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INFLUENCE OF PHYSICO-CHEMICAL CHARACTERISTICS OF LIMESTONE FILLERS ON FRESH AND HARDENED MORTAR PERFORMANCES

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INFLUENCE OF PHYSICO-CHEMICAL CHARACTERISTICS OF LIMESTONE FILLERS ON FRESH AND HARDENED MORTAR PERFORMANCES

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Abstract

In order to meet the specific requirements for fresh Self-Compacting Concrete (SCC), i.e. a high workability together with a good resistance to segregation, the amount of coarse aggregates has to be reduced and replaced by fine material. Since cement is quite expensive and can develop a high heat of hydration with possible problems for thermal cracks in massive concrete, mineral fillers are usually used.

In Belgium, local available materials are limestone fillers; they are very well-adapted for the optimisation of particle packing and flow behaviour of cementitious paste in SCC mixes. These by-products are issued from different sectors, such as the aggregate and lime production industry (quarrying operations) and the ornamental stones industry (sawing operations).

The suitability of these fillers for use in SCC or conventional concrete production was investigated. This paper reports the effect of the nature and the substitution rate of the fillers on the properties of mortars. Some relationship between the physico-chemical properties of the fillers and the properties of mortars were brought forward.

1. INTRODUCTION

To ensure suitable rheological properties for Self-Compacting Concrete (SCC), mineral additions are commonly used. In this research project, six limestone fillers (noted F1 to F6 in table 1) have been collected in Belgium (Walloon Region). They differ from each other through their physical characteristics (Blaine fineness, particle size distribution, water requirement) but also chemical and mineralogical characteristics (presence of impurities such as clay, quartz and dolomite). The suitability of these fillers for production of SCC or conventional concrete has been investigated. These characteristics will influence the mixture proportions and the behaviour of the fresh and hardened mortar and concrete.

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2. 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 milling-drying equipment working in semi-autogenous conditions [1].

Ordinary Portland Cement (OPC) CEM I 42.5 R HES (EN 197-1), 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			

3. 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 (annex A).

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 [2].

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. The consistency and the initial setting time of mortars were determined according to EN 1015-3 (by flow table) and EN 480-2, respectively.

4. RESULTS AND DISCUSSION

4.1 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 [1]. This is confirmed by Methylene Blue Adsorption results.

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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	15.5	1.8	6.5	2.0
Dolomite $Ca(Mg,Fe)(CO_3)_2$ [%]	0.5	0.5	2.5	3.7	7.5	23.0
Chemical analysis (minor components)						
Al_2O_3 [%]	0.15	0.07	2.38	0.63	4.45	1.38
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

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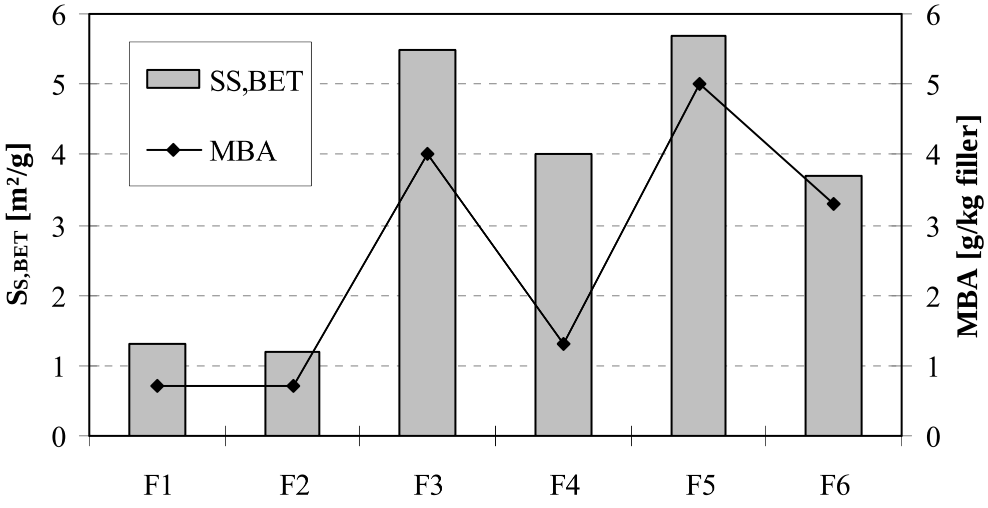

