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Slurry of metakaolin combined with limestone addition for self-compacted concrete. Application for precast industry

Céline Perlot [a,*], Patrick Rougeau [b], Sylvain Dehaudt [b]

[a] SIAME, EA 4581 Equipe Géomatériaux et Structures du Génie Civil/IPRA FR, Université de Pau et des Pays de l'Adour, Allée du Parce Montaury, 64600 Anglet, France
[b] CERIB, Centre d'Études et de Recherches de l'Industrie du Béton, BP 30059, 28231 Épernon, France

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A B S T R A C T

Metakaolin improves the engineering properties of concrete because of its double effect on cementitious matrix (filler effect and pozzolanic properties). Moreover, metakaolin can reduce the environmental impact of concretes due to its lower carbon dioxide emission than clinker. The development of a slurry form of metakaolin opens new fields of investigations, such as its incorporation into self-compacting concretes (SCC). This study compares several SCC formulations that differ in their content of metakaolin and the form of metakaolin (powder or slurry). Limestone filler is included to study the benefit of employing ternary blended binder. As a main conclusion, the use of metakaolin, especially in slurry form, combined with limestone filler incorporation appears particularly suitable for SCC manufacture with high mechanical properties and durability, and very for the precast process optimization: it allows the mixing sequence to be shortened, while maintaining high workability, and more importantly the enhancement of strength at early age due to the particles deflocculating. The incorporation of metakaolin in slurry form appears particularly suitable to elaborate SCC and advantageous for precast product manufacturing as part of a sustainable development approach.

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1. Introduction

The use of fine particles as supplementary or substitution material for cement has largely been reviewed. These studies exposed how they can promote the fresh properties, the mechanical and durability performances of concretes. New fields in concrete formulation have been investigated and then, various specific materials have been set up such as high and ultra high performance concrete (HPC and UHPC) or self-compacting concrete (SCC).

The successful development of SCC has been possible due to the elaboration of performing superplasticizer and the incorporation of inert fine materials, the fillers. Their use is an crucial advance in the civil engineering domain, allowing new constructive technologies, structures with very complex forms and esthetical facing. The suppression of the vibration step in concrete fabrication improves working conditions, principally because of the suppression of noise. With this kind of concrete, security is improved; less equipment and manual labour are required. The service life of the moulds in the precast plants is also enhanced.

In a sustainable development approach through the development of high performance structures, the incorporation of industrial by-products as fillers is more and more investigated and used in practice [1]. The main environmental reason is the limitation of CO_2 emissions, a major preoccupation for the building sector in general, and more particularly for precast industry, that imposes the reduction of the clinker content in concrete products, and therefore in the binder [2,3]. In the processes of material manufacturing, the major part of carbon dioxide emissions, which are mainly responsible to the greenhouse warming, are provided by the thermal treatment stage. The very high temperature of cement elaboration (up to 1450 °C) compromises its sustainability. Furthermore, the reduction of clay to form the clinker engenders important volumes of CO_2 (decarbonation). The production of 1 kg of Portland Cement generates ~1 kg eq. CO_2 [4]. The decomposition of kaolin to elaborate metakaolin released low quantities of CO_2: firstly kaolinite clay is burned in a quite low temperature range (650–750 °C) and secondly, as the raw material is an aluminium silicate, there is no decarbonation during the burning process. The CO_2 footprint of metakaolin is reduced, ~96 kg eq. CO_2/ton, and could reaches values quite equal to zero if the calcination is performed with biogas [5]. Furthermore, fewer raw materials are needed to elaborate metakaolin [6]. For all these reasons, metakaolin could be considered as an environmentally-friendly material [7]. It has been demonstrated that a part of the cement could be successfully substituted by metakaolin, enhancing engineering properties and durability performances [8], and reducing the CO_2 footprint of concrete products [9].

* Corresponding author. Tel.: +33 5 59 57 44 32; fax: +33 5 59 57 44 39.
E-mail address: celine.perlot@univ-pau.fr (C. Perlot).

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The major limitation in the use of SCC resides in the setting of appropriate mix proportions, providing a material with suitable fresh properties and high-quality performances in term of mechanical strength and durability. Besides, from an industrial point of view, the incorporation of additions does not limit the production chain to preserve high productivity and has to guarantee the quality and regularity of the precast products. To ensure the concrete's specificity of self-compaction, the paste must be fluid and viscous to avoid bleeding or segregation. Limestone filler confers flowability, viscosity and stability [10,11]. This mineral admixtures is one of the most used in the French concrete industry. Limestone filler, however, does not present pozzolanic or hydraulic properties. To enhance mechanical and durability performances, ternary mix cement/limestone filler/pozzolanic can be developed [12,13]. As pozzolanic material, metakaolin reacts with calcium hydroxide, a cement hydration product, to form secondary C–S–H, calcium aluminate and aluminosilicate hydrates [14]. Furthermore, the fine size of its particles provides physical filling effect and adequate fresh properties for SCC formulation by using adequate superplasticizer [15–18] and especially for prolonged mixing time [19]. In the precast industry process, the products have to present suitable mechanical performances at early age to be demoulded and handled. In this aspect, the use of metakaolin was examined and is advised [9].

