distribution of added clay particles

	Kaolinite (K)	Bentonite (B)
SS BET [m^2/g]	3.9	45.5
d10 [µm]	3.0	2.1
d50 [µm]	15.5	6.7
d90 [µm]	41.3	27.2

The specific surface was measured by nitrogen adsorption after drying samples at 150 °C (Table 5). Particle size measurement has been studied by means of laser light scattering in aqueous media. kaolinite particles are coarser than bentonite: d_{50} and d_{90} diameters are greater for kaolinite than for bentonite. However, bentonite offers a Specific Surface Area that far exceeds that of kaolinite. These results are explained by the microstructure of particle: analysis of the standard isotherm of nitrogen adsorption of bentonite clearly indicates evidence of intragranular microporosity bentonite while kaolinite is non-porous material.

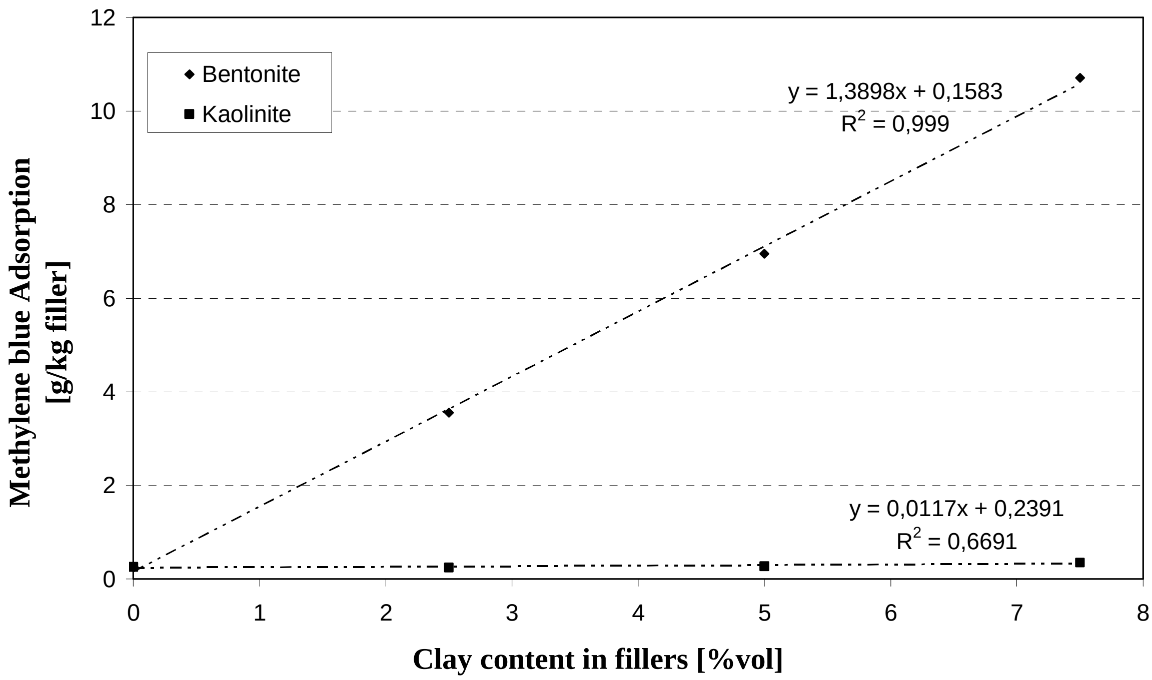

Figure 5 - MBA for modified limestone filler F1 with addition of bentonite (B) and kaolinite (K)

The influence of clays on MBA is directly related to the mineralogy of the particles. X-ray Diffraction Analysis of clays [17] indicates that the activity of bentonite is due to smectite which is a swelling mineral with large basal d-spacing: the increase in MBA may be directly correlated to substitution percentage.

These specific behaviours are confirmed by results of β_P measurements for four paste mixes (Table 6). The clay substitution rates for filler F1 are 2.5% (B1 or K1) and 5% in volume (B2 or K2), respectively. Bentonite tends to adsorb water and restrain the flowing of the paste.

