

Parametric study of the effects of the composition on the setting of self-compacting mortar, using continuous ultrasonic monitoring

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Abstract. The additions and superplasticizers which are responsible for the self-compacting properties of a mortar or concrete can have an important influence on the setting of these mixtures. With the continuous ultrasonic testing method, it is possible to closely follow the setting process, based on the changes of the P-wave velocity of an ultrasonic wave through a hardening mortar sample. The maximal gradient of the wave velocity curve is a good estimator for the start of the percolation of the mixture. In this paper, this testing method is used to characterize the influence of the cement-to-powder ratio (C/P) with constant cement content, the addition type and the superplasticizer quantity and type on the setting of the mortar. The self-compacting mortar mixtures are derived from a standardized mortar mix, using a limestone and a quartz addition and two types of polycarboxylate ether (PCE) superplasticizer. The effects on the wave velocity development are important: While the quartz addition is slowing down the hydration, rising amounts of limestone addition lead to an acceleration of the setting. A rising amount of superplasticizer causes a more significant deceleration of the setting. Despite their similarity, the two types of PCE superplasticizer cause rather different changes in the delay of the setting.

Introduction

Self compacting concretes and mortars rely on a carefully designed combination of a wide array of viscosity modifying agents, superplasticizers and additions to obtain their defining properties [1,2]. Apart from their main functionality, these added components are known to cause secondary effects, influencing the kinetics of the hydration mechanisms in the mixture and consequently the microstructure, the durability and the final mechanical properties. Therefore, much effort is put in to

better understanding and controlling these secondary effects, using a diverse set of techniques and focussing on various influencing parameters [3-5]. Given the elaborate array of possible mixture compositions, the investigated range of the parameters is often narrow and focussed on optimal resulting self-compacting properties. To truly understand the effects of these parameters over a wider range and to be able to anticipate the consequences of the choices made, a wide-range parameter study is needed.

When investigating the effect of the composition on the kinetics of the hydration, continuous measurements at a very early age are indispensable. Indeed, the major part of the fast changes in the mixtures, leading up to the start of the percolation, the setting, and the start of the hardening happen within the first hours after the preparation of the mixture. Few reliable methods exist to follow these events, such as the Vicat and hydration heat tests. Both have however their limitations.

Relying on the dependence of the p-wave velocity of a material on its elastic properties, the ultrasonic transmission method is known to be very sensitive to microstructural changes in a mortar or concrete [6]. Several devices have been developed, extending this method with an automatic driving and data-acquisition unit, and allowing following even the earliest and fastest changes in a fresh hydrating cementitious mixture [7-9]. The relationship between the changes in the p-wave velocity and the development of the microstructure, from suspension to a fully hardened state is very complex. One most important event, the start of the percolation of the hardened matrix, has been proven to correspond well with the inflection point in the velocity curve, easily localized as the point with the maximum velocity gradient [6,10,11].

In this paper, the continuous ultrasonic method is used to perform a parameter study of the influence of the cement-to-powder ratio (C/P) with constant cement content, of the addition type and of the superplasticizer (SP) quantity and type, on the setting of an extensive series of self-compacting mortar mixtures.

Materials and test methodology

For this parametric study, a total of 29 mortar mixtures are produced and submitted to a continuous ultrasonic test to determine the start of the percolation in each mixture. The investigated parameters are: The SP quantity and type, with and without the presence of a limestone addition, the C/P and the type of mineral addition. While the intent is to focus on the behaviour of self-compacting mortars, several of the composed mixtures do not have stable self-compacting properties: In pursuit of a wide range for the investigated parameters, a number of overly dry mixtures are obtained, while others show slight segregation and bleeding.

Mix design

All 29 mixtures are produced using 1.350 kg of normalised sand (according to EN 196-1), 0.45 kg of CEM I 52.5 N and a water cement ratio (W/C) of 0.45.