Figure 1: Relationship between $S_{S,BET}$ and Methylene Blue Adsorption MBA

4.2 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 [4], this effect could mainly be attributed to a less good arrangement of the fine particles in the absence of superplasticizer. In case of fillers F3, F5 and F6, the RLF increases as the content of limestone filler increases from 15 to 35%. For the other fillers, the RLF tends to decrease. This difference in behaviour can be related to the presence or absence of clay fine particles in the fillers, as illustrated in figure 3 for mortars prepared with 65% OPC and 35% limestone filler by mass. Moreover, a good correlation between the mortar consistency and the water requirement of fillers has been found (figure 3).

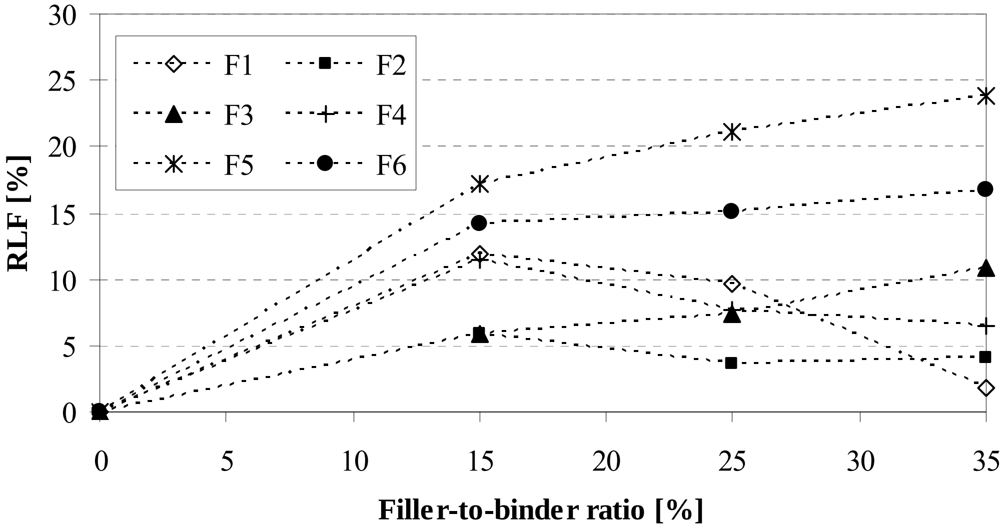

Figure 2: Influence of limestone fillers on mortar consistency

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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.