The present work investigates the development of new SCC which combines limestone filler and metakaolin for specific use in the precast concrete industry. The novel aspect here develops is the use of metakaolin in slurry form: the powder of metakaolin is previously spread into water and superplasticizer. This already premix could facilitate the mixing of concrete compounds from industrially point of view: less and quicker stages in mixing procedure, offer easier storage; and then more and more decrease the environmental impact of SCC using this slurry than simply powder of metakaolin. However, suitable formulation of SCC must be set up and validated. In this aim, firstly the adaptation of the mixing sequence for different metakaolin forms (powder or slurry) is studied. Attention was paid to the setting of SCC mix proportions from the exploitation criterions that the materials have to respect. Secondly, the evaluation of the SCC performances is examined in terms of microstructure, mechanical properties and durability. The samples are prepared in respect with precast process: a thermal curing was applied, which induces specific characteristics to the materials.

2. Materials

2.1. Metakaolin characterisation

Metakaolin is elaborated from natural rocks and is mainly composed of oxides (siliceous, aluminium, iron, etc.) in variable proportions relating to the original extraction lode of the mother rock, the kaolinite. The purity – and thus the reactivity- of metakaolin depends on the physico-chemical characteristics of the kaolinic clay – especially its structure – the thermal treatment to convert kaolinite into metakaolinite, the fabrication process and the final crushing [20,21]. The production of metakaolin is strictly controlled and therefore a high degree of purity and elevated pozzolanic reactivity can be obtained. In France, metakaolins are now covered by a new recent product standard: NF P 18-513 [22]. In this study, we used a commercial metakaolin: its characteristics given by the supplier are presented in Table 1. and were determined in accordance with the NF P 18-513 standard. The loss of Ignition (%) was determined in the manner as the cements [23]: it was deduced from the lost of mass from a sample before and after calcination in an electrical oven (950 ± 25 °C) during 15 min. The pozzolanic activity coefficient was determined by the Chapelle test [22,24]: it corresponds to the amount of calcium hydroxide (initially 2 g) fixed by 1 g of metakaolin after 16 h at 90 °C. The specific surface area was measured by BET gas adsorption and the water demand is evaluated from standard consistence tests on pastes [25]. The grading curve of metakaolin obtained by sedigrapy is presented in Fig. 1.

To evaluate the benefits to use metakaolin in slurry, the both forms – powder and slurry-were tested. The slurry form was obtained by mixing the powder of metakaolin with the superplasticizer used in the SCC formulation and water (concentration of 50% of dry extracts). 20 l were prepared and suitably stocked before the incorporation in concrete, after the mixing stage of dry components.

2.2. Establishing SCC mixture proportions

We explain below the approach to obtain suitable SCC mixtures. Restraints from three origins were token into account, imposed by:

- The NF EN 206-1 (2004) standard [26]: it indicates, in function of the exposure class, the mechanical performances required, the minimal amount of equivalent binder (designed by *E.B.*, calculated with the formula $E.B. = C + k.A$, where C and A are respectively the masses of cement and additions (kg m^{-3}) and k is the activity coefficient of the addition), and the maximal ratio of effective water to E.B. (W_{eff}/E.B.).
- The precast process: given the final use of the product, the size of the moulds, the positions of steel reinforcements and the properties of concrete product, the SCC has to present adapted workability, mechanical and durability performances; a minimal mechanical strength at early age is required for demoulding and handling the products, typically around 15–20 MPa.
- The need from an scientific point of view to compare the performances of the different SCC and to evaluate the influence of metakaolin. It is necessary to maintain constant several parameters (in the accuracy range of the measurements): the E.B. value, the ratios W_{eff}/E.B. and MK/(MK + C) (here *MK* is the mass of metakaolin and C the mass of cement in kg), the rate of cement substitution by metakaolin and the amount of limestone additions; obviously the same compounds (cement, gravels, sand, superplasticizer) must be used in all mixtures.

The Table 2 sums up all these constraints.

