ADAPTATION OF THE STANDARD EN 196-1 FOR MORTAR WITH ACCELERATOR

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Abstract

In certain applications, accelerators are added to favour a rapid evolution of mechanical properties in mortar and concrete. In order to assure adequate performance, it is necessary to test the compatibility between the accelerator and other components of the mixture. The EN 934-5 establishes that such evaluation of accelerators should be performed according with the procedure established in the EN 196-1. However, this standard does not take into account the inclusion of the accelerators or the particularities of the mortar produced with these admixtures. The objective of this paper is to adapt the EN 196-1 in order to characterize the strength of mortars with accelerator. First, an experimental parametric study to evaluate the influence of the production procedure on the results was conducted. Based on the results obtained, a modified production process was proposed. Then, a wide experimental program including a total of 40 mixes of mortars with different formulations and contents of accelerators was performed. Based on a statistical analysis, a new admissible variation used to calculate the compressive strength was proposed.

Keywords: *Mortar, Accelerator, Alkali-free, Compressive strength, Standardization*

1. Introduction

In mortar and concrete with Portland Cement, the setting time and the evolution of mechanical properties are governed by the reaction between the cement and the water [1]. Although the normal evolution of mechanical properties is compatible with the requirements found in most applications, in others it is necessary to accelerate the evolution of properties for safety or productivity reasons [2, 3, 4]. This is the case, for example, of certain underground constructions with sprayed concrete in which the material must resist its self-weight and the external load as soon as it is placed [4, 5]. In such situations, special admixtures known as accelerators may be added to the mixture with the aim of producing a rapid setting or an enhanced gain of strength at very early ages [6, 7]. The behaviour of the concrete placed, the advance of the construction and the safety of the workers involved in the process depend on the dose of accelerator and on its compatibility with the cement or other admixtures present [8, 9, 10, 11, 12].

To assure the adequacy of the concrete and mortar, it is necessary to evaluate such compatibility before the material is applied. Moreover, during the construction process, the quality of the accelerator should be systematically verified to guarantee safe work conditions. Given the difficulties to replicate the real production process in laboratory conditions [13], indirect and simplified tests are used instead. In this sense, the EN 934-5 [134 establishes that the quality of the accelerators must be verified according with the EN 196-1 [15].

Nevertheless, the procedure established in the latter standard is originally conceived for the assessment of the properties of cement using mortar samples without accelerators. In fact, it does not take into account the inclusion of the accelerators or the particularities of the mortar produced with accelerators in terms of the production process. In addition to that, the EN 196-1indicates how the results from each individual test may be used to calculate the representative compressive strength of the tested material. In this calculation, an admissible variation among the results is applied to obtain a reliable average value, to eliminate outliers or to discard the whole set of results if necessary [16]. This admissible variation was not obtained for mixtures with accelerators, which tend to present higher scatter due to the difficulties associated with the production of the samples. Consequently, a bigger number of discarded values may occur leading to problems related with the assessment of the results in practice, compromising the applicability of the characterization procedure.

It is evident that some adaptations are necessary in order to make the EN 196-1 suitable for the characterization of accelerators. Thus, the objective of this study is to perform such adaptation, focusing mainly on the definition of the production process and the procedure for the calculation of the final compressive strength.

In that sense, a two stage experimental program was conducted. The first of them consisted on an experimental parametric study to evaluate the influence of the production procedure on the results. For that, mixes with different doses of accelerator were obtained varying the most relevant parameter of the production procedure established in the EN 196-1. These mixes were tested for compressive strength at early and long ages. The influence both in the scatter and in the absolute result was evaluated in order to identify the most adequate production procedure. In the second stage, 40 mixes of mortars with diverse types of accelerator (alkali/free and aluminate based), dosages of accelerator and types of cements were produced and tested for compressive strength. Based on a statistical analysis of the large database of results obtained, a new admissible variation for the assessment of the representative compressive strength is proposed for the case of mixtures with accelerators.

The conclusions derived from this study sheds light on a topic that was not clearly defined in the literature regarding the evaluation of the performance of accelerators. It provides a common ground that may favour the balanced comparison of the results obtained in different laboratories, serving as a reference for future characterization, quality control and, ultimately, for the development of accelerators.

2. METHODOLOGY

In this section, materials, production process and test methods are described. All tests were performed in the Laboratory of Technology of Structures Luis Agulló from the Univeristat Politècnica de Catalunya (UPC).

Notice that the procedure for the production of the accelerated samples used here follows as much as possible that defined in the EN 196-1. In order to maximize the acceptance of the proposal, only aspects strictly necessary and related with the inclusion of the accelerator were modified in the present study.

2.1. Materials

The efficiency of the accelerators depends on their compatibility with the cement used. Other admixtures included in the mixture may also affect the setting and hardening process in presence of accelerators. This is the case of plasticizers and superplasticizers. In order to adapt the EN 196-1 for testing mixes with accelerators certain changes must be introduced to the standard production procedure. For instance, the composition of the mixture characterized (that includes only cement, sand and water) should be modified to account for other components relevant to the performance. Likewise, the modified production procedure should allow the inclusion of accelerators, as well as chemical and mineral admixtures.

The mortars were composed by cements, water, aggregates, superplasticizer and accelerators. All materials were maintained under controlled temperature (20 ± 2 ^{o}C) and humidity (55 ± 5%) in a climatic room to reduce variations in the tests.

2.1.1. Cement, Water, Aggregates and Superplasticizer

Cement CEM I 52.5 R (I, hereinafter) and CEM II/A-L 42.5 R (II, hereinafter), were used to produce the mixes. The former is widely applied around the world for spraying concrete due to its high clinker content that allows a quick setting of concrete and, therefore, high compressive strength at early ages. On the other hand, the international tendency is to favour the use of blended types of cements to reduce the rate of CO_2 emissions originated during the production of clinker [17]. In that sense, several countries around the world apply cements type II, which includes mineral additions in order to reduce the amount of clinker. Following this trend, this study considered the cement II, which presents a substitution of approximately 10% of clinker by limestone filler. The filler is common in Spain and contributes to reduce the setting time of concrete [18, 19, 20, 21]. The main characteristics of the cements used in this study are presented in Table 1.

Table 1- Main characteristics of the cements used

Cement	CEM II/A-L 42.5 R	CEM I 52.5 R
Clinker (%)	84.10	93.90
Limestone filler	10.00	-
Gypsum (%)	5.90	6.10
Chlorides, Cl^- (%)	0.01	0.04
Blaine specific surface (cm^2/g)	3900	4600
Soundness Le Chatelier (mm)	0.50	0.50

Distilled water was used to avoid either seasonal composition variations or the possible existence of contaminants diluted in tap water. The aggregate was a 0-2 mm standardized sand supplied by the Instituto de Ciencias de la Construcción Eduardo Torroja (CSIC), which follows all the requirements defined by the EN 196-1. Finally, the superplasticizer Viscocrete CS 305 supplied by Sika Group, with an approximate density at 20 ^oC of 1.1 g/cm^3, pH equal to 4.3 and a 37.5% of dry residue, was used in all mixes. Superplasticizers are needed to provide fluidity and workability to concrete and to reduce the incidence of stroke problems in the hoses during the wet-mix spraying process [22]. It also improves the mouldability of the specimens.