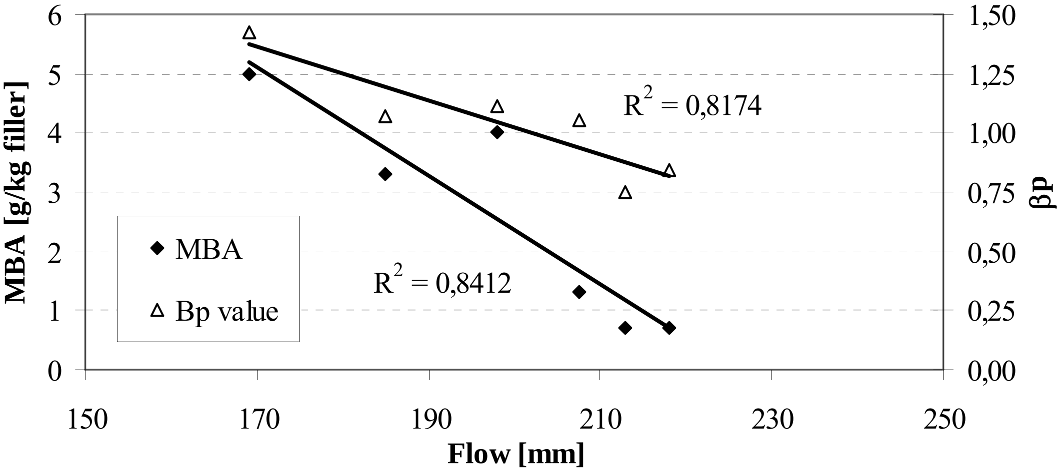

Figure 3: Relationship between mortar consistency and MBA or β_P of limestone fillers (substitution rate of 35% by mass)

The initial setting time of the reference mortar is about 300 minutes. 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. With this latter one, the initial setting time decreases to 255 minutes.

Some limited effects of the limestone fillers have been reported on the 7-day compressive strength for the mixes with a substitution rate of 15%: the average loss of performance has been observed to be as small as 2%, with comparison to the reference mortar. The 28-day compressive strength of mortars containing 0, 15, 25 and 35% of limestone filler (average of six samples) is given in figure 4.

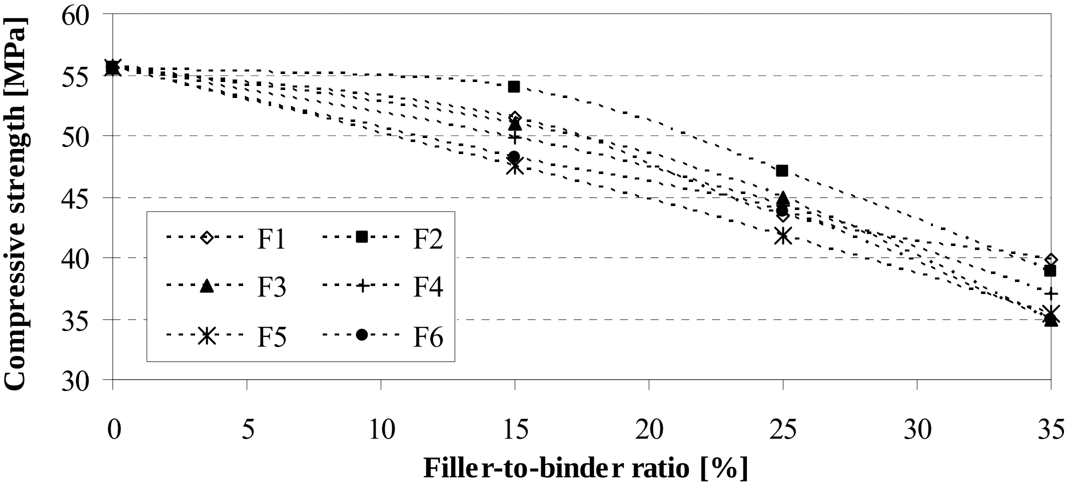

Figure 4: Influence of limestone filler on 28-day compressive strength of mortars

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The strength activity indexes at 28 and 91 days, determined in accordance with French standard NF P18-508, are given in Table 4. Activity index is the ratio of the compressive strength of standard mortar bars, prepared with 75% reference cement and 25% limestone filler by mass, to the compressive strength of standard mortar bars prepared with 100% reference cement, when tested at the same age [5].

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

5. CONCLUSIONS

The following conclusions may be drawn from the present investigation concerning the suitability of local-available limestone fillers for use in mortar and concrete:

- The limestone fillers collected in Belgium differ from each other through their physico-chemical characteristics. The presence of impurities such as clay, quartz and dolomite are observed;
- The water requirement of limestone fillers is mainly influenced by their clay content (indicated here by high MBA and $S_{S,BET}$ values). Therefore, the consistency of fresh mortar decreases as the clay content of limestone fillers increases;
- 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 determined influence on initial setting time is noticed, 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.

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