Two types of SP are considered. Both are third generation PCE superplasticizers, produced by the same company, but show a distinct behaviour. SP1 is produced for the ready-mix concrete industry where slump retention, high strength and durability are required in hot climates. The slump retention is based on the time release behavior of SP1, announced without retardation of the set time [12]. SP2 is used to achieve high early strengths for the precast concrete industry where a high durability and performance is required [13]. SP2 shows significantly higher dispersion properties than SP1. While the technical description of both SP's mentions long lateral polymer chains, their exact composition, and more importantly, the difference in the compositions are not known. SP1 is applied in concentrations between 0 and 3 % of the cement mass, while added SP2 concentrations only range from 0 to 1 % of the cement mass, because of SP2's higher dispersion effect.

Two types of mineral addition are used: a limestone (L) and a quartzite addition (Q). They are added to obtain cement to powder ratio's (C/P) between 0.6 and 1. Figure 1 shows the grading of the two mineral additions. The density and Blaine fineness of these additions is shown in Table I. The geometrical properties of both fillers are much alike, the quartzite addition being slightly finer and lighter.

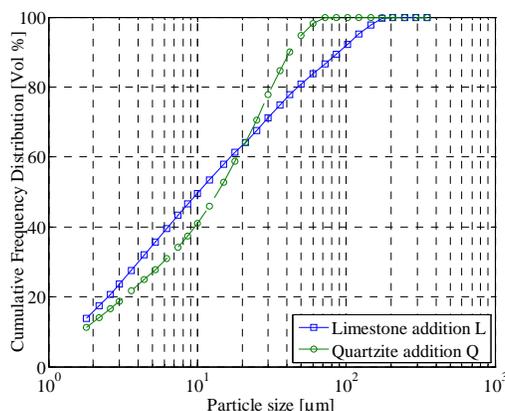


Figure 1. Grading curves of the mineral additions.

Table I. Specific mass and Blaine fineness of the mineral additions

	Specific mass [kg/m ³]	Blaine fineness [m ² /kg]
Limestone addition (L)	2700	338
Quartzite addition (Q)	2640	388

Because of the presence of the additions and the SP, the standardised mixing procedure according to EN 196-1 can not be followed. While maintaining the proscribed mixing speeds, the following procedure is used: The sand, cement and mineral addition are placed in the mixing bowl and mixed at slow speed for 90 s. During the last 30 s, all the water is slowly added to the mixture, followed by another 30 s of slow mixing. The mixer is then stopped for 30 s, during which the SP is added to the paste and after which mixing continues at high speed for 30 s. The mixer is then stopped for 90 s and the mixture is left to rest. Finally, mixing continues for another 60 s at high speed. Immediately after the mixing, the ultrasonic test is started.

Separate batches are prepared for the purpose of the conventional fresh tests. The consistence (by flow table), the bulk density and the air content of the fresh mortar mixtures are determined according to EN 1015-3, -6 and -7. Given the high fluidity of a large part of the mixtures, the slump flow of the fresh mortar is determined as a part of the standardised flow test, by measuring the radius of the mortar cone after the removal of the conical mould and before the application of the shocks. This procedure is similar to the slump flow test as performed on fresh self-compacting concrete [2].

The overview of the mix composition and the results of the conventional (non-ultrasonic) tests on the fresh mortars are shown in Table II. Since the sand and cement quantity, the cement type and W/C are identical in all mixtures, this data is not represented in Table I. The following main groups are considered for the parametric study: In group A and B, the effect of the amount of SP is investigated, for both SP's, in the case of the absence of a mineral addition. The same effect is studied, but now for a mixture with a fixed quantity of limestone addition, in groups C and D. In groups E and F, the effect of the C/P is observed for both types of mineral addition, in combination with a fixed quantity of SP1. In the present case of a fixed cement quantity, the variation of the C/P reduces to the variation of the quantity of mineral addition. Additionally, cross-comparison within these groups allows for the study of the effect of the type of SP and mineral addition.