2.1.2. Accelerators

To cover the wide variety of types generally used and to increase the applicability of the results obtained, 7 accelerators were tested. These accelerators were divided in 4 families depending on their characteristics, as shown in Table 2. Family 0 consisted of 1 alkali-rich accelerator based on aluminates (A-0), which is a common admixture in underground construction in Spain. On the other hand, Families 1, 2 and 3 were composed by 6 formulations of alkali-free accelerators chemically based on hydroxysulphate of aluminum: $Al(SO_4)_x(OH)_{3-2x}$.

These last families are currently used around the world, following the tendency of applying admixtures with better performance in terms of health and safety and lower environmental impact [23, 24]. Family 1 included accelerators AF-1.1 and AF-1.2, representative of those with low molar ratios ($[SO_2^{-4}]/[OH^-]$ and $[Al^{3+}]/[OH^-]$). Family 2 was formed by AF-2.1 and AF-2.2, which represent those with high molar ratios stabilized with inorganic silicates. Finally, Family 3 included AF-3.1 and AF-3.2 that represent accelerators with had high molar ratios stabilized with polycarboxylic acids. All accelerators were supplied in the form of solutions or emulsions.

Table 2- Main characteristics of accelerators

Family	Accelerator	Dry matter (%)	Molar ratio $[Al_2O_3][Na_2O]$	Molar ratio $[SO_4^{-2}][OH^-]$	Molar ratio $[Al^{3+}][OH^-]$	Stabilizer	pH 20ºC
0	A-0	36	0.8	-	-	Polyol	12
1	AF-1.1*	38	-	0.6	0.8	Inorganic acid	3.3
	AF-1.2	48	-	0.8	1.0	Polycarboxylic acid	3.1
2	AF-2.1	39	-	3.4	2.6	Inorganic silicate	2.5
	AF-2.2	42	-	2.8	2.2	Inorganic silicate	2.6
3	AF-3.1	30	-	3.0	2.5	Polycarboxylic acid	2.7
	AF-3.2	30	-	4.5	4.0	Polycarboxylic acid	2.7

*Accelerator tested in Stages 1 and 2. Others were only tested on Stage 2 of the experimental program

Three different accelerator dosages by cement weight (%bcw) were studied for Family 0, 1 and 2, whereas two dosages were evaluated for Family 3. Dosages were established using the results of the initial/final setting time in mixes with cement II and the optimal time intervals defined by former studies [16, 25, 26]. In this sense, the optimal dosage of accelerator - named here "medium dosage" - was the one that entailed an initial setting time lower than 2 min and a final setting time lower than 5 min. The low and high dosages were established to cover the typical content variation found in practice. This criterion considered a variation around the medium dosage of ±2% bcw in case of alkali-free accelerators and ±1% bcw in case of the aluminate based accelerator. Table 3 shows the dosages studied for each family.

Table 3- Accelerator doses tested in the study (% bcw)

Admixtures	Low Dosage	Medium Dosage	High Dosage
Family 0	2	3	4
Family 1	5*	7*	9
Family 2	5	7	9
Family 3	9	11	-

*Doses tested in Stage 1 and Stage 2. Others were only tested on Stage 2 of the experimental program

2.2. Composition

The proportion between components of the base mortar follows as much as possible the proposal of EN 196-1. It includes 450 g of cement and 1350 g of normalized sand. Studies by [2, 4, 27, 28, 29, 30] suggest that the water cement ratio (w/c) applied to the production of mortar with accelerators more representative of practice is 0.45, which is a common value used in sprayed materials. This contrasts with the w/c of 0.50 established originally in the EN 196-1. Given that the aim here is to maximize the representativeness of the tests, a water content of 200 g was fixed in order to achieve a w/c close to 0.45.

Moreover, for this experimental program, 9 g of superplasticizer were added to the composition. To avoid modifying the w/c, the water present in the superplasticizer was discounted from the total water added. The same approach was not adopted for the accelerators, whose content is not discounted from the total water, as usually occurs in practice.

2.3. Production procedure

The order of mixing used in Stage 1 of the experimental program also follows the general guidelines defined in EN 196-1. First, cement and water are mixed for 10 s at slow speed (28.5 rpm) in the standard mixer. The superplasticizer is added at once without stopping the mixer. The material is homogenized for additional 20 s at the same speed. Then, the sand is gradually added during the next 30 s. After that, the mixer is stopped and the material is left to rest for 90 s. The mixer is then restarted at high speed (52.0 rpm) and kept running for 30 s. The accelerator is added steadfastly once this last step is finished. The time and the velocity of mixing used after the inclusion of the accelerator are variables assessed in Stage 1 of the experimental program.

The definition of both variables is particularly relevant in case of highly active accelerators. Longer periods and higher the speed of mixing may promote a better homogenization of the mixture. Conversely, it may break the fragile crystals formed in the first contact between the accelerator and the cement, thus affecting the maximum strength reached. Longer periods could also render more difficult the posterior casting and compaction of the specimens for the tests since a less flowable mixture would be achieved at the end of the production process due to the extended effect of the accelerators. Based on previous studies [29] the mixing times of 20 s and 40 s after accelerator addition were considered in the experimental program. Mixings speeds of either 28.5 rpm or 52 rpm were tested in order to comply with the specifications of EN 196-1 for the standard mixer.

Another variable contemplated in the study is the form of addition of the accelerator, which could be raw or diluted. In the first case, the accelerator is added as provided by the supplier. In the second case, the accelerator is diluted in 20 ml of water that is discounted from the total mixing water. This last approach intends to verify whether a diluted addition would favour the dispersion of the accelerator in the mixture.

It is important to remark that the order of mixing used in Stage 2 of the experimental program was obtained based on the results of Stage 1.

2.4. Tests methods

The evaluation of the influence of the production process in Stage 1 was conducted considering the results of the mechanical properties of the mortar with accelerator. For the short term evolution of properties, the indirect assessment of the compressive strength at short term was conducted with the penetration needle test according with EN 14488-2. The mortar was placed in approximately 4 cm-thick layer in a metallic mould with 10 cm x 40 cm surface. The compressive strength was determined at 15, 30, 45, 60, 75, 90, 105 and 120 min as a result of the average of 10 penetrations, each time.

For the long term assessment, the flexural and the compressive strengths were determined in accordance with the EN 196-1. Prismatic specimens (40x40x160 mm) were cast, compacted and cured in a control chamber at a temperature of 20 ± 2 ^{o}C and humidity of 98 ± 1% until the age of testing (1, 7 and 28 days). At each age, the flexural and the compressive strength are the average of 3 and 6 tests, respectively.

In stage 2, since the aim is to define the admissible deviation for the assessment of the representative compressive strength estimated in accordance with the EN 196-1, only this test was conducted at ages 0.5, 1, 7 and 28 days. The time 0 for all tests was considered the moment of addition of accelerator.

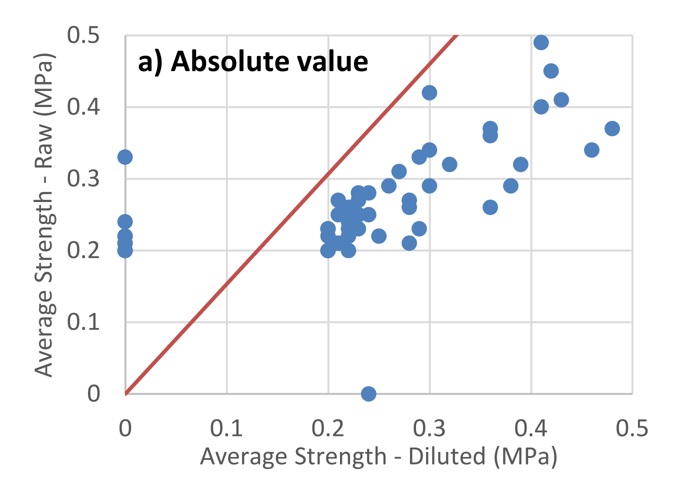
3. Results and analysis of Stage 1: Production procedure

The evaluation of the influence of the production process is performed in terms of the absolute values and the variability of the results. It is assumed that an adequate procedure should yield higher absolute values of mechanical properties, indicating a better interaction between the cement and the accelerator. Moreover, the variability of the results - represented by the coefficient of variation (CV) - should be small, suggesting a better homogenization of the mix.

