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Self-compacting concrete paste constituents: Hierarchical classification of their influence on flow properties of the paste

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ABSTRACT

This paper aims to clarify the influence of the constituent nature and dosages on the rheological properties of cement paste within the framework of self-compacting concrete design. The paste mixes were made with ordinary Portland cement, limestone filler, a superplasticizer (polycarboxylate type) and a viscosity agent (nanosilica). Their flow properties were characterized through spreading diameter, static yield stress and apparent viscosity. In order to take implicit variations of constituent proportioning induced by relational constraints into account, a mixture experiment technique was adopted. A matrix of experiments was build up allowing a polynomial model to express each rheological response according to the dosages of the constituents and some trends about the effect of the various mix constituents and their interactions to be found. A descriptive analysis of the data base only showed that the rheological responses fell into three distinct consistency groups. Consequently, statistical tools (variance analysis, binary tree method coupled with the bootstrap technique) were used to establish a hierarchical classification of the constituents. Results showed that the superplasticizer and the viscosity agent are dominant in yield stress. The apparent viscosity is controlled by cement and superplasticizer at small velocity gradient while it is controlled by powder (cement + filler) and water at higher velocity gradient. The viscosity agent acts at rest rather than during the flow.

1. Introduction

Self-compacting concrete (SCC) requires both high fluidity to flow under the effect of gravity alone and a good resistance to segregation. Contrary to conventional vibrated concrete, chemical admixtures (superplasticizer alone or associated with viscosity agent for horizontal casting applications like slabs) and mineral additions are always necessary to achieve the self compacting abilities [1].

Since controlling the flow properties of cement paste can lead to the control of self-compacting abilities at full concrete scale [2–5], it is necessary to understand the influence of each constituent on the flow behavior at paste scale.

A parametric study consisting in preparing mixtures from the most simple (cement + water) to the most complete (cement + water + superplasticizer + mineral addition + viscosity agent) is not realistic since the compositions of such mixtures are not comparable and not representative of the complete mixture. That is why many authors have studied the influence of constituents on the flow properties of cementitious mixtures (paste, mortar and concrete) using statistical models [6–11]. All these studies use a factorial design approach in order to determine the effects of parameters on the flow properties and mechanical resistance. These methods make it possible to reduce the number of tests, to highlight the dominant parameters and to optimize the choice of materials and the mixture formulation. In such cases, the independent composition parameters are fixed at distinct levels (3 or 5). In this context it is not possible to establish a hierarchical classification taking into account the specific influence of each constituent. Indeed, when designing a composition, implicit variations of constituent proportioning induced by relational constraints should be considered. This requirement can be satisfied by replacing a factorial design approach by a mixture experiment technique [12–14].

Thus, within the framework of the French National Project on SCC (PN B@P), the present paper aims to establish a clear classification of the influence of the constituents on the rheological features of cement-based pastes. Using mixture experiments, it was possible to build up a data base defining a field where constituent dosages could be continuously varied and where the resulting rheological responses were always measurable. A predictive model was derived, allowing some trends to be drawn provided that some constituent dosages were fixed. In order to achieve a classification, it was necessary to analyze the data base by means of statistical tools. In particular the coupled binary tree and bootstrap techniques appeared to be suitable for determining the classification.

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2. Materials and mixing procedure

In order to establish a complete hierarchical classification of all the constituents which may be used for SCC compositions, the paste mixes investigated in this study were prepared with ordinary Portland cement complying with European Standard EN 197-1, limestone filler, a superplasticizer and a viscosity agent. The main physical and chemical properties of the materials are shown in Tables 1 and 2.

Each 1 l batch was prepared using a mixer complying with European Standard EN 196-1. The mixing sequence consisted in introducing first the entire water amount along with the viscosity agent and 1/3 of the superplasticizer. The cement and the limestone filler were then incorporated and mixed for 90 s. After 30 s of rest, mixing was continued for 60 s. The remaining 2/3 of superplasticizer was then added and mixing was continued for 120 s.

3. Apparatus and testing procedures

Immediately after mixing, the pastes were subjected to rheological tests.

3.1. Mini-slump test [15] (spread)

A miniature slump cone whose dimensions are proportional to the ones of the Abrams cone with a ratio of 0.19 was used. The spread diameter was measured on a horizontal plate once the flow had stopped. It corresponded to the average of two diameters taken at right angles.

Table 1
Main physical and chemical properties of constituents.

	Cement	Mineral addition
Nature	CEM I 52,5 N CP2	Limestone filler
Specific gravity	3.11	2.72
Specific surface area (BET N_2) (m^2/g)	1.25	1.09
Mean particle size (μm)	16.9	20.6
Chemical composition (%)		
SiO_2	20.5	0.9
Al_2O_3	4.8	0.5
Fe_2O_3	1.7	0.2
CaO	66.4	55.8
SO_3	3.7	–
MgO	0.9	0.2
Na_2O	0.2	0.1
K_2O	0.3	0.1
LOI (975 °C)	1.4	42.2

Table 2
Main physical and chemical properties of constituents.

	Superplasticizer	Viscosity agent
Specific gravity	1.05	1.14
Solid content (% per weight)	19.9	22.0
pH	7.0 ± 1.0	7.0 ± 1.0
Analysis techniques		
Superplasticizer: Infrared spectrometry, gravimetric thermal analysis, differential scanning calorimetry,RMN ^{13}C spectrometry	Polycarboxylate-type polymer containing graft chains of polyethylene oxide (PEO) together with carboxylic acid groups and sulfonic acid groups	
Viscosity agent: Infrared spectrometry, scanning electron microscopy, energy dispersive X-ray analysis		Solution of hydroxyled silica clusters (100 nm) presenting no pattern with distance

3.2. Static yield stress (yield) and apparent viscosity measurements (vismi and visma)

The viscometer used was a Haake Rotovisco RV2 in a controlled rate configuration. To measure the static yield stress, a six-blade vane (Fig. 1) was immersed and allowed to rotate at a constant rate of 0.4 rpm in a cup containing the paste at rest. The width of the gap between the vane and the cup was large enough (35 mm) for the paste to be considered as an infinite medium. The static yield stress, i.e., the stress required to initiate flow, was determined by considering the peak stress obtained on a stress–time curve (Fig. 2).