It is important to underline that in this study, the incorporation of metakaolin is realized in substitution of a cement part. The rate of cement substitution, MK/(MK + C), expressed as the fraction of cement mass substituted by metakaolin, was fixed at the constant value of 0.15 for all the materials (normalized mortars and SCC) tested in this work. This value was chosen taking into account the results of previous studies dealing with the effect of metakaolin content [27]. This replacement is based on the notion of the equivalent binder described in [26].

In the case of the control material, E.B. is calculated with only limestone additions. The NF EN 206-1 standard gives the activity coefficient of the limestone addition, k_L: $k_L = 0.25$.

For the other SCC, the mass of limestone additions (A_L, kg) taken into account in the E.B. calculation is $A_L = C/3$ (limitation imposed by the NF EN 206-1: the ratio $A_L/(A_L + C)$ must be equal to 0.25). Then, the calculation of the ratio considering the two additions is: $E.B. = C + k_L.A_L + k_{MK}.A_{MK}$, where A_{MK} the total mass (kg) of metakaolin and k_{MK} its coefficient activity.

When the study has been carried, k_{MK} value was not yet fixed by the standard. Also, one of the aims of this study was to quantify what the activity coefficient for metakaolin could be.

Table 1
Characteristics of the metakaolin used.

Chemical analysis (wt.%)		Other properties	
Al_2O_3	40.6	Loss on ignition (%)	1.3
SiO_2	55.8		
TiO_2	1.2	Pozzolanic activity coefficient (mg $Ca(OH)_2$ g^{-1})	1163
Fe_2O_3	1.3		
K_2O	0.8	Specific area (m^2 g^{-1})	21.3
Na_2O	0.02		
CaO	0.1	Water demand (%)	1.08
MgO	0.2	Retained at 63 μm (%)	8
P_2O_5	0.07	d_{50} (μm)	5.3

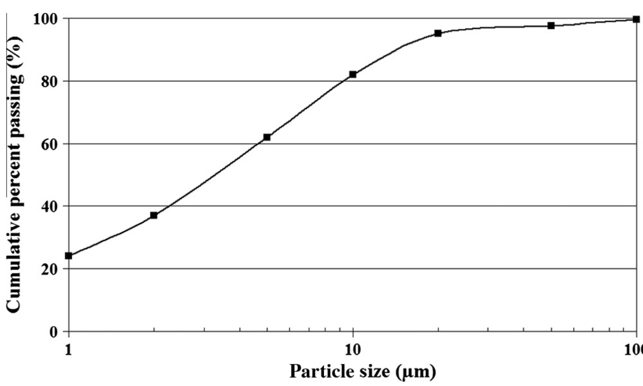

Fig. 1. Particle size distribution of metakaolin.

Table 2
Constraints for SCC mixtures set up.

NF EN 206-1 standard classes XC3, XC4, XF1	Precast process	Experimental constraints
$A/(A+C) \leqslant 0.25$ W_{eff}/E.B. $\leqslant 0.60$	Slump flow: 65 ± 5 cm Mechanical class C45/55: mean compressive strength at 28 days from 55 to 60 MPa	E.B. constant at ±10 kg m^{-3} W_{eff}/E.B. constant at ±0.01
E.B. $\geqslant$280 kg m^{-3}		MK/(MK + C) ratio by mass = 0.15
k-Value for limestone additions: 0.25		Limestone additions = 180 ± 20 kg m^{-3}

Table 3
Activity coefficient determination by compressive strength measures on mortars.

Materials	Compressive strength (MPa)	
	14 days	28 days
Control mortar	48.5	59.05
Metakaolin mortar (15%)	54.5	58.5
Indicator of activity	1.12	0.99

According to NF P 18-513 standard [22], the activity coefficient (in%) is the ratio of the mechanical compressive strength of normalized mortar with 85% of cement and 15% of metakaolin to the compressive strength of a control mortar with only cement (normalized mortar with water, normalized siliceous sand and cement in proportions 0.5:3:1 [28]) at the same age. From our results (Table 3), at 14 days the strength of the blended mortar with metakaolin was 1.12 times the value reached by the control mortar, however they were equivalent at 28 days. According to the NF P 18-513 standard definition, the activity coefficient is 1.12 at 14 days and 1 at 28 days. As a result, metakaolin presents significant reactivity at the early age.