Table 6 - β_P values for modified limestone fillers

Reference	β_P.
F1	0.84
F1B1	1.05
F1B2	1.21
F1K1	0.92
F1K2	0.70

Mortars design and testing

Mortars have been prepared in accordance with EN 196-1; cement has been substituted by 25% in volume of modified limestone filler F1 (CF1xy), where x is B or K and y represents clay content (1 = 2.5% and 2 = 5%, in volume). Volume substitution was preferred to mass substitution in order to avoid any change of global volume that could influence the results of the tests. Consistency and compressive strength were determined according to EN 1015-3 and EN 196-1, respectively.

Fresh mortar performances

The highest flow value is obtained for unsubstituted cement mortar: when clay is incorporated into F1, flow decrease is systematically observed (Fig. 6). Partial substitution of F1 by bentonite (CF1B1 and CF1B2) induces a higher decrease of consistency, probably due to higher water adsorption, while presence of kaolinite (K) doesn't seem to have major effect.

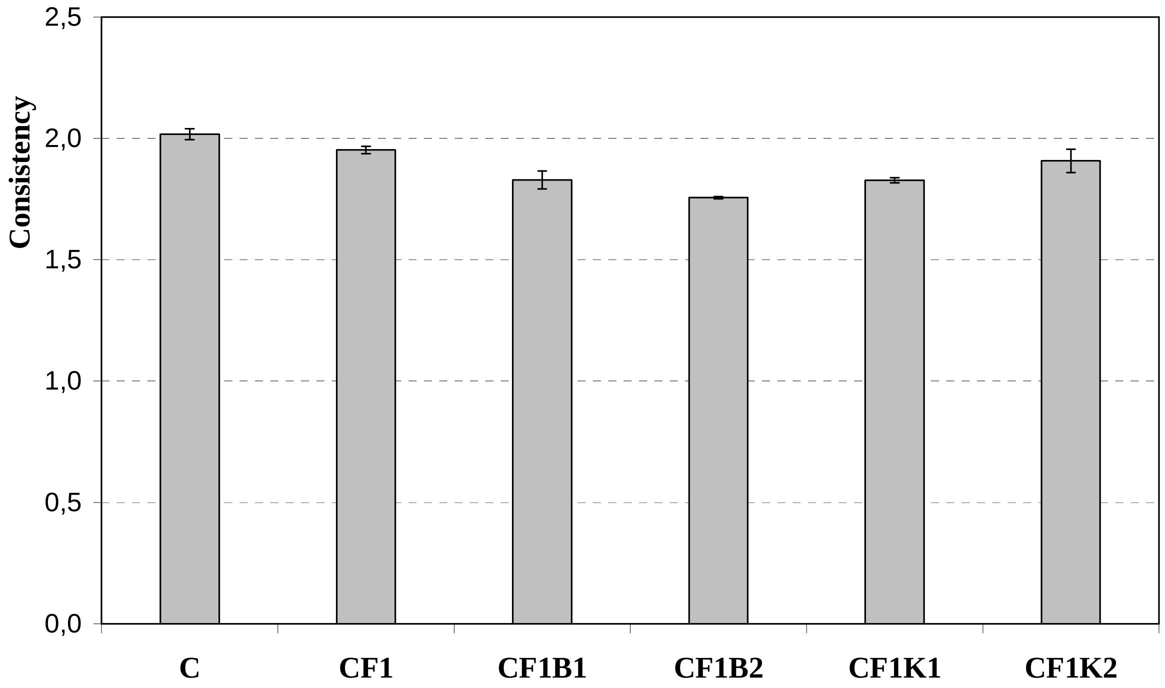

Figure 6 - Consistency of mortars with modified limestone fillers

Three parameters – MBA, β_P and mortar consistency – are obviously affected by the presence of swelling clay like bentonite material.