Continuous ultrasonic testing

Test device. The apparatus used for the continuous ultrasonic tests is the Ultratest IP-8 [14]. The device, as shown in Figure 2, consists of a PC-connected controller allowing up to 8 simultaneous measuring channels. In this research, up to 4 simultaneous measurements were made. Each measuring channel is composed of a cylindrical flexible silicone mould and an ultrasonic sender and receiver pair. The mould can hold cylindrical concrete or mortar samples measuring up to 70 mm across and 60 mm high, for a maximum sample volume of 230 ml. This volume is a compromise between the representativity of the sample and the signal to noise ratio of the received signal, which is in direct relation with the sender to receiver distance. For a mortar the sample volume is of the order of magnitude of a standardised mortar prism (256 ml) and thus perfectly acceptable. The mould allows the lateral fitting of the sender-receiver pair, in direct contact with the fresh mortar sample, for the measurement of the ultrasonic wave transit time in through-transmission. All tests were performed with a sender-receiver distance of 50 mm +/- 5 mm. To ensure an optimal contact quality and an improved signal-to-noise ratio, as well as to avoid demoulding problems, the inside of the moulds and the contact surface of the ultrasonic testers are covered with a thin layer of spray-on silicon grease. The sample can be sealed from the air with a mastic-fixed cover. This avoids excessive water evaporation and reduces drying shrinkage, which can lead to a loss of the contact of the sample with the ultrasonic testers. While this flexible mould system is very user-friendly and reduces spurious through-the-mould signal transmission, it renders compaction of dryer samples rather arduous and difficult to reproduce.

The p-wave narrow-band ultrasonic tester pair has a resonant frequency of 25 kHz, which makes it well fitted for testing fresh mortar. At very early age, this low range of ultrasonic frequencies has an optimal transmission ratio [15]. The testers have a flat, 25 mm diameter contact surface with the sample.

Table II. Mix composition and results of conventional fresh mortar tests

Name	Group	Addition type	C/P [/]	SP type	SP [Mass%]	Slump Flow [mm]	Flow [mm]	Fresh air Content [Vol%]	Fresh density [kg/m ³]
S-0	A/B	/	1	/	0	100	135	4.9	2245
S1-1	A	/	1	SP1	0.25	100	164	7.2	2150
S1-2	A	/	1	SP1	0.5	113	184	5.0	2223
S1-3	A	/	1	SP1	0.75	134	209	3.4	2252
S2-1	B	/	1	SP2	0.2	104	157	7.4	2178
S2-2	B	/	1	SP2	0.25	105	167	4.9	2236
S2-3	B	/	1	SP2	0.35	155	216	2.2	2286
S2-4	B	/	1	SP2	0.4	234	266	5.2	2222
S2-5	B	/	1	SP2	0.5	266	276	4.0	2242
LS1-1	C	L	0.65	SP1	1	110	176	4.5	2260
LS1-2	C	L	0.65	SP1	1.5	187	240	5.0	2239
LS1-3	C	L	0.65	SP1	2	241	261	2.7	2257
LS1-4	C	L	0.65	SP1	2.5	271	283	1.7	2299
LS1-5	C	L	0.65	SP1	3	284	291	0.8	2326
LS2-1	D	L	0.65	SP2	0.4	100	133	5.8	2256
LS2-2	D	L	0.65	SP2	0.6	182	222	5.9	2243
LS2-3	D	L	0.65	SP2	0.8	285	> 300	3.1	2268
LS2-4	D	L	0.65	SP2	1	> 300	> 300	0.75	2350
L-1	E	L	0.6	SP1	1	105	151	5.3	2256
L-2	E	L	0.65	SP1	1	110	176	4.5	2260
L-3	E	L	0.7	SP1	1	111	182	4.7	2242
L-4	E	L	0.75	SP1	1	136	208	4.4	2245
L-5	E	L	0.8	SP1	1	175	239	5.1	2232
Q-1	F	Q	0.65	SP1	1	100	124	5.2	2235
Q-2	F	Q	0.7	SP1	1	104	150	5.4	2239
Q-3	F	Q	0.75	SP1	1	108	180	5.2	2248
Q-4	F	Q	0.8	SP1	1	142	217	4.7	2241