Nevertheless, for this study we propose to perform the experiments by setting two values for metakaolin activity coefficient: $k_{MK} = 0.6$ (medium value) and 1, rather high value that could be justified with the mechanical and durability performances measured. In literature some significantly higher k_{MK} values are found [29,30], despite here we consider two values in the range of those indicated in the NF EN 206-1 standard for other additions (higher k value is 2 for silica fume) and at which could pretend metakaolin in this context. Four SCC mixtures were characterized: one control material without metakaolin (named as Ref) and three SCC with different rates and/or forms of metakaolin. The second and the third SCC incorporate metakaolin in powder giving a respective k_{MK} value of 0.6 (named as P 0.6) and 1 (named as P 1), and the last SCC incorporates metakaolin in slurry with $k_{MK} = 1$ (named as S 1). The mixture proportions are presented in Table 4 (amounts really introduced).

The amount of superplasticizer was adapted for each mixture to provide a near constant workability between the different materials (slump flow of 65 ± 5 cm).

The behaviour of metakaolin in contact with water or superplasticizer is a key point to assess the involvement of the ultra fines with the concrete rheology. The increase in water demand is mainly attributed to the high fineness of metakaolin as well as their narrow particles size distribution [31], their shape [32] and consequently the important specific area developed by their ultra fine particles [33]. To maintain constant the fluidity of the mixtures with metakaolin, the amount of superplasticizer has to be increased [34]. We noticed that less superplasticizer is required when metakaolin are used in slurry form, because the slurry already contained superplasticizer in which metakaolin fines particles are deflocculated to react more rapidly [35].

To simulate concrete precast processes, the samples were cast and placed in a thermo-regulated oven (±2 °C) for 8 h. The heat treatment was: 2 h at 30 °C, temperature increase from 30 °C to 65 °C at 0.5° min^{-1} for 1 h, 3 h at 65 °C, after which the oven was switched off and opened: the samples slowly cooled at ambient temperature for 2 h. After demoulding, the samples were cured in a 20 °C tempered room at a relative humidity of up to 95%.

3. Mixing time adaptation

The first part of the study aims at adapting mixing sequence, crucial point in the precast process: the duration of SCC mixing must be as short as possible (to gain productivity) without, nevertheless, decreasing the fresh and mechanical properties of the products. It is based on the maintenance of constant workability as determination criterion.

The same procedure was employed for the four SCC studied to establish the total mixing duration required (Table 5).

The mixing sequence includes different steps. Firstly, the introduction of the components: step one the dry components mixing (gravels + sand + cement) and after, step two, the water addition. Each of these steps lasts 45 s and cannot be shortened, so they are considered together in the sequence named M0. Secondly, the superplasticizer is added. The second sequence (M1) corresponds to the mixing time necessary to confer the SCC with the suitable rheology (slump of 65 ± 5 cm) after superplasticizer introduction. It could be optimized because it depends on the mix proportions and on superplasticizer content. So, for each SCC we measured the minimal period required to obtain the target slump through slump tests. At the end of M1 sequence, concrete was taken from each SCC mix for casting 12 cubic samples

Table 4
Mixture proportions of the SCC studied.

Mixture proportions (amounts introduced)					
Constituents (kg m^{-3})		Ref.	P 0.6	P 1	S 1
Cement CEM I 52.5 N	385	351	335	342	
Additions	Limestone	182	183	184	188
	Metakaolin (powder)	–	62	59	–
	Metakaolin (slurry)	–	118		
Siliceous sand 0/5 mm	899	875	887	878	
Siliceous gravel 5/12 mm	736	719	728	717	
Superplasticizer (% of cement mass)	2.02	4.06	3.87	2.25	
Efficient water (W_{eff})	159	162	160	157	
E.B. = C + k.A + k_{MK} A_{MK}	417	417	422	429	
W_{eff}/E.B.	0.38	0.39	0.38	0.37	
W_{eff}/C	0.41	0.46	0.48	0.46	

Table 5
Mixing sequence for the four SCC studied.

		Ref.	P 0.6	P 1	S 1
M0	Gravels + sand + cement	45 s			
	Water addition	45 s			
M1	Superplasticizer addition	1 min 30 s	2 min	2 min 30 s	45 s
M2	Additional mix	2 min			
Total	M0 + M1 + M2	5 min	5 min 30 s	6 min	4 min 15 s

(10 × 10 × 10 cm) in order to evaluate the homogeneity of the mixture by mechanical measurements. Finally, a supplementary sequence (M2) of 2 min was applied on all the mixtures to ensure homogeneity. Twelve more cubic samples (10 × 10 × 10 cm) were casted.

The mechanical compressive strength f_{cm} (MPa) was measured on the two sets of samples (M1 and M2), 24 h after mixing (16 h after heat treatment) according to NF EN 12390-3 standard [36] (Table 6). The homogeneity of the materials was estimated through the standard deviation of f_{cm} calculated from the results of the 12 samples. Nevertheless, this number of samples seems insufficient and could be criticized in the case of a rigorous statistical approach.

