RATIONAL USE OF FLASH METAKAOLIN APPLIED TO INDUSTRIAL DESIGN OF SELF-COMPACTING CONCRETE

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ABSTRACT

Supplementary cementitious materials (SCM) are becoming essential in the replacement of cement to reduce the cost and the environmental impact of concrete. Recently, metakaolin was introduced as a new compound in SCC design. The challenge of using metakaolin was the high water demand of this powder. This issue can be overcome by using both a lower purity metakaolin, reducing the water demand, and considering the higher water demand of this type of product in an appropriate way. This study is based on a design method adapted for the use of metakaolin as the only SCM in SCC. The diphasic approach consists of optimizing the quantity of water in the paste and aggregates. The results show that the design of SCC using several types of cements and for several cement replacement percentages with metakaolin is possible in a variety of cases, both in the laboratory and in industry.

Keywords: Metakaolin; Mix design; Self-compacting concrete (SCC); Industrial application

INTRODUCTION

The flow of self-compacting concrete (SCC) is usually achieved through a reduction in the coarse aggregate content, an increase in the powder content and the use of chemical admixtures. For reasons of preservation of the environment, reduction of cost and improvement of concrete properties, supplementary cementitious materials (SCM) are often used in substitution for cement. Limestone filler, fly ash and slag are the main SCM used for manufacturing SCC [1]. Metakaolin (MK) is less common in this

kind of application, even though it improves the properties of hardened concrete through its early pozzolanic reaction. The main reason for this is probably related to its high water demand [2], which can imply either an increase in the water-binder ratio or in the quantity of high range water reducing agent (HRWRA) [3] needed to maintain a given workability. It has been shown that MK probably modifies the rheological properties of the concrete. Static [2] and dynamic [4] yield stresses are increased when a part of the cement is replaced with metakaolin, the increase being particularly marked over time [5]. This increase can be considered as a negative factor regarding the flow of SCC, but proper use of HRWRA can strongly reduce this effect [2]. Higher viscosity has also been observed [3,4], generally related to the increased specific surface area of MK compared to the cement [5] This effect can be considered as positive since it could allow the coarser particles to be stabilized in the suspension and limit the use of viscosity modifying agents.
Considering the effects of MK on concrete rheology, and since more highly reactive materials such as MK can present some advantages compared to inert/less reactive SCM (early age hardening, durability, etc.), it was decided to assess the technical feasibility of incorporating metakaolin in SCC as a partial replacement of cement. Special attention was paid to industrial constraints inherent in the use of such an SCM: need for a formulation method for SCC adapted to the use of MK for industrial purposes, management of the water demand of MK, respect of the requirement of standards EN 206-1 and EN 206-9 in terms of binder content and concrete specifications, and effect of last minute changes of formulation parameters on the properties of the concrete.