To plot a flow curve, coaxial cylindrical geometry was used (Fig. 1). The rotating inner cylinder with a rough surface of 200 μm in depth sheared the paste contained in the outer cylinder. The gap between the inner and outer cylinders was small enough for the shear stress and shear rate to be assumed to be constant across the gap for a given rotational rate. Because of the time-dependent behavior of the paste at rest, a single flow curve cannot represent the complete rheological behavior, so the paste was sheared at a high shear rate in order to achieve the best structural breakdown in the sheared zone [16]. Two up and down shear histories were applied to be sure to obtain structural breakdown (Fig. 3). Then, a pseudo flow curve was obtained from the second shear history by decreasing the velocity. The viscometer was manually operated to wait for the steady state to be reached (torque

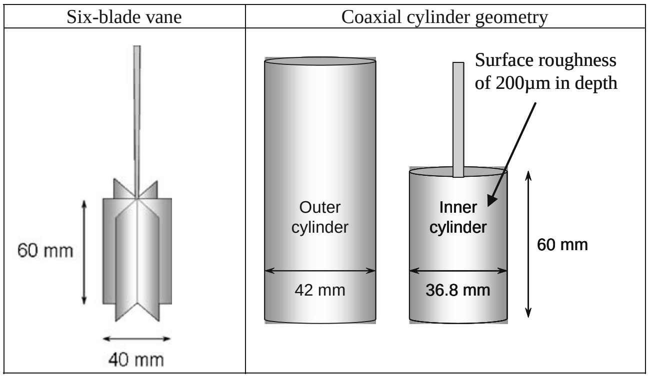


Fig. 1. Dimensions of shear geometry used for yield stress (left) and flow (right) measurements.

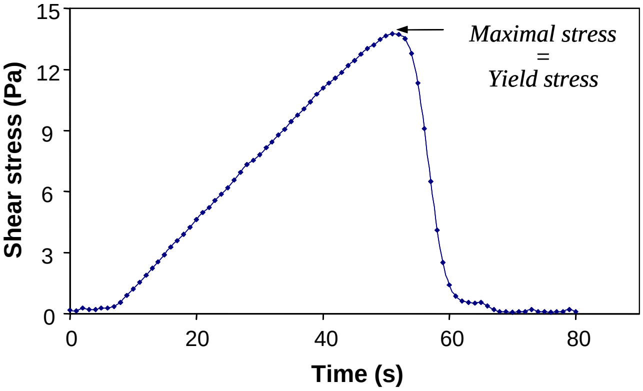


Fig. 2. Typical stress–time curve for yield stress measurement.

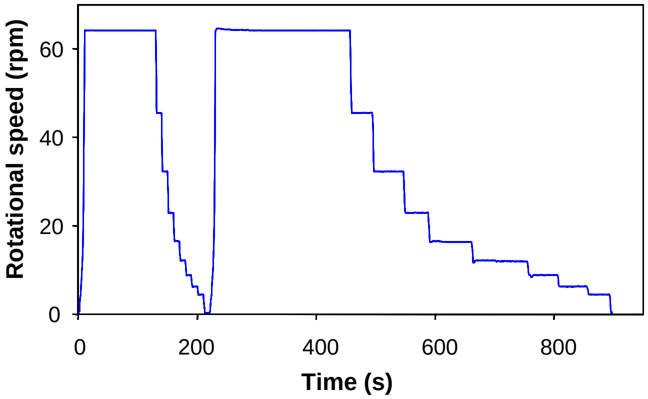


Fig. 3. Example of shear history of cement pastes for flow measurements.

stabilization) at each rotational rate. The apparent viscosity was calculated from the flow curves as the ratio of shear stress to shear rate. For this study, the apparent viscosity was determined at shear rate values of 4 s^{-1} (vismi) and 18 s^{-1} (visma), which corresponded to the common limits of all the mixtures investigated. These values were within the range of typical shear rates encountered in the placement of concrete [2,17]: 4 s^{-1} represents traditional casting in formwork, whereas 18 s^{-1} is representative of a pumping context.

The dimensions of the shear geometry related to yield stress and flow measurements, respectively, are given in Fig. 1.

The test sequence and the corresponding age of the paste at each measurement were as follows:

$$(1)\ \underset{T_0}{\text{End of mixing}} \rightarrow \underset{T_0+1\ \text{min}}{\text{Mini-slump test}} \rightarrow \underset{T_0+4\ \text{min}}{\text{Static yield stress}} \rightarrow \underset{T_0+9\ \text{min}}{\text{Apparent viscosities}}$$

4. Experimental strategy

4.1. Experimental domain

Preliminary experiments enabled a range to be determined for the proportion of each constituent so that the resulting mixes always exhibited a homogeneous aspect, without excessive sedimentation, and measurable rheological properties. In addition, the proportions remained in the range recommended by manufacturers for SCC (Table 3).

4.2. Determination of the experiment matrix

In the mixture experiment technique, the consequence of varying the dosage of any constituent on the others is taken into account through the following relation:

$$C + F + SP + VA + W = 1$$

where *C*, *F*, *SP*, *VA* and *W* are the volumetric proportions of cement, limestone filler, superplasticizer, viscosity agent and water, respectively.

Table 3
Experimental domain.

Limestone filler = 20%–30% of the cement mass
Superplasticizer = 0.9%–1.1%[a] of the mass (cement + limestone filler)
Viscosity agent = 3%–4.5%[a] of the mass (cement + limestone filler)
$0.61 \leqslant$ solid volumetric concentration $\left(\frac{V_{\text{solids}}}{V_{\text{total}}}\right) \leqslant 0.63$

[a] Dosages are referred to the admixture as delivered (commercial solution).

In that case, the relations defining the experimental domain (Table 3) implicitly generate limits in the dosage of each constituent.

Hence, a set of experiments, i.e., a matrix of experiments, has to be sought so that the variation of the rheological properties can be described as good as possible by a polynomial relationship expressing each dependent variable (yield, spread, vismi and visma) according to the dosages of the constituents.

The degree of the polynomial function must be chosen as a compromise between the desired precision and the limited

Table 4
Experiment matrix (volumetric proportions).