The variations between the standard deviations for the SCC blended with metakaolin and the reference SCC are comparable: the presence of metakaolin does not affect the homogeneity of the material and the superplasticizer content appears suitable.

Furthermore, all the standard deviations decrease from M1 to M2 and are low values, so we could consider that the mixing sequences are validated.

The results establish that the incorporation of metakaolin under powder form needs longer mixing duration, up to 60 s, to obtain the same workability. The employment of metakaolin in slurry compared to powder allows a saving in time, 1 min and 45 s by comparing P 1 and S 1 that represents about 29%, a real benefit at the precast industry scale. As the homogeneity of the material is not altered by employing slurry, we observed its properties to assume this use.

4. Metakaolin contribution to SCC properties

The second part of this work dealt with the study of metakaolin in slurry contribution to SCC properties: mechanical strength, microstructure and durability.

Several batches of 0.15 m^3 of each material (Ref, P 0.6, P 1 and S 1, Table 4) were cast following the mixing sequences detailed above (Table 5). The same heat and curing treatments than the previous ones were applied.

4.1. Metakaolin influence on fresh properties

The initial time (t_0) was defined as the end of the total mixing sequence. At this moment, fresh concrete density and entrapped air content were measured in a concrete aerometer (Table 7). The evolution of SCC workability over time was followed by a slump flow test with Abram's cone (Table 7). The tests were lead according with the NF EN 206-9 standard, specific for SCC characterization [37].

From these results, we can assume that:

- SCC blended with metakaolin could reach slump values up to 60 cm, also there is no difficulty in formulating SCC with metakaolin in association with limestone filler, from the moment that mixture proportions are adapted.
- The incorporation of metakaolin does not modify the air entrapment into SCC.
- At t_0, the slump of the SCC with metakaolin in slurry form is comparable with those of the other SCCs despite a lower superplasticizer content.
- After 1 h, all the slump flow are higher than 50 cm; the highest values have been obtained for Ref and S1 SCCs.
- The rheological behaviour of the SCC P 1 demonstrates that it is possible to elaborate SCC with metakaolin, the flowability of which is maintained over time in a highly satisfactory way: the slump flow slightly decreases for the first hour, that shows the suitable rheological comportment of this SCC for casting of large elements or its transport.

The natural behaviour of the slump decreases with the use of metakaolin for a given water-binder ratio-already described- was observed here too [38].

From the observations of behaviour of fresh mixes, it can be concluded that metakaolin contributes to preventing segregation and in this way to make the SCC more robust. With the incorporation of metakaolin, we observed that the SCCs are more consistent. This confirms previous investigations: metakaolin supplies good consistency to SCC by especially limiting the bleeding and the granular segregation, and improves the viscosity of the mixture [15–18].

It has been reported that for low rates of cement substitution by metakaolin as employed here (0.15), the initial and final setting time of blended cement with metakaolin are similar to those of ordinary Portland cement [32]. This trend was observed as well in our measurements.

The examination of the SCC fresh properties leads to the following conclusions:

- The evolution over time of the SCC workability is not significantly influenced by the incorporation of metakaolin.

Table 6
Mechanical compressive strength for different mixing sequences.

	Ref.		P 0.6		P 1		S 1	
	M1	M2	M1	M2	M1	M2	M1	M2
Mean f_{cm} (MPa)	39.0	40.5	37.0	39.5	28.0	31.0	35.5	40.0
Standard deviation of f_{cm}	1.5	1.0	1.2	0.6	1.0	0.6	2.2	1.6

Table 7
SCC fresh properties and evolution of workability after mixing.

	Ref.	P 0.6	P 1	S 1
Fresh concrete density (kg m^{-3})	2380	2375	2375	2360
Entrapped air (%)	2.5	2.4	2.4	2.6
Slump (cm)				
t_0	64	62	67	61
t_0 + 15 min	62	62	67	61
t_0 + 30 min	62	58	66	58
t_0 + 45 min	60	57	66	57
t_0 + 60 min	59	51	63	55

Table 8
Development of the SCC compressive strength.

f_{cm} (MPa)	Ref.	P 0.6	P 1	S 1
9 h	10.5	11.0	8.0	14.0
23 h	38.0	45.0	38.0	46.5
56 h	42.0	50.5	42.5	50.5
7 d	55.0	60.5	61.5	63.5
28 d	67.0	65.0	71.5	71.5

- The metakaolin incorporation in powder form requires a supplementary amount of superplasticizer to balance the workability attenuation, the use of metakaolin in slurry form enables this addition to be decreased.