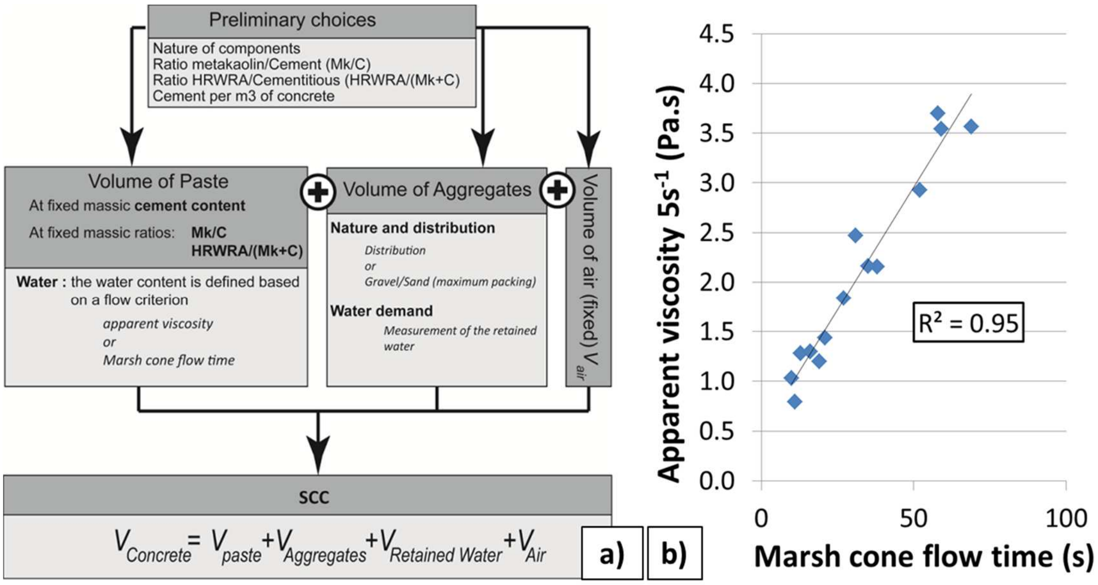
DESIGN METHOD

The design of SCC containing metakaolin as the only mineral addition was derived by adapting a method already used for the design of limestone powder-based SCC, presented at SCC 2010 in Montreal [6]. This method is based on a diphasic approach considering the association between a paste and a wet aggregate skeleton (Figure 1a).

- The volume of **paste** is directly related to the binder content in the concrete mixture (in kg/m^3), itself fixed by the class of the concrete. The water content of the cement paste is optimized on the basis of a flow criterion, by using either the apparent viscosity at low shear rate or the Marsh cone flow time. Preliminary laboratory tests showed that a viscosity criterion between 2 Pa.s and 4 Pa.s, corresponding to a flow time between 40 and 75 s (Figure 1b), was suitable for the design of SCC. When limestone powder SCC was designed [6], a paste viscosity of 1 $Pa.s^{-1}$ was used. This difference in viscosity criterion could be related to the ability of the metakaolin-based paste to present thixotropic behavior leading to an increase in the measured viscosity at low shear rates because of the structural rebuild, or to an insufficient mixing energy during the preparation phase of the metakaolin/cement paste despite the use of the HRWRA. Initially, the design method was developed using apparent viscosity measurements to optimize the water content of the paste. However, for an easier application in the concrete industry, this test could be replaced by Marsh cone flow time, which shows a significant linear relationship with the viscosity measurements (Figure 1b).

- Two main characteristics concerning the **aggregates** must be taken into account: the optimization of the grading curve (obtained from an existing composition or through a maximum packing optimization [7]), and the water demand of the aggregate skeleton to ensure that the water volume determined for the cement paste remain unchanged because of water absorption by the aggregates (obtained by a test measuring the retained water [8]).

Figure 1. a) Design method for SCC [6], b) relationship between values of apparent viscosity at 5s⁻¹ and marsh cone flow time.



MATERIALS

The cements used were commercially available in the south of France and complied with EN 197-1. Their main characteristics are given in Table 1. Table 2 summarizes the characteristics of the metakaolin used in this study and the limestone powders used in reference concretes. The metakaolin, obtained by an industrial flash calcination process [9], presented an impurity content (mainly quartz) of about 50% by weight, thus reducing the specific surface area and causing a reduction of the water demand [9]. The aggregates, coming from southern France, are used by several concrete manufacturers for the design of SCC (Table 3).

Table 1: Cement properties

	Denomination	% clinker	% of main constituents*	Main constituents*	Density (kg/m^3)	Specific surface area (Blaine) (cm^2/g)
Cement C1	CEM I 52.5N	98.5	-	-	3190	3550
Cement C2	CEMII A 42.5 R	85	15	limestone	3040	4196
Cement C3	CEM II A 42.5 R	92	6	limestone	3120	3850
Cement C4	CEM III A 52.5 N	57	40	blast furnace slag	3010	4300

* other than clinker

Table 2: SCM properties

	Mineralogy	Density (kg/m^3)	Specific surface area (cm^2/g)	D_{50}(μm)
Metakaolin	50% amorphous 50% quartz	2510	140 000 (BET)	19
Filler F1	97.6% $CaCO_3$	2700	4 850 (Blaine)	13
Filler F2	97.5% $CaCO_3$	2710	3 520 (Blaine)	---
Filler F3	97.7% $CaCO_3$	2700	4 510 (Blaine)	15

Table 3: Aggregate properties

	Nature	Grading (mm)	Rolled or crushed	Absorption coefficient (wt. %)
Sand S1	Siliceous	0-4	rolled	1.5
Gravel G1	Siliceous	4-14	rolled	1.2
Sand S2	Siliceous-limestone	0-4	rolled	0.7
Gravel G2	Granite	6.3-10	crushed	0.7
Sand S3	Siliceous	0-4	rolled	1.2
Gravel G3	Siliceous	4-14	rolled	1.0

RESULTS AND DISCUSSION

The design method briefly described above was used for various industrial applications.