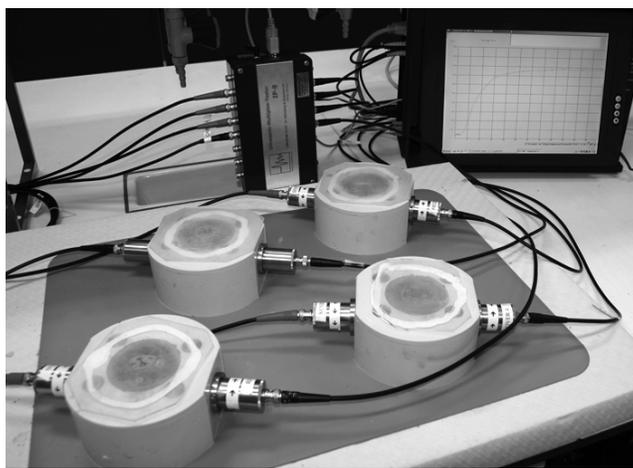


Figure 2. The Ultratest IP-8 in a 4-channel test setup

The device is controlled by the WinUltraSonic/IP-8 software application. It allows programming the pulse generation and data acquisition of the continuous monitoring experiment up to a total of 3600 measurements at chosen time intervals. The transmission time is measured with a precision of 0.1 μs , using a threshold onset picking algorithm. Because of the flexible nature of the mould, the sender to receiver distance cannot be determined a priori. At the end of the test, after demoulding, the exact distance between sender and receiver is measured on the hardened sample with a precision of 0.1 mm, which allows the calculation of the wave velocity in function of time.

Test procedure. For each mixture, 3 to 4 channels are used, for as many simultaneous measurements. After the mix preparation, the moulds are filled and closed as quickly as possible, in order to reduce the blind time interval of the test. Each test is started not later than 12 minutes after the start of the adding of the water during the mixing procedure. This time interval is taken in to account during the treatment of the data. This blind time interval has no influence on the measurements in this study, since hardly any variations in the wave speed are measured during the first 60 minutes after the adding of the mixing water. Each test is run for at least 48 hours. For slower mixtures, the continuous measurements are run for 72 hours. The time interval in between measurements is set at 72 seconds.

Data treatment. For each mixture, the mean of the time histories of the p-wave velocity of each recorded channel is calculated and replaced for further treatment by a higher-order polynomial fit with a root mean squared error of calibration lower than 10 m/s. Next, the time history of the gradient of this polynomial fit is calculated, as well as the moment in time at which the gradient is maximal, which is considered to correspond to the start of the percolation of the mixture [6,10,11].

Results and discussion

The start of the percolation of each mixture is determined as described in the previous paragraph. Within each mixture group, the effect of the relevant parameters can be studied. Furthermore, relevant comparisons between groups of mixtures are made for group A to D and for group E and F.

Effect of the SP concentration and type

These parameters are investigated with and without the presence of the limestone addition. Figure 3 shows the percolation start time in function of SP concentration with and without addition, using both SP's.

For all mixture groups, a gradual retardation of the setting with rising SP concentrations is measured, as is expected [16]. The dispersion of the cement particles, by both electrostatic repulsion and steric hindrance, will lead to a slower hydration and development of the microstructure. The retardation of the start of the percolation seems to increase more or less linearly with rising SP concentrations, except for the highest concentrations obtained in mixture groups C and D, where a sudden increase of the retardation can be observed. This effect is not noticeable for the mixtures without additions, since the mixtures start to show segregation and bleeding before these highest SP concentrations can be obtained.