Experiment	*C*	*F*	*SP*	*VA*	*W*
1	0.4851	0.1114	0.0155	0.0475	0.3406
2	0.4846	0.1113	0.0189	0.0474	0.3379
3	0.4431	0.1529	0.0187	0.0470	0.3383
4	0.4810	0.1104	0.0153	0.0704	0.3228
5	0.4399	0.1518	0.0152	0.0698	0.3234
6	0.4805	0.1103	0.0187	0.0703	0.3201
7	0.4394	0.1516	0.0186	0.0697	0.3208
8	0.5010	0.1150	0.0160	0.0490	0.3189
9	0.5004	0.1149	0.0195	0.0490	0.3162
10	0.4962	0.1139	0.0194	0.0726	0.2979
11	0.4417	0.1524	0.0153	0.0584	0.3322
12	0.4508	0.1555	0.0156	0.0478	0.3302
13	0.4466	0.1541	0.0189	0.0708	0.3096
14	0.4579	0.1580	0.0176	0.0486	0.3180
15	0.4557	0.1572	0.0193	0.0603	0.3076
16	0.4750	0.1352	0.0193	0.0723	0.2982
17	0.4775	0.1360	0.0158	0.0606	0.3100
18	0.4714	0.1342	0.0191	0.0480	0.3272
19	0.4793	0.1365	0.0177	0.0488	0.3178
20	0.4907	0.1127	0.0174	0.0599	0.3194
21	0.4831	0.1238	0.0183	0.0661	0.3087
22 (T.P.1)	0.457	0.145	0.018	0.067	0.313
23 (T.P.2)	0.4567	0.1434	0.0163	0.0533	0.3303
24 (T.P.3)	0.4564	0.1433	0.0180	0.0533	0.3290
25 (T.P.4)	0.4854	0.1244	0.0166	0.0543	0.3193
26 (T.P.5)	0.4832	0.1239	0.0166	0.0662	0.3101

Table 5
Experiment matrix (proportions in % per weight).

Experiment	*f/c*	*w/(c + f)*	*va/(c + f)*[a]	*sp/(c + f)*[a]
1	20.085	18.800	2.989	0.898
2	20.087	18.670	2.986	1.097
3	30.180	18.858	2.987	1.095
4	20.074	17.971	4.468	0.894
5	30.180	18.158	4.468	0.896
6	20.077	17.839	4.466	1.094
7	30.175	18.034	4.467	1.098
8	20.076	17.045	2.986	0.898
9	20.082	16.920	2.989	1.096
10	20.076	16.077	4.467	1.099
11	30.176	18.577	3.723	0.898
12	30.169	18.094	2.986	0.898
13	30.178	17.123	4.464	1.098
14	30.178	17.154	2.989	0.997
15	30.170	16.674	3.726	1.098
16	24.894	16.163	4.467	1.098
17	24.910	16.712	3.724	0.894
18	24.898	17.869	2.988	1.095
19	24.908	17.069	2.988	0.998
20	20.087	17.429	3.726	0.997
21	22.413	16.785	4.097	1.045
22 (T.P.1)	27.750	17.239	4.207	1.041
23 (T.P.2)	27.462	18.245	3.356	0.945
24 (T.P.3)	27.461	18.185	3.359	1.045
25 (T.P.4)	22.415	17.278	3.350	0.943
26 (T.P.5)	22.426	16.855	4.102	0.947

[a] Ratios between the mass of the admixtures as commercial solutions and the mass of powder.

number of experiences. Here, a second degree polynomial function was applied. For each response Y (flow property), the 2-degree model was composed of 15 coefficients (β_i and β_{ij}) to be determined by a multilinear regression. This function can be represented by

$$\begin{aligned} Y = {} & \beta_1 \cdot C + \beta_2 \cdot F + \beta_3 \cdot SP + \beta_4 \cdot VA + \beta_5 \cdot W + \beta_{12} \cdot C \cdot F \\ & + \beta_{13} \cdot C \cdot SP + \beta_{14} \cdot C \cdot VA + \beta_{15} \cdot C \cdot W + \beta_{23} \cdot F \cdot SP \\ & + \beta_{24} \cdot F \cdot VA + \beta_{25} \cdot F \cdot W + \beta_{34} \cdot SP \cdot VA + \beta_{35} \cdot SP \cdot W \\ & + \beta_{45} \cdot VA \cdot W \end{aligned} \tag{1}$$

Table 6
Experimental responses.

Experiment	Yield (pa)	Spread (cm)	Vismi (Pa s)	Visma (Pa s)	Consistency
1	4	17.5	1.1	1.8	Fluid
2	<1	16.6	0.5	0.5	Fluid
3	<1	16.6	0.5	0.7	Fluid
4	852	12.0	3.8	7.2	Stiff
5	204	13.5	1.4	2.8	Plastic
6	5	16.9	0.8	1.5	Fluid
7	<1	16.5	0.5	0.7	Fluid
8	1142	12.8	7.3	10.5	Stiff
9	<1	16.8	1.4	1.5	Fluid
10	857	14.7	4.3	5.4	Stiff
11	2	16.8	0.7	1.3	Fluid
12	<1	17.3	0.9	1.4	Fluid
13	1	16.6	0.7	0.8	Fluid
14	3	16.1	0.7	0.8	Fluid
15	<1	17.3	1.0	1.0	Fluid
16	6	16.7	2.0	2.7	Fluid
17	1015	11.8	7.5	22.1	Stiff
18	<1	16.1	0.6	0.8	Fluid
19	<1	16.8	0.9	1.2	Fluid
20	12	18.6	1.9	2.6	Fluid
21	155	14.3	2.7	6.4	Plastic
22 (T.P.1)	13	16.5	2.0	3.1	Fluid
23 (T.P.2)	21	16.7	1.1	2.1	Fluid
24 (T.P.3)	2	16.7	0.9	1.3	Fluid
25 (T.P.4)	939	14.0	5.2	7.2	Stiff
26 (T.P.5)	260	13.4	2.4	4.9	Plastic

Based on repeatability tests on fluid (experiment no. 22) and stiff (experiment no. 25) mixes, standard deviations were deduced on each rheological response. Yield: ±2.7 Pa (fluid), ±20 Pa (stiff); etal.: ±0.4 cm (fluid or stiff); vismi: ±0.4 Pa s (fluid or stiff); visma: ±0.4 Pa s (fluid or stiff).

The experiment matrix (i.e., the list of the experiments) was generated with the assistance of the NemrodW software, and satisfied three criteria [13,14] for: final information quality, model coefficient quality, and model prediction quality.

It was composed of 21 points (Table 4) which are taken on the domain boundaries. The first column of Table 4 is the number of the mixture; the others give the volumetric proportions of the constituents. This basic experiment matrix was aimed at the determination of the coefficients β_i and β_{ij}. Other experiments (test points, T.P. in Table 4) were also selected by NemrodW within the experimental domain to validate the mathematical model.