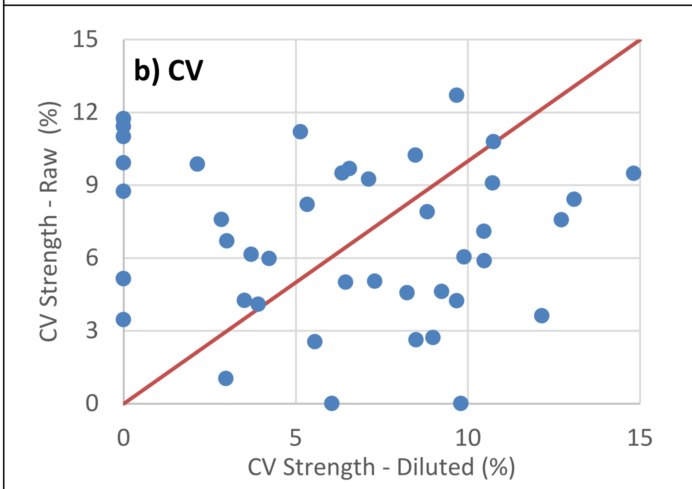
3.1. Form of addition of accelerator

Fig. 1 shows the influence of the form of addition of the accelerator in the absolute values and the coefficient variation (CV) of the strength at short term. Equivalent average results for the same time of measurements are displayed for the diluted (x-axis) and the raw addition (y-axis). Beside each graph, a table is presented with statistical parameters related with the results obtained.

In terms of absolute values (see Fig. 1.a), the average compressive strength of mixes with raw addition is bigger than that of equivalent diluted mixes. This is confirmed by a bigger concentration of points above the equivalence line (x = y) included in the graph and the bigger average value of the mixes with raw addition, which is 0.03 MPa bigger than that of diluted ones on average. Moreover, in 56.6% of measurements, the penetration resistance of mixes with raw addition is bigger than that of diluted addition. In turn, only in 28.3% of the measurements the opposite occurs.



Parameter		Value
Average (MPa)	Raw	0.27
	Diluted	0.24
	Raw-Diluted	0.03
N (%)	Raw> Diluted	56.6
	Raw= Diluted	15.1
	Raw< Diluted	28.3
p (Raw= Diluted)		0.019



Parameter		Value
Average (%)	Raw	6.98
	Diluted	7.30
	Raw-Diluted	-0.01
N (%)	Raw> Diluted	47.2
	Raw= Diluted	0.0
	Raw< Diluted	52.8
p (Raw= Diluted)		0.990

Fig. 1- Influence of form of addition of accelerator in absolute values (a) and CV (b) of indirect compressive strength at short term

A paired Student's t-test was performed with the average measured at each time for equivalent mixes to evaluate wheatear the differences mentioned previously are statistically significant. This test was conducted with alpha of 0.05 considering 2-tailed distribution. To reject the null hypothesis (Raw addition equal to Diluted addition in terms of absolute values) – which is the same as concluding that both forms of addition yield statistically different results – the p-value should be smaller than 0.025. In the case of the absolute penetration resistance, the p-value obtained is 0.019. This confirms with a 95% probability that the raw addition provides bigger results than the obtained in the case of diluted addition.

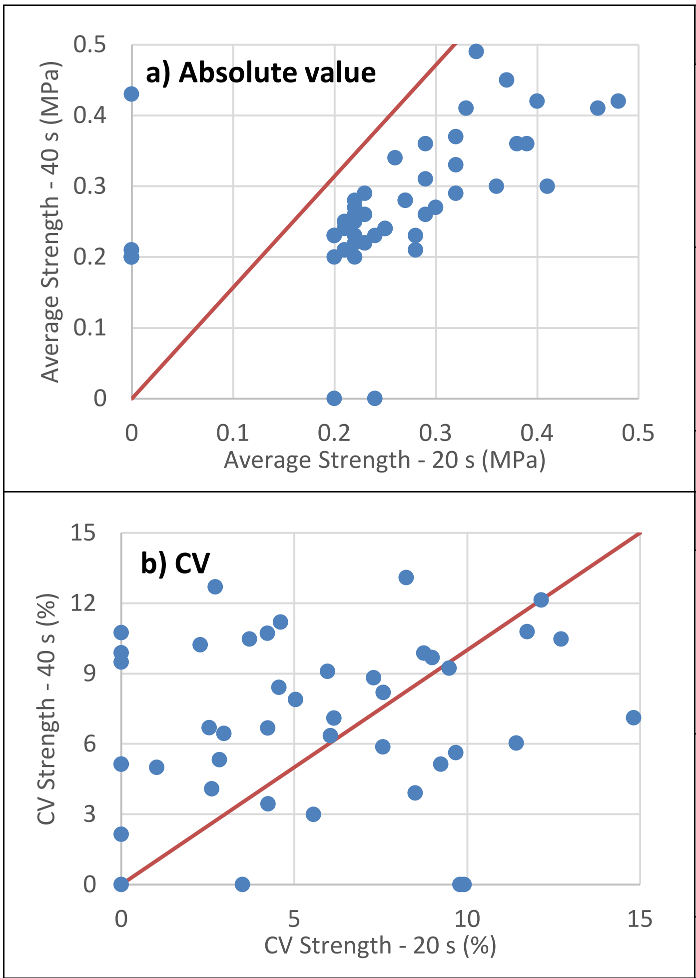
A similar analysis for the CV yields a different conclusion (see Fig. 1.b). In fact, the p-value in this case is 0.990, which indicates that the CV of the measurements with the raw addition and the CV of the diluted addition are not statistically different. This is indirectly observed by evaluating the average difference in the CV of raw and diluted forms of addition that is only 0.01%. Furthermore, the numbers of times that the mix with raw addition showed bigger CV is nearly the same as the number of times that the diluted addition showed bigger CV (47.2% for the former against 52.8% for the latter).

Based on the analysis of the results, even though the form of addition does not cause statistically significant differences in the variability (CV) of the results, it has a significant repercussion in the absolute values. This may be related with the higher flowability of the mix just prior of the addition of the raw accelerator since more water would already be available since the first stages of the mixing procedure to fluidify the mortar, thus favoring the distribution of the accelerator when it is added. Conversely, in the diluted form of addition, the reduction of the amount of water added in the first stages of the mixing procedure (notice that part of the water is saved to dilute the accelerator) would yield a stiffer mix. Therefore, at the moment of adding the accelerator, it would be more difficult to distribute the admixture in the whole mortar volume.

The fact that raw addition provides higher results than the diluted one suggests that a better interaction between accelerators and cement happens in the former. Considering that this would make the observation of differences between accelerators more evident, the use of the raw addition is recommended.