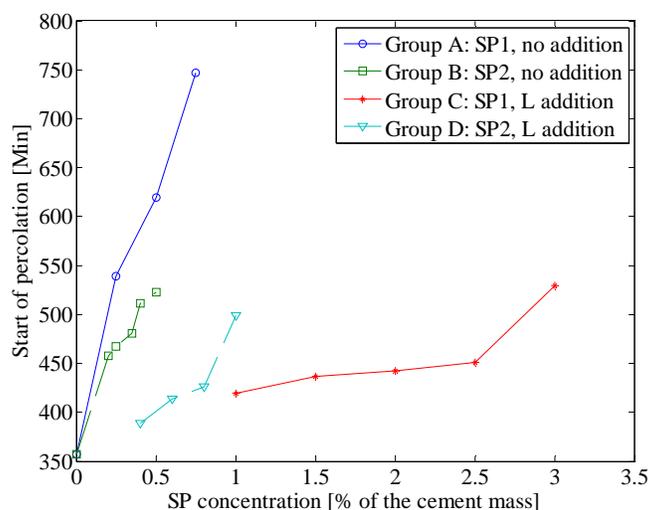


Figure 3. Start of percolation i.f.o. SP concentration for mixture groups A, B, C and D

While the conventional fresh tests show the distinctly higher dispersion effect of the SP2, this does, unexpectedly, not necessarily result in a higher retardation of the start of the percolation, as can be observed when comparing group A to B. The technical description of the SP's mentions a "time release" effect for the SP1 [12], indicating that, though the immediate dispersion due to the use of SP1 may be lower, its effect is extended in time. The results show that, in contradiction to [12], this effect is clearly accompanied by a prolonged retardation of the hydration, at least in comparison with SP2. This effect seems to disappear when observing the comparison of group C and D. This approach is however treacherous because of the large difference in the applied SP concentrations in the presence of an addition. In this case, considering a constant addition, cement and water content, the Flow value of the mortar mixtures is a better indicator of the dispersion effect. It thus indicates the total immediate dispersion effect of a certain quantity of one SP with a certain dispersion efficiency. The qualification "immediate" specifies that the Flow value can only give an indication of the dispersion effect of the SP immediately after the mixing, and thus ignores a possible extended consistence retention by the use of SP1. Figure 4 shows the percolation start time in function of the Flow value for mixture groups A to D. Flow values exceeding 300 mm are plotted at 300 mm. It confirms the earlier statement regarding the higher retarding effect for an equal immediate cement particle dispersion of SP1 compared to SP2. It also shows a linear relationship between the Flow value and the start of the percolation, except for the lowest Flow values, corresponding to the absence of SP. The representativity of these lowest Flow values can be questioned, since they rely highly on the manual compaction of the relatively dry mortar in the Flow cone, as compared to the other, self-compacting mixtures.

For the mixture groups C and D, containing a fixed amount of limestone addition L, the start of the percolation arrives significantly earlier compared to mixture groups A and B. This is due to the accelerating effect of the limestone addition on the hydration reactions, as described by [17,18]. While the exact mechanism is not yet clear [2], limestone filler is confirmed to cause a faster formation of the microstructure and consequently, an earlier percolation of the mortar matrix. The extent of this acceleration is investigated in the following paragraph.

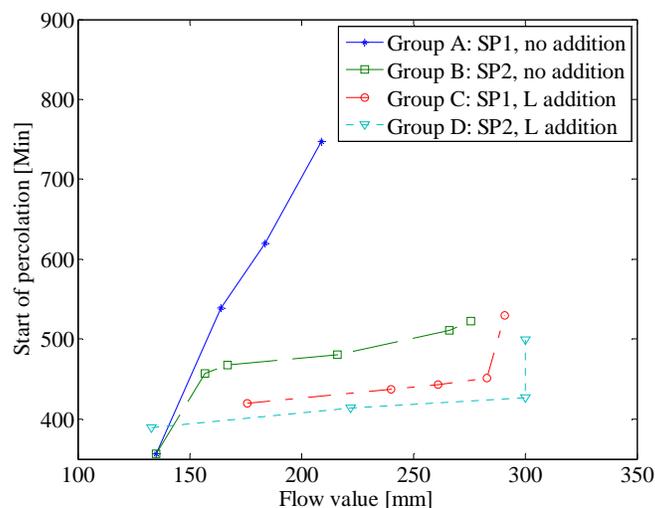


Figure 4. Start of percolation i.f.o. Flow value for mixture groups A, B, C and D

Furthermore, the presence of the filler has reduced the difference between the retardation effect of the two SP's, from a steadily diverging difference, reaching up to 275 minutes, to a mere 20 minute difference, more or less constant over a wide consistence range.