Determined in terms of volumetric proportions, the experiment matrix can also be expressed in terms of proportions per weight c, f, sp, va and w generally used by the designers. Table 5 shows the f/c, $w/(c+f)$, $va/(c+f)$ and $sp/(c+f)$ ratios.

5. Results

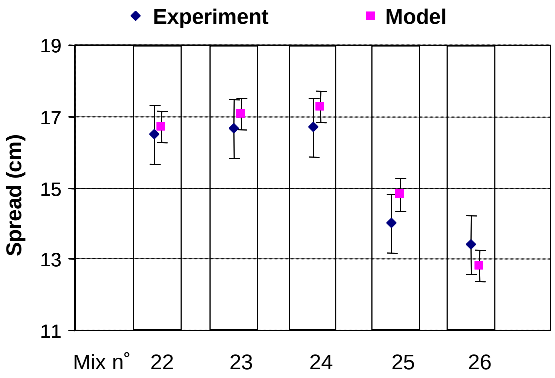
Table 6 gives the experimental responses of all the mixes represented in Table 4 or Table 5.

The mixture experiment technique offers two possibilities. On the one hand, it gives the designers the means to predict the effect of the dosage of the constituents on the variation of the rheological responses and also to predict a mixture with pre-selected properties. On the other hand, it gives the researchers a database where relations between either the rheological responses and the design parameters or between the design parameters themselves can be looked for through what is called descriptive analysis. Both concerns are now examined.

5.1. Model prediction

Once the coefficients β_i and β_{ij} were determined thanks to the test results of 21 mixes of the experiment matrix, the reliability of the model pertaining to each response was confirmed by experiment, as shown for example by Fig. 4 in the case of spread response.

The model (Eq. (1)) can also be useful to point out trends about the effect of the various mix constituents and their interactions,

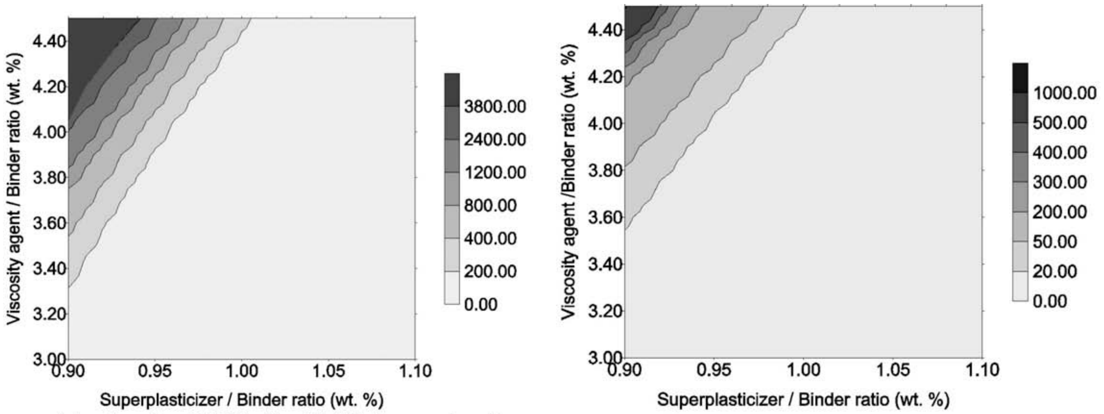


<u>Scatter intervals</u>

Experiments = standard error at the bilateral 95% confidence limit calculated from repeatability tests;

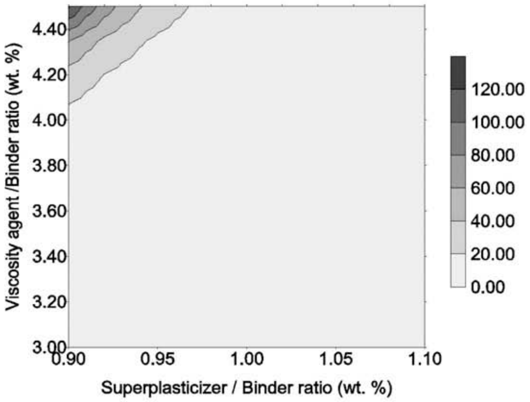
Model = average uncertainty value of all mixes studied, calculated from uncertainties about the mass of constituents.

Fig. 4. Comparison model/experiment for mini-slump test.



(a) w/(c+f) = 17.0%, f/c=22.0% (lowest level)

(b) w/(c+f) = 17.4%, f/c=25.0% (mean level)



(c) w/(c+f) = 18.0%, f/c=30.0% (highest level)

Fig. 5. Isocurves of yield stress (Pa) versus *va/(c + f)* and *sp/(c + f)* ratios per weight when *w/(c + f)*and *f/c* ratios per weight are fixed.

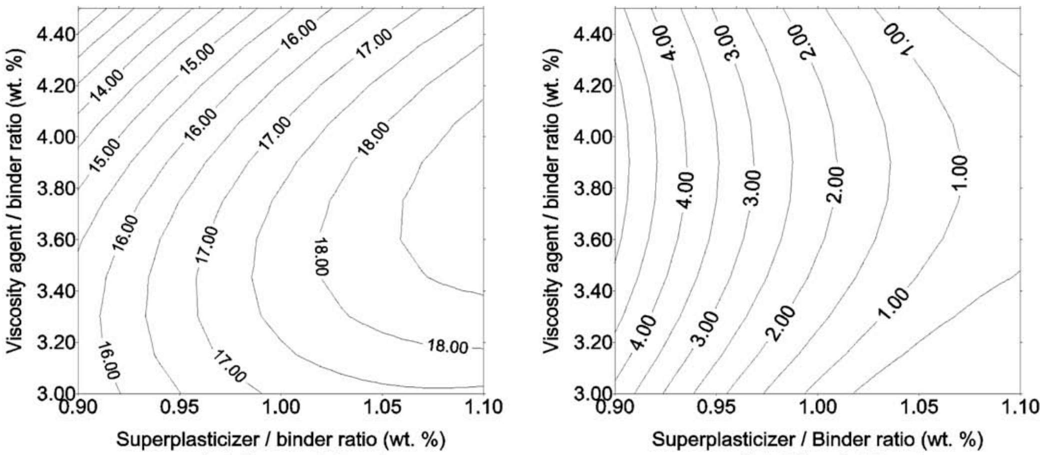
provided that some constituent dosages are maintained at a given value. Here, for design purpose, the analysis was carried out by fixing *w/(c + f)* and *f/c* ratios and examining the influence of *sp/(c + f)* and *va/(c + f)* ratios on the rheological responses such as yield, spread, vismi and visma. Details of the resulting isocurves are only given about yield response (Fig. 5a–c) since it was found that modifying *w/(c + f)* and *f/c* ratios (at the smallest, mean and highest levels within the limits of the experimental domain) did not change the way of variation of any response. The isocurves plotted in Fig. 5 show that the more *w/(c + f)* and *f/c* ratios, the more the fluidizing effect traduced by a decrease in the maximum value and in the extend of the interval variation. At the same time, the spread is found to have an increase in its minimum value and a decrease in the extend of its interval variation whereas a decrease in the extreme viscosity values are observed.