3.2. Mixing time after accelerator addition

The influence of the mixing time after accelerator addition (20 s or 40 s) is depicted in Fig. 2. The analysis performed is similar to that described in section 3.1. In terms of the absolute values (see Fig. 2.a), the average strength achieved by mixing for 20 s is slightly smaller than that achieved by mixing 40 s. This is observed in 56.6% of the measurements, whereas the opposite happens in 35.8% of the measurements. The p-value of the absolute penetration resistance is 0.028, that is, faintly above the limit established to consider the difference is statistically significant. Despite that, it is reasonable to suppose that mixing for 20 s is more likely to provide slightly smaller results than mixing for 40 s.



Parameter		Value
Average (MPa)	20 s	0.24
	40 s	0.27
	20 s – 40 s	-0.03
N (%)	20 s > 40 s	56.6
	20 s = 40 s	7.5
	20 s < 40 s	35.8
p (20 s = 40 s)		0.028

Parameter		Value
Average (%)	20 s	6.04
	40 s	7.93
	20 s – 40 s	-1.72
N (%)	20 s > 40 s	33.3
	20 s = 40 s	2.1
	20 s < 40 s	64.6
p (20 s = 40 s)		0.021

Fig. 2- Influence of the mixing time in absolute values (a) and CV (b) of indirect compressive strength at short term

In terms of the CV (see Fig. 2.b), the differences between both mixing procedures become more evident. In 64.6 % of cases the variability achieved in the procedure by mixing 20 s is smaller than that of the procedure by mixing 40 s. The opposite situation only is observed in 33.3% of the measurements. In fact, the average difference between the CV for the mixing time of 20 s and 40 s is -1.72%. In other words, the average CV for the mixing period of 20 s is smaller than that for the mixing period of 40 s.

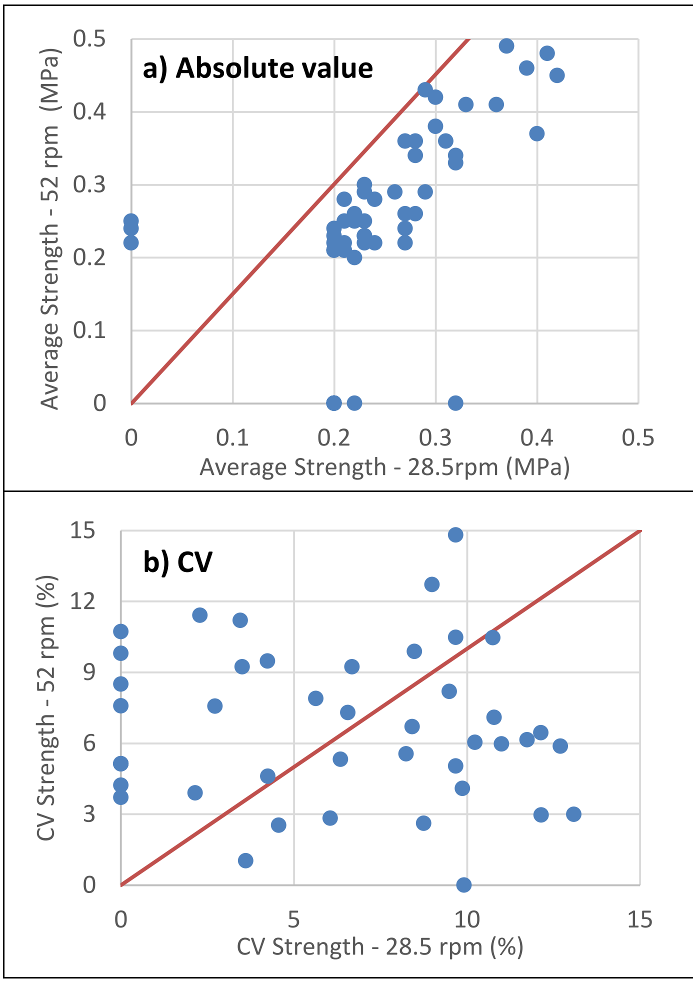
Contrarily to what was observed for the absolute penetration resistance, the Student's t-test indicates that the differences observed in the CV are statistically significant as a p-value of 0.021 is obtained. Even though the increase of the mixing time seems to lead to slightly bigger strength, the influence over the scatter of the results is more significant in favour of the mixing time of 20 s, which leads to smaller CV.

The influence on the CV may be explained by the increased difficulty to manipulate the mortar and distribute it in the mould prior to the test in case longer mixing times are adopted. Especially if highly active accelerators are used, doubling the mixing time after accelerator addition might mean that a stiffer sample is obtained since more time is left for the admixture to react before sample manipulation, which is a downside for the procedure with mixing time of 40 s. Therefore, considering the positive and more pronounced influence in the scatter as well as the need to reduce the production time, it is advisable to adopt a mixing time of 20 s.

3.3. Mixing speed

Fig. 3 presents the influence of the mixing speed after the addition of the accelerator in the absolute and the CV of the strength at short term. In average values (see Fig. 3.a), a difference of only -0.01 MPa is observed between both procedures. The Student's t-test shows a p-value of 0.483, indicating that from a statistical standpoint the differences between the absolute strength of both mixing speeds are not significant. Interestingly, it is more likely that a speed of 52 rpm will yield higher penetration resistance than if a speed of 28.5 rpm is used.

In terms of the variability (see Fig. 3.b), again the differences observed are not statistically significant given that a p-value of 0.436 is obtained in the Student's t-test. A similar outcome is observed when analysing the number of timer that a speed of 28.5 rpm provides bigger CV than that of 52 rpm. This happens 52.1% of times, against the 47.9% of times of the opposite situation.



Parameter		Value
Average (MPa)	28.5 rpm	0.25
	52 rpm	0.26
	28.5 – 52	-0.01
N (%)	28.5 > 52	28.3
	28.5 = 52	9.4
	28.5 < 52	62.3
p (28.5 = 52)		0.483

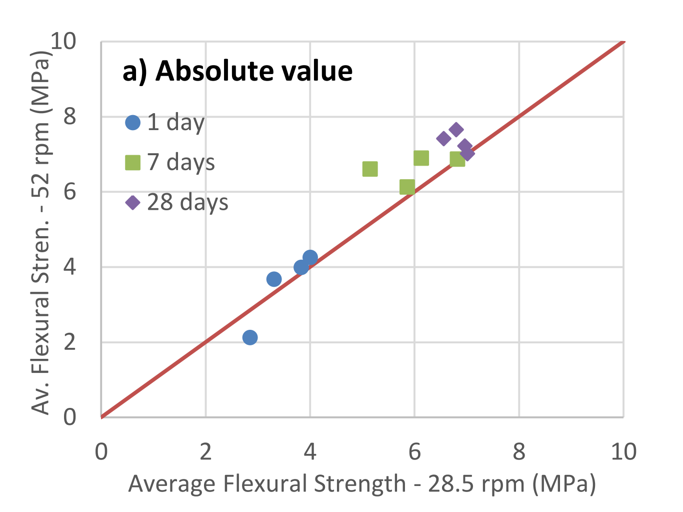
Parameter		Value
Average (%)	28.5 rpm	7.35
	52 rpm	6.62
	28.5 – 52	0.67
N (%)	28.5 > 52	52.1
	28.5 = 52	0.0
	28.5 < 52	47.9
p (28.5 = 52)		0.436

Fig. 3- Influence of the mixing speed in absolute values (a) and CV (b) of indirect compressive strength at short term