For that, metakaolin in slurry is particularly recommended for SCC production.

4.2. Mechanical properties development

The mechanical compressive strength was measured on three cylinders (11 × 22 cm) at five ages: 9, 23 and 56 h after the end of mixing (bearing in mind that the heat treatment lasts 8 h), 7 and 28 days. The means of these results are presented in Table 8.

Several points can be underlined.

At the early age (9 and 23 h) the SCC P 0.6 and S 1 are more resistant than the reference SCC without metakaolin. This result could be attributed to the pozzolanic reactions at early ages [39]. Furthermore, metakaolin favours cement hydration through a physical effect due to their high surface area (easier germination) and accelerated cement hydration through their chemical composition and modification of ionic composition of the pore solution [40,41]. In the short term, this activation of anhydrous cement compounds in the presence of metakaolin accelerates the hardening of cementitious materials [42]. This beneficial effect of metakaolin is more pronounced if the cement amounts of the different mixtures are considered. The cement contents in SCCs P 0.6 and S 1 are lower than the control SCC nevertheless, they lead to similar or even higher mechanical performances after 7 days: the lesser quantity of cement is balanced by metakaolin blending.

It has long been established that reducing the W_{eff}/E.B. ratio supports mechanical strength development. S 1 presents the smaller W_{eff}/E.B. ratio, but this parameter alone does not explain the increase in mechanical properties. The elevated performances obtained with metakaolin in slurry form are probably attributable to the better deflocculating of the metakaolin particles. In the case of the mix P 1, the mechanical compressive strength at early age is lower than the values of control sample and S 1 despite it presents very similar proportions of water and metakaolin to these mixes. This result could be explained in terms of accessibility to the reaction sites. Khatib et al. observed for a high rate of metakaolin incorporation that the particles in powder tended to agglomerate and did not spread [43]. As a consequence, metakaolin reactivity is reduced because the contact with water is restrained. The more the ultra fines are dispersed, better is the access to them and faster the hydration reaction. The mechanical strengths at the early age for P 1 are low because in this form metakaolin particles are less separated, in comparison with the slurry form, and the pozzolanic reactions have not yet compensated the difference of cement amount-this material contains a lower amount of cement than the control SCC and P 0.6-. These conclusions could be supported by the calculation of the coefficient activity for the mixes at different ages, according to the method described by Wong and Razak [30]: k is calculated from the relative mechanical strength of the material with metakaolin to control one, corrected by the part of cement substitution through cement and pozzolanic masses in the materials. At 23 and 56 h, the values for k for P 1 are respectively 0.8 and 0.9 whereas for S 1 they reach higher values, 2.2 and 2.0, that confirms the great activity of metakaolin in slurry form. So, the deflocculating state of the metakaolin particles appears as a determinant point for the compressive strength development at early age [44].

The mechanical performances of P 1 and S 1 are equivalent at 7 days.

After 7 days, the blended SCC with the high rate of metakaolin show greater mechanical strengths than the control sample, whatever the incorporation form (powder or slurry). Late pozzolanic reactions take place in these SCCs after 7 days and generate very dense products, essentially high density C–S–H, which reinforce the cementitious matrix [45].

The strength efficiency of metakaolin in concrete, broadly related [46,47], is one more time observed.

Coupled with compressive tests, flexural mechanical strength f_{fm} (MPa) was measured on three samples (mean results in Table 9). The flexural and compressive results could be interpreted in the same way. The most important information resides in the fact that the flexural strength is ameliorated with the cement substitution by metakaolin.

As far as mechanical properties are concerned, we only focus on compressive strength and flexural tests in this work, but the influence of metakaolin on other mechanical performances is related in literature [48,49]. Among, another important point for the precast industry is the limitation of dimensional variations of concrete products. It has been observed that the replacement of cement by metakaolin provides a decrease of the shrinkage [50] that confirms the advantage to use metakaolins to ensure a good quality of precast products.

4.3. Water porosity and bulk density development with metakaolin

Water porosity and bulk density were determined on three samples (tests described in AFPC-AFREM recommendations [51]) at 42 and 90 days (Table 10).

The accuracy of these measurements is estimated as ±0.5% for the water porosity and as ±10 kg m^{-3} for the bulk density. Given these precisions, the water porosity appears to be slightly higher for the concretes with metakaolin. For P 1 the decrease of water porosity between 42 and 90 days traduces the evolution of this material in time and the fact that metakaolin – the more inaccessible particles – is still reacting. These results will be discussed in the following paragraph.

4.4. Water absorption coefficient

Water absorption is a key point in assessing SCC performances because this property is often examined to accord quality label (NF or CE marks) to the precast products.