Hardened mortar performances

Compressive strength was evaluated after 7 and 28 days of hardening, respectively. The highest values are again obtained for unsubstituted cement mortar i.e. 43 MPa (7 days) and 56 MPa (28 days) (Figs. 7 and 8). Limestone filler F1 induces a decrease of performances: clay material content doesn't seem to have major influence on 7-day compressive strength, with regard to the influence of limestone filler itself. That means that the effect of cement substitution by limestone filler is dominant over the effect of clayey materials.

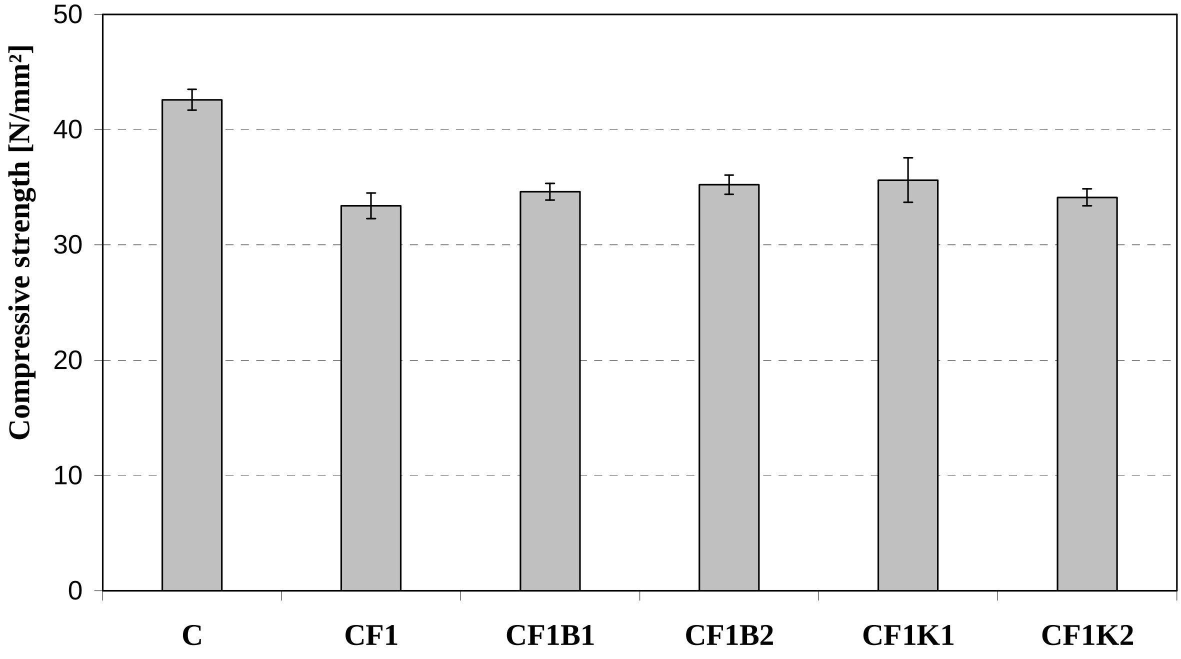

Figure 7 - 7-day compressive strength of mortars with modified limestone fillers

Similar conclusions may be given for the 28-day compressive strength of the different mortars. The decrease in strength, when substituting filler F1 by clay (Fig. 8), is however higher and increases with clay content: the less quantity of reactive material is inducing less hydrated products and, consequently, less cohesion.