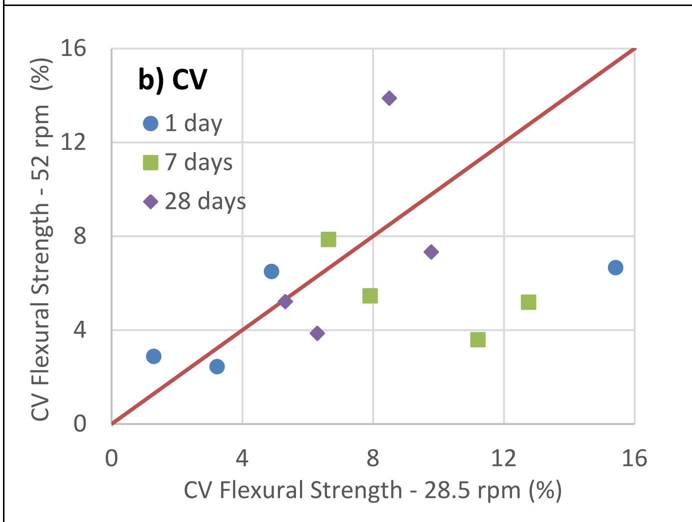
To go deeper in the analysis of the influence of the mixing speed, additional tests for the assessment of the long term flexural and compressive strengths were performed. In stage 1, this was only done with mixes produced with a raw addition of accelerator and a mixing time of 20 s after accelerator addition since these parameters were already clearly defined in accordance with the penetration test in sections 3.1 and 3.2.

Fig. 4.a depicts the flexural strengths of mortars produced with a mixing speed of 28.5 rpm and 52 rpm for both types of cement included in the experimental program. Results at long term

suggest that, in absolute values, the mortar produced with mixing speed of 52 rpm is more likely to lead to higher flexural strength in comparison with equivalent mortar produced with a speed of 28.5 rpm. This occurred in 83.3% of the determinations performed in Stage 1. The difference between both procedures is nearly statistically significant since the p-value achieve is 0.036, that is, close to 0.025.



Parameter		Value
Average (MPa)	28.5 rpm	5.44
	52 rpm	5.82
	28.5 – 52	-0.38
N (%)	28.5 > 52	8.3
	28.5 = 52	8.3
	28.5 < 52	83.3
p (28.5 = 52)		0.036

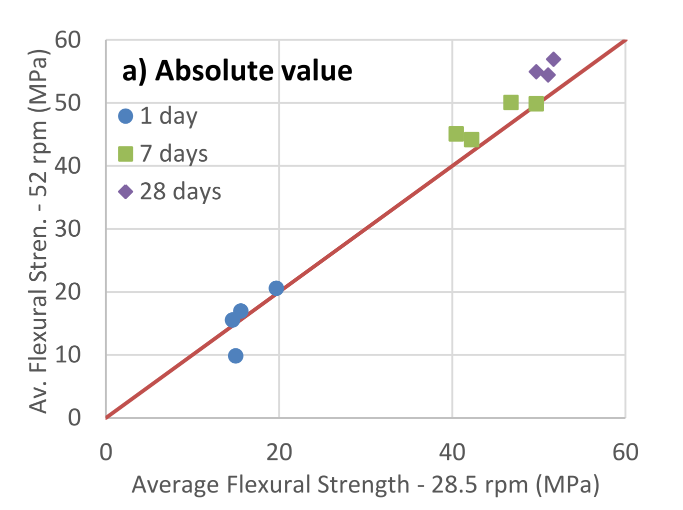


Parameter		Value
Average (%)	28.5 rpm	7.78
	52 rpm	5.90
	28.5 – 52	1.88
N (%)	28.5 > 52	66.7
	28.5 = 52	0
	28.5 < 52	33.3
p (28.5 = 52)		0.160

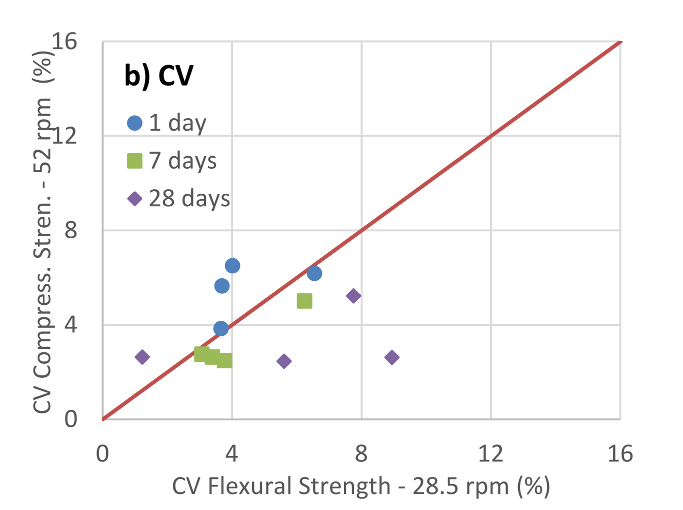
Fig. 4 - Influence of the mixing speed in absolute values (a) and CV (b) of the flexural strength at 1, 7 and 28 days

In the analysis of the variability of the flexural strength (see Fig. 4.b), even though higher average CV are found for the mixing speed of 28.5 rpm in comparison with that of 52 rpm, the difference between both procedures is not statistically significant (p-value of 0.160).

Fig. 5 shows the results of the compressive strength at long term for both mixing speeds. The analysis for the absolute values and the CV are the same as the presented in previous paragraphs for the flexural strength. A slightly bigger compressive strength is expected in mortars produced with mixing speed of 52 rpm, although the values are close to those obtained with equivalent mortar produced with mixing speed of 28.5 rpm. In terms of the variability, results indicate that both procedures provide practically identical CV.



Parameter		Value
Average (MPa)	28.5 rpm	37.62
	52 rpm	40.22
	28.5 – 52	-2.60
N (%)	28.5 > 52	8.3
	28.5 = 52	0
	28.5 < 52	91.7
p (28.5 = 52)		0.027



Parameter		Value
Average (%)	28.5 rpm	4.83
	52 rpm	4.00
	28.5 – 52	-0.84
N (%)	28.5 > 52	66.7
	28.5 = 52	0
	28.5 < 52	33.3
p (28.5 = 52)		0.256

Fig. 5 - Influence of the mixing speed in absolute values (a) and CV (b) of the compressive strength at 1, 7 and 28 days

Results suggest that the use of 52 rpm tend to be more adequate under the assumption that higher values of mechanical strength could indicate a better interaction between cement and accelerator in this case. However, it is important to stress that comparisons in the case of the mixing speed are not as conclusive as in the case of the form of addition (section 3.1) and the mixing time (section 3.2). Moreover, differences regarding the variability of the results were not statistically significant in this experimental program.

4. Results and analysis of Stage 2: Admissible variation

The results of compressive strength are presented considering the four variables of the study (type of cement, type and dosage of accelerator and age of specimens). Subsequently, these are compared with the results obtained from the non-accelerated mortars. Then, a statistical analysis is performed to evaluate a new admissible deviation for mortars with accelerators.

The procedure adopted for the production of the mortar in Stage 2 followed that established in section 2.3. The accelerator was added in a raw form and mixed during 20 s with a speed of 28.5 rpm. The admissible variation obtained here could also be taken as a reference if a mixing speed of 52 rpm was used since both speeds have similar average values and CV.

4.1. Analysis of the experimental results

To highlight the impact of the addition of the accelerator on the variability, mixes with the same compositions and without accelerator were also tested for comparative purposes. Table 4 presents the compressive strength measured at different ages for mortars with both cement types and without accelerator. The CV of the results are shown between parenthesis.