As expected, the viscosity agent and the superplasticizer act on yield stress in an antagonist way. Indeed, yield response decreases when the proportion of *sp* increases and the dosage of *va* decreases. In addition, the contribution of *sp* seems to be slightly preponderant, regarding the slope of the isocurves in Fig. 5a and b. Particularly, in the limits of the experimental domain, the dosage of *va* must grow slightly faster than the one of *sp* to maintain a yield stress value of 50 Pa (Fig. 5b). Fig. 5b also shows that a yield stress value less than 20 Pa can be achieved with a minimum 1% *sp/(c + f)* ratio and any given *va/(c + f)* ratio.

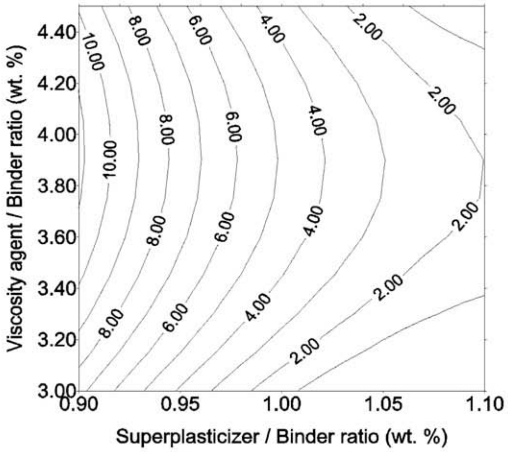
Fig. 6 presents the isocurves of the variation of the rheological responses spread, vismi and visma with the *va* and *sp* contents, when *w/(c + f)* and *f/c* ratios are fixed at the mean level, i.e., at the centre of the experimental domain.

Concerning spread diameter response (Fig. 6a), an antagonist action also exists between *sp* and *va*. However, the influence of *va* on the spread variation is noticeably marked when the dosage of *sp* is close to its lower limits. Otherwise, for a given proportion of *va*, the spread diameter variation is mainly governed by *sp*. When considering 1% of *sp* by mass of (*c + f*) in order to target a yield stress less than 20 Pa (Fig. 5b), the spread diameter ranges from approximately 15.5 to 17 cm (Fig. 6a). Fig. 6b and c show that the antagonist action still stands about viscosities. For any given *va/(c + f),* the variation of the viscosities depends on the dosage of *sp*. Conversely, the greater the *sp/(c + f)* ratio, the smaller the viscosity variation when the proportion of *va* is modified. It is a well-known fact that high doses of superplasticizer must be used to reach a correct flowability. Then, it is most often necessary to increase the viscosity of the paste in order to avoid severe segregation and to maintain the stability of SCC at rest. In the experimental context of this study, a minimum spread diameter value of 16 cm was assessed to target self-compacting abilities, which corresponds to a minimum *va* proportion of 4.3% if the proportion of *sp* is always fixed at 1%. Hence, viscosity values are close to 2 and 4 Pa s for vismi and visma responses, respectively.

Despite the trends made above are consistent with previous studies, notably for yield stress and mini-slump test responses [8], there is no doubt that they are not sufficiently reliable in order to be extended to the whole experimental domain. In fact, the isodiagrams presented in Figs. 5 and 6 should have been plotted for all the combinations between the *w/(c + f)* and *f/c* ratios, which would be a time-consuming and laborious task. This latter remark calls



(a) Spread (cm) (b) Vismi (Pa.s)



(c) Visma (Pa.s)

Fig. 6. Isocurves of spread, vismi and visma responses versus *va/(c + f)* and *sp/(c + f)* ratios per weight of mixes made with *w/(c + f)* and *f/c* ratios per weight fixed at 17.0% and 25.0%, respectively.

for a global approach which will be done in Section 6 by means of a statistical analysis.

5.2. Descriptive analysis

The descriptive analysis was approached by considering the distribution of mixtures in the planes representing the volumetric proportions of the constituents and the responses. When any response (yield, spread, vismi and visma) was plotted versus constituent dosages, the results showed no marked relationship. The low correlation coefficients (Table 7) between responses and constituents confirmed this observation. In fact, the expected relations are hindered by the implicit variations of constituent proportioning induced by relational constraints considered in the mixture experiment. Conversely, it appears that each response was divided into three quite distinct groups as illustrated for the yield-stress response (Fig. 7a–c for example): five points with a high yield stress (average value of 1000 Pa), three points with an intermediate yield stress (average value of 200 Pa) and 18 points with a weak yield stress (average value of 4 Pa). This is not an unexpected result because most of the points belong to the experimental domain boundaries, which induces a large variation of the rheological responses.

The arrangement of points observed among the constituents (*C*, F, SP, VA and *W*) does not show any singularity except for that between cement and filler (Fig. 7d). In this case, the arrangement is very particular since the points are laid out in five distinct groups

Table 7
Correlation matrix.