These parameters are investigated by mixtures with increasing amounts of limestone or quartzite addition. Figure 5 shows the percolation start time in function of C/P for both mixture groups. It is clear that both additions have a significantly different effect on the hydration kinetics of the mortar mixtures. While both mineral additions are considered to be chemically inert, it is known that the presence of limestone filler has a certain catalytic effect on the hydration [17,18].

For the highest C/P, and thus the lowest quantities of addition, both mixture groups behave similarly, by a retardation of the start of the percolation. When addition quantities increase (and C/P decreases), the accelerating effect of the limestone addition becomes visible, resulting in a gradual acceleration of the hydration and a shortening of the induction period. The acceleration seems to diminish towards the lower C/P values, indicating that a maximum acceleration is nearly reached at C/P = 0.6. For a more detailed view on the behaviour of the mortar with C/P around 0.75, a test series with a higher resolution of the C/P parameter is necessary.

Effect of the C/P and addition type

For an increasing amount of quartzite addition, the start of the percolation is gradually more retarded. The increase of the retardation is gradually flattening out for the lower C/P ratios. While quartzite powder is generally known to be inert and to have no significant influence on the kinetics of the hydration [17], the retardation shown by these results can not be ignored. Its causes need to be investigated in a more detailed study of this specific parameter.

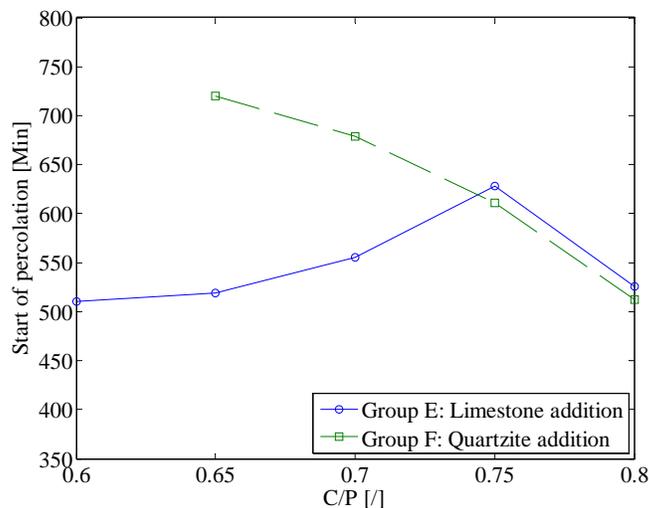


Figure 5. Start of percolation i.f.o. C/P for mixture groups E and F

Conclusion

The continuous ultrasonic testing method confirms to be a very sensitive tool to determine the effect of the composition of a mortar mixture on the kinetics of the formation of the microstructure in general and the time of the start of the percolation in particular.

The time to the start of the percolation increases linearly with an increasing SP concentration. The relationship more generally, independent of the SP type, when the SP concentration is expressed through its effect on the Flow value of the mixture. For Flow values nearing 300 mm (and thus for very high SP concentrations), a faster increase of the retardation is observed

Though SP2 has a higher dispersion effect than SP1, it causes a lower retardation, due to the time release behaviour of SP1. In the presence of limestone addition, the retarding effect of both SP's is reduced and the difference in the retardation caused by the two SP's is rendered constant over a large Flow value domain.

For C/P close to 1, both types of mineral addition cause an increase of the retardation. For C/P's lower than 0.75, the accelerating effect of limestone addition on the hydration kinetics results in decreased start times of the percolation of the microstructure. Adding higher amounts of quartzite addition results in an ever increasing delay of the start of the percolation, which is in contrast with its expected inert behaviour.

Though the results give a good impression of the effects of these composition parameters on the time of the start of the percolation of the microstructure of a mortar, they need to be investigated at a higher resolution.

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