Table 4- Compressive strength results of the non-accelerated samples (MPa)

Cement	**Age (d)**			
	0.5	**1**	**7**	**28**
I	21.78 (2.35%)	35.08 (12.99%)	47.24 (2.78%)	54.04 (2.49%)
II	10.57 (6.68%)	29.84 (2.28%)	36.18 (1.83%)	46.86 (3.19%)

The absolute values of compressive strength are consistent with the requirements established for both cement types [1]. The average values of CV are 5.12% and 3.49% for mixes produced with cement I and cement II, respectively.

Tables 5 and 6 present the compressive strength obtained for mixes produced with accelerator using cement I and cement II. Again, the results of their CV are presented between parenthesis. Considering the type and dosage of accelerator, the average CV is 14.78% for mixes produced with cement I and 8.74% for those with cement II. The comparison between these values and the ones found for mixes without accelerator (see Table 4) confirms that the introduction of accelerator entails higher scatter. In fact, on average the CV of mixes with accelerator are 1.8 and 1.5 times bigger than the ones presented by equivalent mixes with accelerator using cement I and II, respectively.

Table 5- Compressive strength results of the accelerated samples produced with cement I (MPa)

Low Dose							
Age (d)	**A-0**	**A-1.1**	**A-1.2**	**A-2.1**	**A-2.2**	**A-3.1**	**A-3.2**
0.5	3.36 (42.45%)	14.98 (8.86%)	5.21 (17.56%)	19.38 (6.48%)	11.14 (9.00%)	21.26 (3.72%)	16.75 (8.14%)
1	13.02 (1.14%)	27.27 (6.36%)	24.73 (10.07%)	25.37 (11.27%)	28.26 (4.76%)	28.66 (7.86%)	23.81 (15.88%)
7	35.83 (6.70%)	42.58 (19.76%)	51.03 (5.86%)	49.35 (6.91%)	48.19 (5.88%)	45.99 (13.62%)	45.76 (7.38%)
28	51.47 (3.37%)	51.36 (5.79%)	57.57 (5.68%)	45.84 (20.11%)	62.76 (5.06%)	53.05 (10.71%)	40.43 (28.89%)
Medium Dose							
Age (d)	**A-0**	**A-1.1**	**A-1.2**	**A-2.1**	**A-2.2**	**A-3.1**	**A-3.2**
0.5	4.52 (20.17%)	15.67 (6.87%)	7.54 (7.51%)	19.32 (3.95%)	15.21 (2.71%)	20.05 (4.48%)	15.70 (8.41%)
1	13.68 (3.52%)	20.71 (18.58%)	18.44 (20.61%)	25.30 (12.74%)	29.52 (7.20%)	28.08 (29.80%)	26.58 (8.36%)
7	32.97 (13.31%)	42.78 (12.02%)	44.05 (3.58%)	46.53 (5.63%)	42.74 (19.87%)	47.56 (11.62%)	42.31 (14.61%)
28	46.61 (2.83%)	44.78 (24.07%)	50.18 (11.23%)	47.58 (10.57%)	52.54 (8.17%)	42.16 (26.49%)	46.07 (8.20%)
High Dose							
Age (d)	**A-0**	**A-1.1**	**A-1.2**	**A-2.1**	**A-2.2**	**A-3.1**	**A-3.2**
0.5	6.56 (38.77%)	14.23 (14.15%)	7.68 (5.15%)	17.28 (29.59%)	16.21 (7.51%)	- -	- -
1	10.23 (31.06%)	16.68 (17.95%)	18.18 (21.67%)	18.21 (31.69%)	22.59 (17.75%)	- -	- -
7	30.15 (13.47%)	35.63 (28.47%)	28.13 (15.71%)	23.66 (57.59%)	38.75 (23.36%)	- -	- -
28	45.83 (2.94%)	22.74 (23.08%)	27.28 (13.71%)	30.20 (31.38%)	44.42 (14.92%)	- -	- -

Table 6- Compressive strength results of the accelerated samples produced with cement II (MPa)

Low Dose							
Age (d)	**A-0**	**A-1.1**	**A-1.2**	**A-2.1**	**A-2.2**	**A-3.1**	**A-3.2**
0.5	3.36 (12.22%)	7.87 (11.11%)	6.15 (12.82%)	7.72 (7.10%)	5.99 (12.93%)	11.58 (2.47%)	9.90 (11.83%)
1	15.52 (6.06%)	14.81 (3.22%)	15.73 (3.95%)	12.23 (16.01%)	15.32 (9.00%)	15.94 (6.05%)	14.05 (7.25%)
7	37.58 (21.21%)	36.74 (7.29%)	40.06 (3.95%)	37.43 (3.92%)	33.35 (6.38%)	23.17 (29.81%)	32.07 (4.30%)
28	41.11 (6.73%)	47.75 (3.09%)	40.38 (2.63%)	44.77 (3.35%)	40.38 (7.33%)	45.72 (4.02%)	40.98 (3.07%)
Medium Dose							
Age (d)	**A-0**	**A-1.1**	**A-1.2**	**A-2.1**	**A-2.2**	**A-3.1**	**A-3.2**
0.5	7.05 (5.61%)	8.60 (7.39%)	5.80 (11.29%)	9.71 (7.50%)	8.42 (10.49%)	10.57 (7.14%)	9.41 (14.90%)
1	15.28 (5.72%)	13.11 (9.11%)	14.86 (6.91%)	13.62 (15.64%)	17.29 (7.89%)	15.41 (7.84%)	13.73 (4.56%)
7	33.66 (7.81%)	34.71 (8.37%)	40.91 (5.17%)	34.51 (5.56%)	36.53 (6.13%)	34.68 (3.37%)	31.74 (3.14%)
28	40.21 (2.82%)	40.91 (14.36%)	50.76 (3.51%)	35.50 (22.10%)	43.17 (3.22%)	39.66 (3.53%)	41.22 (6.33%)
High Dose							
Age (d)	**A-0**	**A-1.1**	**A-1.2**	**A-2.1**	**A-2.2**	**A-3.1**	**A-3.2**
0.5	6.47 (5.64%)	8.63 (5.59%)	4.74 (9.95%)	9.89 (4.79%)	7.90 (10.15%)	- -	- -
1	14.93 (3.40%)	9.36 (16.44%)	8.84 (25.97%)	15.46 (15.58%)	15.86 (5.32%)	- -	- -
7	30.27 (5.50%)	26.62 (18.66%)	29.76 (9.14%)	31.97 (17.41%)	35.97 (7.50%)	- -	- -
28	36.29 (5.22%)	38.33 (20.01%)	39.71 (7.61%)	40.87 (7.38%)	47.03 (4.13%)	- -	- -

Considering the results of the accelerated mixes, Fig. 6 shows the deviation from the average depending on the different variables: type of cement, type and dosage of accelerator and age. The values are represented in box plots through their four-number summaries: lower quartile (Q_1), median quartile (Q_2), upper quartile (Q_3), and largest observation (Max).

A continuous line represents the admissible deviation from the average allowed by the EN 196-1 (10%). In all cases the box plots show that the upper whisker is bigger than such limit.

Consequently, more than 25% of the results show deviations above the admissible value allowed by the standard, which is observed regardless of the variable considered. If the same admissible deviation established in the EN 196-1 was used (10%), most of the results obtained would be eliminated. This would entail the rejection of the majority of the tests performed.