Variable	*C*	*F*	*SP*	*VA*	*W*	Yield	Spread	Vismi	Visma
C	1.000	−**0.899**	0.096	−0.100	−0.271	0.473	−0.261	0.535	0.374
F	–	1.000	−0.013	−0.032	0.041	−0.392	0.228	−0.392	−0.258
SP	–	–	1.000	0.116	−0.376	−0.365	0.422	−0.335	−0.379
VA	–	–	–	1.000	−0.643	0.147	−0.277	0.134	0.157
W	–	–	–	–	1.000	−0.292	0.281	−0.391	−0.334
Yield	–	–	–	–	–	1.000	−**0.830**	**0.942**	**0.806**
Spread	–	–	–	–	–	–	1.000	−**0.774**	−**0.774**
Vismi	–	–	–	–	–	–	–	1.000	**0.910**
Visma	–	–	–	–	–	–	–	–	1.000

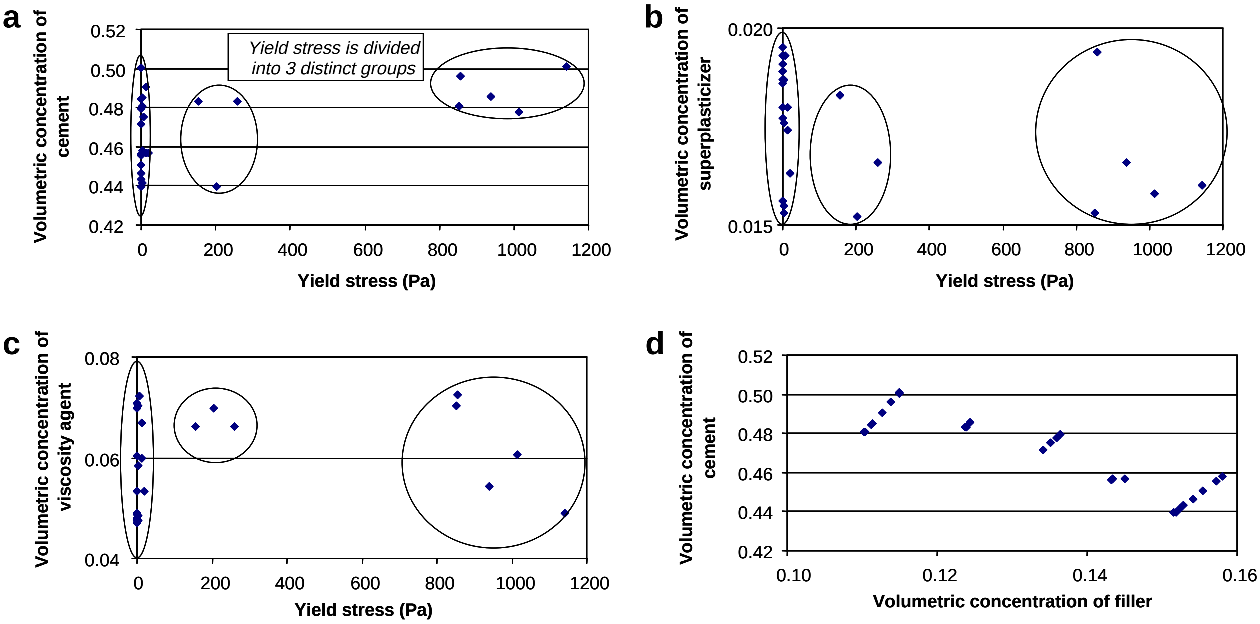


Fig. 7. Descriptive analysis for yield stress response.

and regularly distributed, with an increasing linear function in each group, and a variation among the groups that is also linear but decreasing. A high correlation coefficient of approximately -0.9 confirms this particular connection between the two constituents: cement and limestone filler (Table 7).

Finally, Table 7 clearly shows that the responses were strongly correlated, since the correlation coefficient is close to one.

The descriptive analysis did not give more information about the influence of each constituent upon the rheological responses of the pastes. Consequently, a statistical analysis was undertaken to establish a hierarchical classification of the constituents.

6. Statistical analysis

As proposed above, a statistical approach was carried out, allowing a global analysis of the database to aim at a classification of the influence of each constituent on flow properties of the resulting mix. This process was worked out in two steps.

First, the variance analysis was used in order to validate the arrangement of the rheological responses in three groups in terms of consistency. Second, the binary trees highlighted the constituent nature and dosages which distributed the mixes into groups. The last-mentioned technique, along with the bootstrap technique, gave a hierarchical classification of the constituents by their effect on the flow properties. Two software packages, SAS and Splus, were used for the various processing carried out in the study.

6.1. Variance analysis

Through the descriptive analysis, the results indicated that the mixture responses were distributed into three distinct groups. Three qualitative consistency states had already been attributed to the mixtures: fluid, plastic and stiff (Table 6). The variance analysis for each response checked whether this distribution was relevant or not. The method was based on a statistical linear model representing each response Y through

$$Y = K_1 + K_2 \times \begin{pmatrix} 1 & \leftrightarrow & \text{stiff} \\ 0 & \leftrightarrow & \text{not stiff} \end{pmatrix} + K_3 \times \begin{pmatrix} 1 & \leftrightarrow & \text{fluid} \\ 0 & \leftrightarrow & \text{not fluid} \end{pmatrix} + \varepsilon \tag{2}$$

where (K_1), $(K_1 + K_2)$ and $(K_1 + K_3)$ are the average values of the responses assumed to belong to plastic, stiff and fluid consistencies, respectively, ε is the error value.

Student's and Fisher's tests evaluated reliability and quality, respectively, of the partition of the responses.

The Student's t-test determined whether the average values defining the groups were significantly different. The quality of the relationship is expressed through the coefficient of determination R^2. It represents the variance percentage explained by the consistency:

if $0.8 < R^2 \leqslant 1$ then there is a very strong relationship,
if $0.6 < R^2 \leqslant 0.8$ then there is a strong relationship.

Student's and Fisher's tests were carried out with the significance level of 0.05. The results are shown in Table 8.

Vismi and particularly yield stress responses were very strongly represented by the values estimated for each level of consistency. The consistency parameter was also adequate to represent the two other responses (spread and visma). Accordingly, variance analysis showed that the partition of the data into groups was relevant, which enabled the binary tree method to be employed.

6.2. Binary tree analysis

This method [18] was used to find the constituent dosages for which the mixes were allocated to one of the three defined groups.

Basically, a binary tree is a structure which consists of a succession of elements called nodes N_i (Fig. 8). This structure begins at a root node (N_1 in Fig. 8). Following nodes are either internal nodes (N_2, N_3 and N_4 in Fig. 8) or final nodes (leaf, L_i in Fig. 8).

A binary tree is built by dividing the space of the constituents by hyper planes. In turn, each side can be divided until a consistency state is assigned to a leaf. A node is above all defined by the choice of a constituent and a condition on its dosage defining the associated hyper plane.

The final tree must have the optimal divisions among all those acceptable. From a given node, the calculation algorithm chooses the division which minimizes the disorder of the two child nodes. The disorder is described by the entropy function D. For instance, the following equation is applied to a node k:

Table 8
Variance analysis results.