The water absorption coefficient by capillary rise was determined (NF EN 13369 standard [52]), at the same date as the bulk density and porosity to water (Table 10).

Considering the standard error of this measurement, around 0.5%, no significant evolution can be observed between 42 and 90 days for all the SCCs.

Water absorption in a porous media is induced by a capillary absorption phenomenon in the opening macro porosity of the cementitious material. We observe in our study the general trend of water absorption variations correlated with water porosity.

By comparing the results from control and blended SCC, the presence of metakaolin appears to slightly increase the water porosity and the water absorption. At first sight, these results could seem opposite to the beneficial use of metakaolin largely related in the literature and measured in this work, namely enhancement of mechanical properties and durability performances, as resistance to aggressive ions penetration or chemical attacks [53]. In fact, metakaolin acts on different scales of cementitious matrix porosity: by the physical filler effect and the development of supplementary hydrates, it refines microstructure. Mercury intrusion porosimetry tests revel that metakaolin shifts the main peak of porosity towards small sizes, in the range from 10 to 20 nm [16] and that the proportion of pore with radii smaller than 20 nm increases with metakaolin content [54]. This refinement explains the improvement of mechanical and durability performances. On the other hand, the intrinsic porosity of metakaolin added to concrete capillary porosity [55] increases water absorption, without affecting mechanical and durability performances that are governed by the finest pore structure and the tortuosity of the pathways. This increase is related to the metakaolin content [56] and could be insignificant for lowest incorporation levels and W_{eff}/E.B. ratios. In the mixture studied here, this ratio is around 0.38 (medium value) and these concretes present matrix from current compactness, not comparable with High or Ultra-High Performance Concrete (HPC or UHPC) using metakaolin [57].

These points need additional investigations to precisely describe microstructural development with metakaolin in the studied materials. In this aim, pore size distribution measurement with mercury intrusion porosimetry over time could enable micro (fine pores, pozzolanic filling) and macro (ITZ, own metakaolin porosity, percolation pathways) structures to be distinguished and the impact of metakaolin amount and form to be detailed [58]. These measures could be coupled with SEM and microprobe characterisations.

Table 9
Evolution over time of the SCC flexural strength.

f_{fm} (MPa)	Ref.	P 0.6	P 1	S 1
9 h	1.6	2.0	–[a]	2.1
23 h	4.0	3.8	3.5	3.8
56 h	4.2	5.1	3.8	4.6
7 d	5.8	5.9	5.7	6.3
28 d	6.6	7.0	6.9	7.1

[a] Measure impracticable.

4.5. Durability

Durability performances of a cementitious material could be approached by many experimental ways: through durability indicators such as permeability or diffusivity or by the evaluation of material resistance in aggressive environments. The influence of metakaolin on traditional concrete durability has been largely investigated [27]. The pozzolanic products and the fine particles of metakaolin improve microstructure by filling the capillary porosity: average pore size is reduced and also the penetration of water, gas, salts or acidic is restricted. These results were confirmed by Asbridge et al. through their investigation of civil engineering structures: metakaolin was used to formulate concretes, which were exposed for a long time to aggressive environments such as tidal water, high sulphate soils and acidic water [59]. Consequently the microstructure refinement, compared with ordinary Portland concrete, cementitious materials incorporating metakaolin exhibit significantly lower chloride diffusivity, gas and water permeabilities [60]. As all these properties govern the behaviour in aggressive environments and through that, the durability performances. It has been logically proved, and for similar cement substitution rates as we tested, that metakaolin restricts chloride penetration [61], reduces the risk of delayed ettringite formation [62,63] and prevents thaumasite formation by increasing the resistance to sulphate attack [64,65]. The modification of the chemical composition of the pore solution due to metakaolin action, especially in alkali content, significantly reduces expansion due to alkali-silica reaction [66,67].

Since pozzolanic reactions progress at the expense of portlandite amount, calcium hydroxide content is reduced or even totally consumed in function of the metakaolin content [68]. Cementitious materials blended with metakaolin are naturally less sensitive to all the attacks in which calcium hydroxide dissolution is at the origin of the concrete integrity loss: acidic attack, leaching in pure water, carbonation, etc. Previous studies have shown that for an optimized clinker/metakaolin proportion in concrete and low W_{eff}/E.B, this constituent does not induce a negative impact on the corrosion resistance [69–71].

Regarding durability management, the low Portlandite content could be a drawback in the cases where the progression of the degradation is slowed down by the reaction with this compound: carbonation in rich CO_2 atmosphere, sulphate attack in magnesium sulfatique environments, etc. In the context of steel reinforced products development, SCC behaviour under carbonation is a useful durability indicator to validate its design and manufacturing process. For this purpose, we propose testing our materials under carbonation.