Case study 1: formulation method for SCC adapted to the use of MK for industrial purposes

Context – In order to improve the properties of hardened concrete (e.g. durability), a concrete producer needed a formulation of SCC containing a reactive SCM like MK. Since a direct replacement of the cement and/or limestone filler was not suitable due to the difference of water demand of the constituents, an appropriate design method for MK-SCC was required. In this case, the method illustrated in Figure 1a and initially developed for limestone filler was followed strictly.
Design of the paste (design effort: 1-2 hours) - The paste was designed with the cement C1, a binder content of 400 kg/m^3, a metakaolin/(cement+metakaolin) ratio of

0.20 [9] and an HRWRA (polycarboxylate type) content of 1.3% by mass of powder. After some tests performed to achieve a paste flow time of 40-45 s (Marsh cone, opening of 8 mm) the water content was fixed at a value of 112 kg/m^3 of concrete.

Aggregate skeleton (design effort: 24 hours for the prewetting of aggregates and ½ hour for the retained water test) - This paste was then associated with aggregates (0-4 mm sand S1 and 4-14 mm gravel G1, siliceous and rounded). An optimal Gravel/Sand ratio = 1.1 was determined by means of a maximal experimental packing test [7]. A retained water/aggregates volumetric ratio of 13.3% was measured, meaning that 85 L/m^3 of concrete of water was necessary to wet the aggregates (both the porosity and a thin surrounding layer). This value is approximately 4 times the water quantity measured following standard EN 1097-6 (22 L/m^3) and is necessary to avoid an underestimation of the aggregate water demand, which could lead to pumping of the paste water.

The two phases were associated (considering an air content of 20 L/m^3) and the concrete composition is presented in Table 4. The fresh properties of the concrete were tested following standard EN 206-9, using the flow spread (both diameter and the time needed to reach a concrete spread diameter of 500 mm), the L-box test (with 3 rebars, result expressed as the ratio H2/H1) and sieve stability. When the criterion of the standard was applied, this concrete was found suitable for both horizontal and vertical applications.

Table 4: Detailed concrete design

Paste				aggregates		Fresh properties				28-d strength (MPa)
Cement (kg/m^3)	Mk (kg/m^3)	HRWRA (kg/m^3)	Water (kg/m^3)	Sand + Gravel (kg/m^3)	Water (kg/m^3)	Spread (cm)	T_{500} (s)	L-box	Sieve stability (%)	
320	80	5.2	112	1680	85	66	<2	0.85	8	65

Case study 2: designs of MK-SCC in comparison to industrial LF-SCC

Context – The aim of this work was to increase the number of concrete formulations of concrete producers by developing SCC with MK, which were compared with existing formulations of SCC with limestone filler. One important constraint was that SCC with MK should have the same technical and economic performance as existing SCC.

In this case, the objective was to show that the flow characteristics of industrial SCC incorporating limestone filler were not impaired when limestone filler was replaced by metakaolin. Since the replacement was to be made considering the activity index of each SCM, a lower content of binder was targeted for the design of MK-SCC (MK being more reactive than filler). In addition, with the aim of staying in an economically viable situation, the quantity of binder had to be kept as low as possible. This constraint increased the difficulty of achieving the requested fresh-SCC properties because of the decrease of the flowability with the reduction of the paste content.

All the designs (LF-SCC and MK-SCC), together with basic properties (slump flow and 28-day compressive strength), are given in Table 5. A first observation is the large reduction in the binder content achieved when limestone powder is replaced by

metakaolin in SCC (respectively 13%, 34% and 24% for case studies 1 to 3). Considering the experimental dispersion of the results (± 3 cm), it can be said that the flow spread remained unchanged (comparing LF-SCC_i with MK-SCC_i), except for the mixture MK-SCC3. Nevertheless, this mixture still met the EN 206-9 criterion for the slump flow (class SF1). This latter case highlighted the difficulty of designing low-powder SCC, such as those studied in laboratory applications [10], in an industrial context because of the limits of the standards (e.g. EN 206-1) in terms of Water/Binder ratio and compressive strength, and also because the amount of HRWRA was limited in the aim of keeping down costs. The quantity of 350 kg/m^3 of cement+metakaolin seemed to be a strict minimum, below which there was not sufficient paste and the friction between coarse aggregates became too high for a high level of slump-flow to be achieved.
The MK-SCC presented improved compressive strength (mixes 1 and 2) or did not change the strength class (Mix 3). The improvement in compressive strength for mixes 1 and 2 could be explained by an optimization of the concrete design by giving appropriate consideration to all the components, leading to a reduction in the water/binder ratio (mix 1) despite the high water demand of the metakaolin. It can also be related to the quantity of reactive powder in the mixtures, since MK-SCC1 and MK-SCC2 contained 350 and 390 kg of cement+MK, respectively, compared to 300 and 350 kg for LF-SCC1 and LF-SCC2. The use of more active binder increased the pozzolanic C-S-H content, leading to an improvement in the matrix performance.