Response	K_1 (plastic)	$K_1 + K_2$ (stiff)	$K_1 + K_3$ (fluid)	Partition reliability (Student)	R^2 (Fisher)
Yield (Pa)	110.6	960.9	1.7	Yes	0.97
Spread (cm)	15.5	13.1	16.8	Yes	0.63
Vismi (Pa s)	1.9	5.6	0.9	Yes	0.84
Visma (Pa s)	3.8	10.5	1.2	Yes	0.61

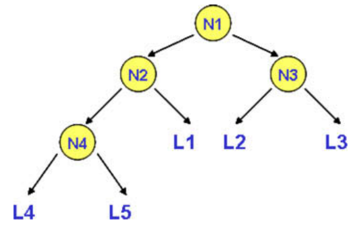


Fig. 8. Binary tree representation.

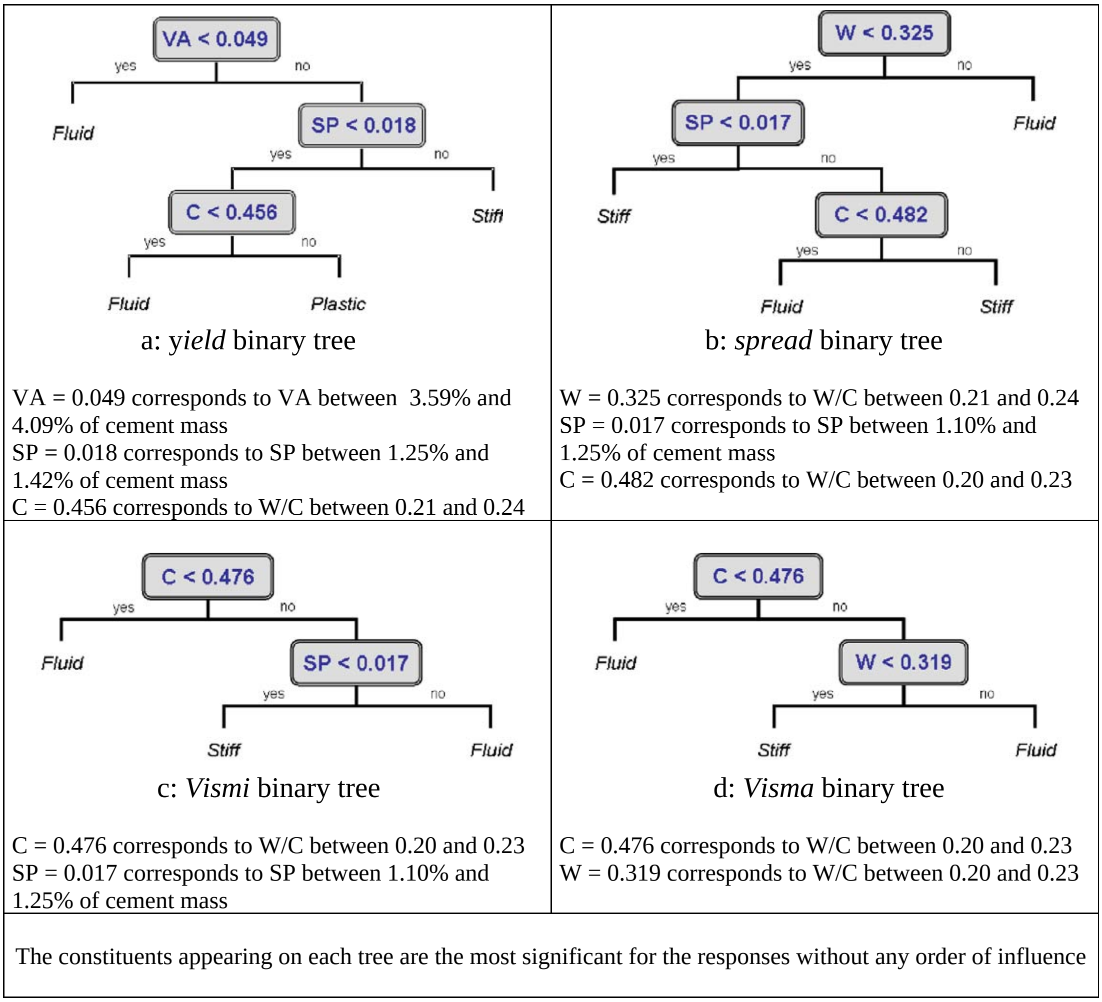
$$D_k = -2n_k \sum_{1}^{m} p_{ik} \log(p_{ik}) \tag{3}$$

where n_k is the number of data at node k, p_{ik} is the probability of obtaining a state i among m at the node k. If K is the total number of nodes, the most representative tree will be built by choosing the associated divisions which minimize the total entropy D, according to

$$D = \sum_{k=1}^{K} D_K = \min\left\{-2\sum_{k=1}^{K} n_k \sum_{i=1}^{m} p_{ik} \log(p_{ik})\right\} \tag{4}$$

To avoid unnecessarily fine division of the tree, a minimum number of data has to be fixed for a leaf. Here, the selected stop rule is to have three data at least per node which becomes a leaf. A consistency is assigned to a final node considering the most representative state in the data group. This implies that some data may not be properly classified in the final tree. Here, trees which did not classify more than a quarter of the data were rejected.

Optimal binary trees are given in Fig. 9a–c and d for yield, spread, vismi and visma, respectively. It must be stressed that no more than three constituents appear in the final trees. This means that these constituents are the most significant for the corresponding responses without any order of influence. The associated



a: *yield* binary tree

VA = 0.049 corresponds to VA between 3.59% and 4.09% of cement mass
SP = 0.018 corresponds to SP between 1.25% and 1.42% of cement mass
C = 0.456 corresponds to W/C between 0.21 and 0.24

b: *spread* binary tree

W = 0.325 corresponds to W/C between 0.21 and 0.24
SP = 0.017 corresponds to SP between 1.10% and 1.25% of cement mass
C = 0.482 corresponds to W/C between 0.20 and 0.23

c: *Vismi* binary tree

C = 0.476 corresponds to W/C between 0.20 and 0.23
SP = 0.017 corresponds to SP between 1.10% and 1.25% of cement mass

d: *Visma* binary tree

C = 0.476 corresponds to W/C between 0.20 and 0.23
W = 0.319 corresponds to W/C between 0.20 and 0.23

The constituents appearing on each tree are the most significant for the responses without any order of influence

Fig. 9. Final binary trees.