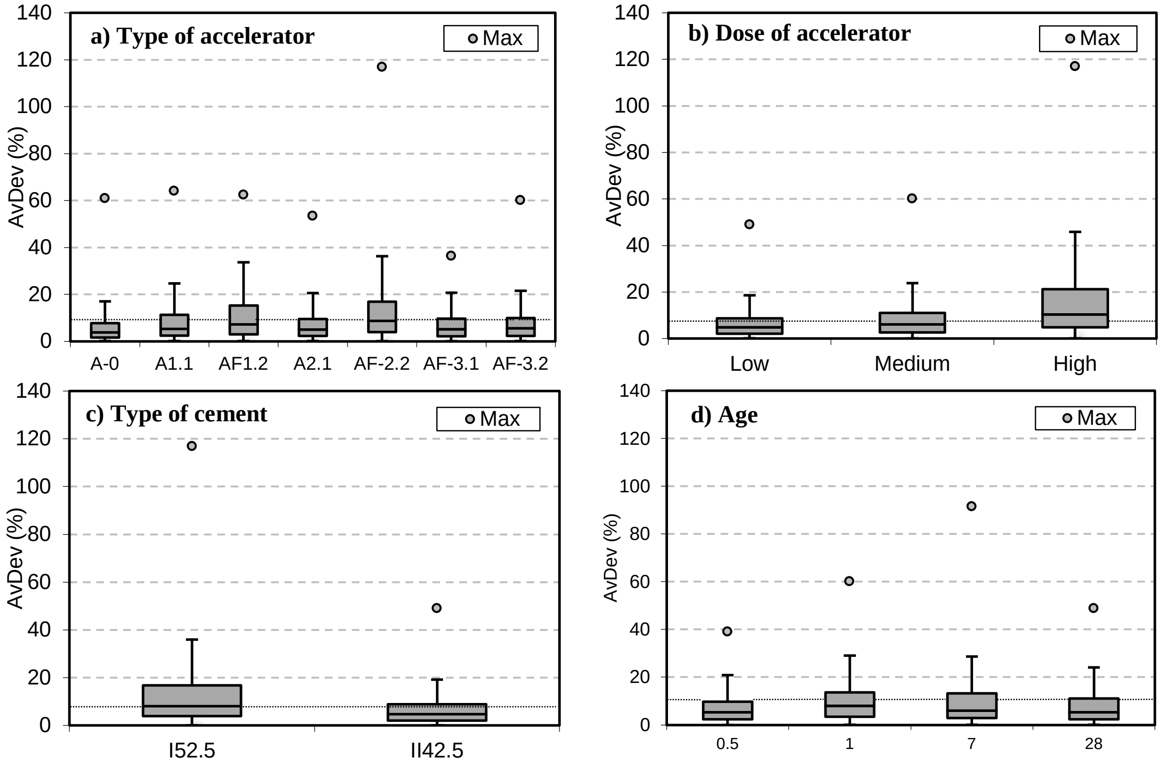


Fig. 6- Box plot of the deviations over the average

The increase in scatter is attributed mainly to the difficulties of homogenization, casting and compaction process due to the rapid setting promoted by the accelerators, which leads to higher variability. Notice that this difficulty is intrinsic to the use of accelerators and would be present even if the production process was changed. In other words, under the same conditions, compositions with accelerator should present a scatter higher than that obtained for compositions without them.

As shown in Fig. 6.1, mortars with alkali-free accelerators display deviations that are around that found for compositions with the aluminate-based accelerator tested. Smaller maximum values are obtained for compositions with AF-3.1 and higher maximum values are obtained for compositions with AF-2.2. Therefore, no clear influence of the type of accelerator (alkali-free or based on aluminates) was found.

Apart from that, the results from Fig. 6.b show that higher dosages of accelerators entail higher deviations. This is possibly caused by difficulties to homogenize the accelerators, to cast and to compact the samples of mixes with higher dosages due to their faster setting. For a similar reason, the type of cement also affects the results of deviation obtained, as shown in Fig. 6.c. Mixes with cement I present higher deviations than the ones with cement II. This is probably due to the higher content of clinker and of C_3A in cement I that leads to higher reactivity, making the casting and compaction process more difficult.

In a general analysis, the maximum scatter measured increases with the age of the specimen (see Fig. 6.d), except for the results at 28 days. This trend is not so clear if the average scatter for each age are compared since very similar values are obtained at 1, 7 and 28.

4.2. Statistical verification for mixes with accelerator

The analysis of the results showed that the addition of the accelerators implies an intrinsic scatter higher than that of conventional mortar without accelerator. These results confirm that an adaptation of the standard in terms of criteria for the statistical verification of the results is needed. This adaptation requires the assessment of new admissible deviation from the average considering the new production process established in section 3 and the typical scatter associated to the use of accelerators.

Fig. 7 shows the steps of the statistical verification defined in the EN 196-1 to assess the representative long term compressive strength. The standard allows discarding 1 result among the 6 measurements obtained in each sample, which is equivalent to a maximum discard rate of 16.66%. A statistical analysis was performed with the 960 values of deviation from the average calculated experimentally to derive a new admissible deviation. The new admissible deviation was estimated considering that the probability of having outliers should be 16.66%. This means that the deviation obtained in the statistical analysis for mortars with accelerators is approximately analogous to that established for the test of conventional mortar without accelerator.

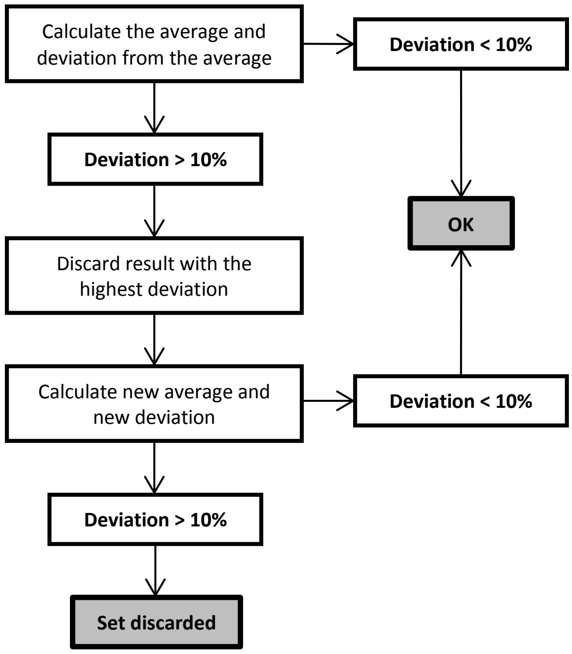
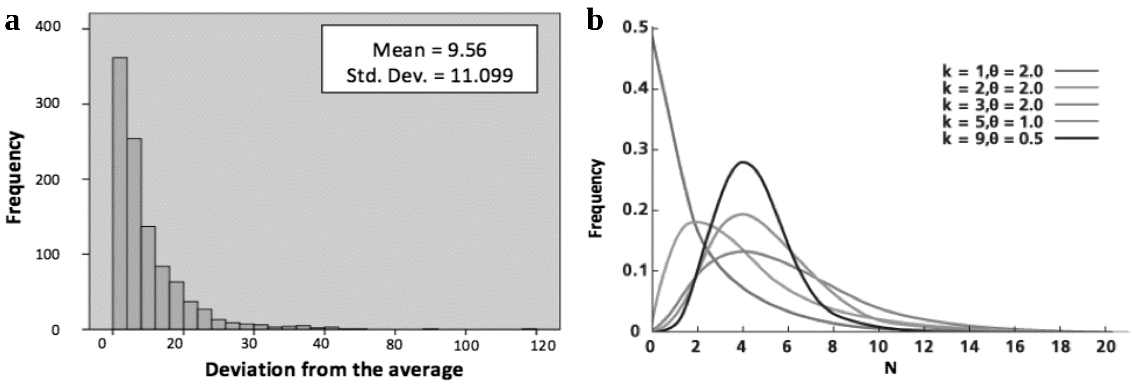


Fig. 7 - Statistical verification defined in the EN 196-1

For that purpose, first a histogram was obtained (see Fig. 8.a) considering all the experimental data. Then, the probabilistic law that best fits the histogram was found. Although different distributions were analyzed, the best fit was obtained with the Gamma Distribution (see Fig. 8.b).