Table 5: Metakaolin based SCC versus Limestone based SCC

	Cement (kg/m^3)	SCM (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)	Total Water (kg/m^3)	Efficient Water (kg/m3)	HRWRA (kg/m^3)	AEA (kg/m^3)	W/B	Spread (cm)	28-d strength (MPa)
LF-SCC1	C2;300	F1;100	S2;895	G2;825	197	184	2.4	0.3	0.57	65	27.2
MK-SCC1	C2;290	60	S2;924	G2;871	190	177	2.2	0.3	0.52	65	34.5
LF-SCC2	C3;350	F2;243	S3;798	G3;681	210	200	6.3	0	0.50	77	56.7
MK-SCC2	C3;321	68	S3;832	G3;818	216	205	5.9	0	0.53	74	61.0
LF-SCC3	C4;295	F3;173	S4;831	G4;789	204	186	31	0.5	0.58	70	38.2
MK-SCC3	C4;290	60	S4;906	G4;860	192	177	3.0	0.7	0.52	62	32.4

LF-SCC: reference concretes with filler (industrial formulation)
W/B: calculated using Efficient Water / equivalent binder following NF EN 206-1 (LF – k=0.25 and SCM/binder ≤ 30%; MK – k = 1 and SCM/binder ≤ 15%)

<u>Case study 3: Influence of paste content and gravel/sand ratio</u>

Context – On the basis of concrete MK-SCC1 (Table 5) designed to match the properties of concrete LF-SCC1, the concrete manufacturer made adjustments to the design in order to increase the slump flow. Maintaining the nature of the components, three adjustments were explored and the basic properties of the concretes are presented in Table 6.
First, the binder content was increased (Mix MK-SCC1 to MK-SCC4) to improve the workability, in accordance with the previous statements on the limit on the binder of 350 kg/m^3 of concrete for the design of SCC. It can be observed that the water requirement had to be strongly increased (+28 L/m^3) to maintain equivalent fresh state

properties. This could be explained by the simultaneous increase in the gravel content (G/S passing from 0.95 to 1.1), using crushed coarse aggregates which greatly increased the friction between the grains. The influence of the coarse aggregates can be observed when changing from mix MK-SCC4 to MK-SCC6, where the decrease in the G/S ratio from 1.1 to 1 (the variation in experimental packing is not significant, i.e. 0.490 to 0.488) while using the same total water leads to a significant increase in flow-spread. Concerning the hardened properties of the concretes (MK-SCC4 and MK-SCC6), similar compressive strengths were measured and the concretes remained in the same strength class.

Table 6: influence of design on SCC properties

	Cement C2 (kg/m^3)	MK (kg/m^3)	Sand S2 (kg/m^3)	Gravel G2 (kg/m^3)	G/S	Total Water (kg/m^3)	HRWRA (kg/m^3)	AEA (kg/m^3)	W/B	Spread (cm)	28-d strength (MPa)
MK-SCC1	290	60	924	871	0.95	190	2.2	0.3	0.52	65	34.5
MK-SCC4	310	70	795	874	1.1	218	3.2	0.3	0.57	65	42.3
MK-SCC5	310	70	813	854	1.05	218	3.2	0.3	0.57	66	---
MK-SCC6	310	70	854	854	1	218	3.2	0.3	0.57	70	38.8

CONCLUSIONS

The feasibility of employing metakaolin-based SCC was studied in an industrial context by adapting an existing design method developed for limestone powder SCC. It has shown that it is possible to design MK-SCC with equivalent fresh state, hardened state and economic properties by making rational use of the metakaolin. A basic one–to-one replacement of one mineral addition by another is not appropriate.

The following conclusions can be drawn:

- The method employed uses quick and easy tests (Marsh cone, retained water test) that are peculiarly suitable for an industrial application.
- If the high water demand of metakaolin is properly taken into consideration during the design process, it is no longer an issue for the realization of SCC.
- For reasons of economy, the powder content has to be lowered for MK-SCC, but concrete with a minimum powder content of 350 kg/m^3 was successfully produced.
- Both rounded and crushed aggregates could be employed until the G/S ratio has been adjusted to reduce grain friction.
- The use of metakaolin has a beneficial impact on the hardened properties because of its pozzolanic nature.

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