Table 9
Hierarchical classification of constituent influence.

Bootstrap results				
Static yield stress (yield)				
SP (70%)	*VA* (60%)	*C* (45%)	*W* (40%)	*F* (20%)
Mini-slump test (spread)				
SP (60%)	*W* (50%)	*C* (45%)	*VA* (30%)	*F* (15%)
Apparent viscosity at 4 s^{-1} *(vismi)*				
C (60%)	*SP* (40%)	*W* (25%)	*VA* (20%)	*F* (15%)
Apparent viscosity at 18 s^{-1} *(visma)*				
C (60%)	*W* (40%)	*F* (30%)	*SP* (25%) and *VA* (25%)	

C: cement, *F*: limestone filler, *SP*: superplasticizer, *VA*: viscosity agent, *W*: water.

dosage values are also mentioned in Fig. 9. They are significant in our experimental context but they are not necessarily valid for any cement-based material.

To establish a hierarchical classification, the bootstrap technique [19] was used. This re-sampling technique consisted in randomly choosing a set of 26 data with replacement among the 26 initial data. This operation was repeated 300 times to build a great number of samples on which the stability of the trees was checked. In fact, beyond 250 samples, the final classification did not change any more. Finally, the hierarchical classification was derived from the number of times each constituent intervened in the resulting trees.

This classification is represented in Table 9.

7. Discussion

This study takes into account the simultaneous variation of all the dosages of constituents within the experimental field. The results gathered together in Table 9 show different hierarchical classifications according to the responses. This point might be expected since each of them gives a partial but specific feature of the flow. The static yield stress is representative of a more or less strong structure hindering flow initiation. The spread is linked to the deformation capacity of the material [20]. The apparent viscosities express the resistance to flow against the shear stress once the yield stress is exceeded.

Accordingly, the following comments are proposed for each type of response.

i. Static yield-stress response
SP and *VA* play the main roles in the yield stress variation of the paste. This confirms that the need for superplasticizer to enhance fluidity is firmly established in SCC composition rules [1,4,21]. The superplasticizer, which acts by electrostatic and steric effects [22], moves the solid particles in the paste apart and prevents flocculation, thus causing the yield stress response to fall. Conversely, the high affinity between the viscosity agent and water (Table 2) gives rise to a network in the liquid phase which increases the force necessary to initiate the flow of the paste [23]. The antagonist effects of *SP* and *VA* explain why they are found to have a similar order of significance. From a practical point of view, it is necessary to find adequate dosages of *VA* and *SP* so that *VA* stabilizes the dispersed system of particles generated by *SP*. In the case of a self compacting concrete mix with a large amount of water, this mechanism ensures that fluidity and stability are maintained [24]. To the best of our knowledge, empirical combinations are still proposed.

ii. Mini-slump response (spread)
Despite the well-known relationship between yield stress and slump flow [25,26], the orders of influence of *VA* and *W* are permuted. A low yield-stress value allows the paste to spread, which is why the superplasticizer is the dominant constituent. Once structural breakdown occurs (i.e. yield stress is exceeded), water and cement or, implicitly, the *W/C* ratio rank second. This observation is consistent with previous studies on different material scales stating that the higher the water to binder ratio, the greater the spread diameter [27]. The viscosity agent does not seem to play an important role in the spread response variation. Considering the above comments on yield stress, *VA* acts on the stability at rest rather than during flow.

iii. Apparent viscosities (vismi and visma)
Even though the dosage and nature of the other constituents may have some effects on viscosity according to the velocity gradient, cement proportioning has the most important role for both responses, vismi and visma. The amount of cement is the main factor governing the volume concentration of solids, which has a direct consequence on the mechanical aspect of the flow resistance because friction among particles is more or less reduced by water and the addition of superplasticizer and viscosity agent. Even though limestone filler plays a part in the volume concentration of solids, it acts more as a lubricant than a reactive powder within the first minutes after mixing [28]. The influence of the superplasticizer is particularly marked (second rank) at low velocity gradients (vismi) while it is of minor importance at high velocity gradients (visma). When there is a rise in the shear rate, the existing chain-like polymers tend to be aligned in the shear direction [29] thus reducing the spacing of solid particles. Interparticle friction is then enhanced and viscosity is controlled by both powder and water contents, which is relevant to the fact that the water and the limestone filler appear in second and third position, respectively (Table 9). Finally, the analysis shows a weak influence of *VA* under dynamic conditions, particularly at high velocity gradients. Considering the hierarchical classification of yield and spread responses, the main effect of the viscosity agent remains in static conditions.

Generally speaking, the proposed methodology based on simultaneous variation of all the constituents gives results that strengthen the trends exposed in parametric studies where independent composition parameters were fixed at distinct levels. These trends were observed on different scales, particularly on full concrete scale. Hence, controlling the rheological properties of cement paste remains a major concern in SCC composition as suggested by previous studies [30], and recently confirmed by others [2,4].

8. Conclusion

In comparison with vibrated concrete, self-compacting concrete (SSC) can only be obtained with the use of additional constituents such as chemical admixtures and mineral additions. Considering that the flow properties of cement paste govern the self-compacting abilities on the concrete scale, it is necessary to understand the influence of each constituent on its own flow behavior. This paper has proposed a classification of the influence of the constituents on the rheological properties of cement pastes.

The paste mixes, investigated through a mixture experiment technique, were prepared with ordinary Portland cement, limestone filler, a superplasticizer (polycarboxylate type) and a viscosity agent (nanosilica).

The following conclusions can be retained.

- The superplasticizer and the viscosity agent play the main roles in the yield stress. The antagonist effects of such constituents explain that they are found in similar orders of significance.

- Concerning spreading ability, the superplasticizer remains the dominating constituent. Once structural breakdown is achieved (i.e. yield stress is exceeded), water and cement, or implicitly the water/cement ratio, rank in second position.
- Cement proportioning has the most important effect on apparent viscosity values at different velocity gradients. The influence of the superplasticizer is particularly marked (ranking second) at low velocity gradients while it is of minor importance at high velocity gradients. In the latter case, interparticle friction is enhanced and the viscosity is controlled by the powder (cement + limestone filler) and the water content, which is related to the fact that water and limestone filler become more significant (ranking second and third, respectively).
- The analysis shows a weak influence of the viscosity agent under dynamic conditions, particularly at high velocity gradients. It acts on the stability at rest rather than during flow.

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