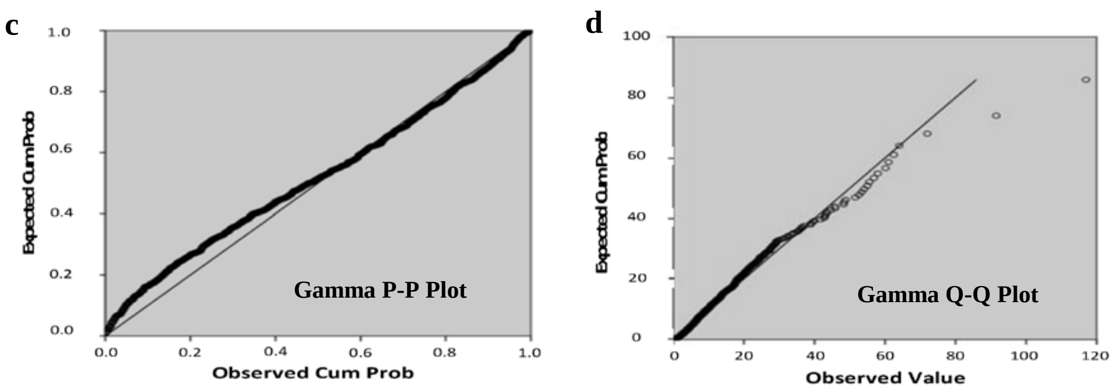


Fig. 8- Gamma distribution (a); Histogram of the values of deviations from the average (b); Results of the P-P plot (c) and Results of the Q-Q plot (d)

The goodness of the fit was evaluated through the P-P and the Q-Q curves plotted in Fig. 8.c and Fig. 8.d, respectively. Both of them indicate a good fit of the values of deviation from the average calculated experimentally and the probability distribution Gamma since values approach the equivalence line given by x = y.

The Gamma distribution depends on two parameters: shape (k) and range (θ). Whereas k affects the shape of a distribution, θ determines the statistical dispersion of the probability distribution, as observed in Fig. 8.b. Eq. 1 presents the probability density function, which depends on Γ(k) (Eq. 2). Values of parameters k and θ were calculated using the cumulative distribution function (Eq. 3) that depends on the lower incomplete function (Eq. 4).

$$f(x;k;\theta) = \frac{1}{\theta^k} \cdot \frac{1}{\Gamma(k)} \cdot x^{k-1} \cdot e^{-\frac{x}{\theta}} \ for\ x > 0\ and\ k, \theta > 0 \tag{1}$$

$$\Gamma(k) = (k-1)! \tag{2}$$

$$F(x;k;\theta) = \int_0^x f(u;k;\theta) \cdot du = \frac{\gamma\left(k, \frac{x}{\theta}\right)}{\Gamma(k)} \tag{3}$$

$$\gamma\left(k, \frac{x}{\theta}\right) = \int_0^x t^{k-1} \cdot e^{-t} \cdot d\left(\frac{x}{\theta}\right) \tag{4}$$

Once these parameters are determined for a set of data, the Gamma function is used to calculate the deviation that occurs with a likelihood of 16.66%. Table 7 present the values of k, θ and admissible deviation (Admissible AvDev(%)) calculated considering the different variables of the study and the results for the whole set of data from the experimental program.

The Admissible AvDev(%) calculated are higher than 10% in all cases, ranging between 11.89 and 27.65%. Table 7 also reveal that Admissible AvDev(%) increases with the dose of accelerator. Moreover, cement I present higher Admissible AvDev(%) than cement II. Such results are consistent with the observations included in section 4.1.

Table 7- New admissible deviations considering variables studied

Variable		Shape (*k*)	Range (θ)	Admissible AvDev(%)
Accelerator	A-0	0.476	0.064	14.25
	AF-1.1	0.733	0.084	16.22
	AF-1.2	1.045	0.097	19.18
	AF-2.1	0.973	0.138	12.67
	AF-2.2	0.738	0.057	24.06
	AF-3.1	1.031	0.137	13.43
	AF-3.2	0.722	0.085	15.82
Dosage	Low	0.977	0.144	12.19
	Medium	1.040	0.129	14.37
	High	0.933	0.061	27.65
Cement	I	0.949	0.079	21.67
	II	1.003	0.151	11.89
Age (d)	0.5	1.164	0.166	12.30
	1	1.231	0.124	17.28
	7	0.740	0.076	18.08
	28	0.853	0.097	16.07
All data		0.741	0.078	17.65

Considering all set of data obtained in the study, the new value of admissible deviation from the average is 17.65%. In this sense, a new admissible deviation equal to approximately 17% should be taken into account when using the EN 196-1 for the test of mixes with accelerators.

5. Conclusions

The following conclusions were derived from this study based on the extensive experimental program conducted and the analysis performed.

<u>Regarding the production process</u>

- The study of the influence of the form of addition of the accelerator suggests that the raw addition (without dilution with part of mixing water) shows higher compressive strength than that of the diluted addition (obtained by mixing the raw accelerator with part of the mixing water). The scatters in the compressive strength of both approaches are not statistically different. In this context, the raw addition is recommended since it is expected to provide higher strength, indicating a better interaction between accelerator and cement.
- The study of the influence of the mixing time after accelerator addition indicates that mixing for 20 s tend to give compressive strength smaller than mixing for 40 s. Nevertheless, mixing for 20 s yields smaller scatter in the results in comparison with 40 s. Since the influence in the scatter is more statistically significant than in the absolute value (p-value of 0.21 against 0.28), mixing for 20 s is recommended. This also contributes to reduce the production duration, which is important in mortars with highly active accelerators given the difficult to manipulate the sample with time.
- The analysis of the mixing speed after accelerator addition shows that the speed of 52 rpm tend to give higher compressive and flexural strengths than mixing with 28.5 rpm. The variability of the results is similar in both cases. Therefore, the speed of 52 rpm is recommended.
- Considering all the above, the production of the mortar should follow the production process established in section 2.3. The accelerator should be added in raw at the end, being actively mixed for 20 s at 58 rpm.

<u>Regarding the admissible variability of the compressive strength:</u>

- The high scatter of the compressive strength is intimately related with the production process and the difficulty to homogenize, to cast and to compact the samples. Notice that this is intrinsic to the compositions with accelerators.
- The variables studied had an influence on the scatter of compressive strength at long term. An increase in the reactivity of the composition led to higher scatter. In this sense, higher doses of accelerators entail higher deviations. Moreover, mixes with cement I present higher deviations than the ones with cement II.
- A new admissible deviation from the average of the results is estimated to account for the higher variability of the mix with accelerator. A value of 17% is suggested after studying all the results from the present work. This value is 70% bigger than the established in the EN 196-1.

It is important to remark the inherent difference between the microstructure of the sprayed material and the material produce through a mechanical mixing of the components. Therefore, comparison with results obtained with sprayed material should also be performed in case more accurate comparisons are needed. Even though the accelerators characterized here represent a significant part of the currently used in many applications, it is important to remark that other types are available in the market. Considerations different from the ones proposed here may be required in case special types of accelerators are used.

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