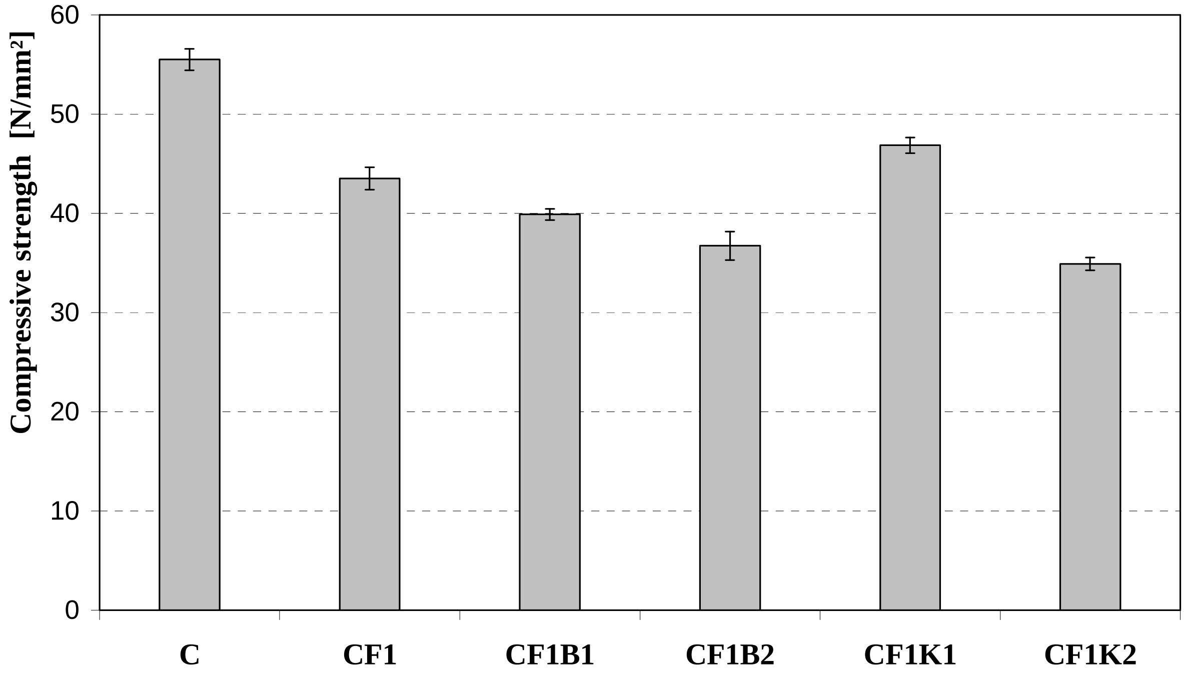

Figure 8 - 28-day compressive strength of mortars with modified limestone fillers

Moreover, capillary suction and water absorption results show an increase of the rate of absorption when limestone fillers are incorporated into mortars. But clay content doesn't seem to have any effect [18].

CONCLUSIONS

The following conclusions may be drawn from the present investigations concerning the suitability of local-available limestone fillers for using in cement based composites:

- the limestone fillers are generally characterized through their physico-chemical characteristics (granulometry, $CaCO_3$ content, …). The presence of impurities, such as clay, sulphates, quartz and dolomite, has also to be investigated as it may influence mortar and concrete properties;
- the water requirement β_P of limestone fillers is mainly affected by their swelling clay content;
- water requirement is directly correlated to MBA and $S_{S,\,BET}$ values;
- the consistency of fresh mortar decreases as the swelling clay content of limestone fillers increases.

That means that three main parameters – MBA, β_P and consistency – are obviously affected by the presence of clay like bentonite material. Research project also clearly shows that only swelling clays are affecting fresh properties of mortars. Next conclusions are related to the behaviour of hardened mortars:

- some limited effects on 7-day compressive strength are observed, when substituting 15% mass of OPC by limestone filler;
- the activity index of the six limestone fillers varies from 0.75 to 0.85 at 28 days. No clear or specific effect of clayey material content is noticed;
- no determined influence on initial setting time is pointed out, with exception of the finest filler. For this one, the setting time continuously decreases as the substitution rate increases from 0 to 35% by mass;

However, by means of the complementary research we performed, we may confirm that, even if it affects fresh mortar behaviour, there is no major influence of clay fine material on the behaviour of hardened mortars. Even swelling clays don't present any major effect on the porosity of the microstructure of limestone fillers modified mortars: if superplasticizers may solve rheology problems, it means that fillers from aggregate industry of ornamental stone sawing may be used in concrete manufacturing.

AKNOWLEDGEM ENT

The authors would like to acknowledge the Regional Government of Wallonia (Belgium), which partly financially supported the research (Filltech research project nr 616472) and Florence Schmitz, who performed experimentation.

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