The carbonation phenomenon is based on the carbon dioxide diffusion into concrete porosity, so conditioned by the CO_2 concentration of the surrounding environment. Under natural conditions, this progression is very long. To predict long term performances, the testing duration has to be shortened: acceleration can be achieved by increasing the concentration of carbon dioxide in the exposed environment. We carried out carbonation accelerated tests as described in AFPC-AFREM recommendations [51]: four prisms (7 × 7 × 28 cm) of each material were exposed to an environment enriched with carbon dioxide (regulated concentration of 50 ± 5% by volume), with 65 ± 5% relative humidity controlled by NH_4NO_3 saturated solution. At each date fixed by the standard (14 and 28 days of exposure to carbonation), a sample was extracted from the carbonation medium, half-broken along the section and pulverised with phenolphthalein indicator. To determine

Table 10
SCC water porosity, bulk density and water absorption 42 and 90 days.

Age	Measure	Ref.	P 0.6	P 1	S 1
42 days	Water porosity (%)	11.7	12.2	12.8	12.5
	Bulk density (kg m^{-3})	2260	2260	2240	2250
	Water absorption (%)	4.6	5.0	5.2	5.2
90 days	Water porosity (%)	11.8	12.3	12.2	12.6
	Bulk density (kg m^{-3})	2260	2260	2260	2250
	Water absorption (%)	4.6	5.0	5.1	5.2

Table 11
Carbonation depth of the SCC after 14 and 28 days.

	Ref.	P 0.6	P 1	S 1
14 days	No carbonation observed	No carbonation observed	No carbonation observed	No carbonation observed
28 days	<0.5 mm	1 mm	1 mm	1 mm

the depth of carbonation, several measures were performed all around the circumference of the broken material. The mean values of these data are presented in Table 11.

For 28 days we discern a slight carbonation in the metakaolin blended SCC. The origins of this difference between blended and not blended SCC are twofold:

- The mean cause is linked to the limited amount of portlandite in metakaolin blended SCC due to their consumption in pozzolanic reactions [72]; subsequently, the carbon dioxide migration is less impeded compared to the control SCC.
- The second source is the supplementary porosity in the metakaolin blended materials that could facilitate carbon dioxide penetration.

The concrete carbonation depends mainly on two parameters: portlandite content and W_{eff}/E.B ratio. When the W_{eff}/E.B. ratio is low (that is the case of the materials here studied) this latter parameter governs the degradation progression: the degradation depth remains weak despite the low portlandite content in the material.

Meanwhile, the low carbonation depths confirm the good quality of durability of all these materials.

5. Conclusions

The advantage of using metakaolin in slurry for self-compacting concretes was examined in this work. To observe the influence of this product, the properties of SCC blended with metakaolin in slurry were compared to these of SCC with metakaolin in powder or without metakaolin (control SCC).

The formulations of SCC were developed according to engineering and standardization constraints, respecting manufacturing processes-including thermal treatment-in order to pass the scientific domain and to be applied to precast industry.

The study of the mixing sequences proves that the use of metakaolin in slurry is a real benefit because it permits to shorten the mixing sequence (about 29%) while maintaining high workability and without inducing heterogeneity in the material, that represents a real save at industrial scale.

Secondly, the premix in slurry with superplasticizer allows the deflocculation of the agglomerated particles of metakaolin in an optimal way. Thus, metakaolin dispersed becomes more reactive since it is more accessible. As a consequence, it improves compressive strengths in the early age, another advantage for precast industry where products must be fast demoulded to preserve productivity, transported, placed under pre-tension or incorporated into the building structures. A reduction of temperature and the duration of heat treatment could be envisaged. Further experiments should be performed to optimize this process step aiming at enhancing the productivity and preserving natural resources.

To validate the use of the slurry, fresh properties, microstructure mechanical and durability performances the SCC blended with metakaolin were compared with a control SCC without metakaolin. The use of ternary blended mix (cement-metakaolin and limestone filler) appear to be a real benefit for mechanical and durability performances, mainly due to the refinement of pore structure conferred by the two different particle size distributions of additions and intensified by the products of metakaolin pozzolanic reaction.

Considering environmental sustainability, SCC with ternary binder metakaolin/limestone/clinker appears as an environmentally-friendly material, even more so for the precast industry. The addition of limestone filler and replacement of a part of clinker by metakaolin preserves natural resources by limiting the use of raw materials, reduces energy consumption and reduces the release of CO_2 into atmosphere.

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