Use of superabsorbent polymers to mitigate autogenous shrinkage in ultra-high performance concrete

L. De Meyst[1], B. Debbaut[1], M. Araújo[1,2], K. Van Tittelboom[1], S. Van Vlierberghe[2], N. De Belie[1]

[1] Magnel Laboratory for Concrete Research, Ghent University, Tech Lane Ghent Science park, Campus A, Technologiepark-Zwijnaarde 60, 9052 Ghent, Belgium – email: laurence.demeyst@ugent.be; brenda.debbaut@ugent.be; adelaide.araujo@ugent.be; kim.vantittelboom@ugent.be; nele.debelie@ugent.be;
[2] Polymer Chemistry and Biomaterials Group, Centre of Macromolecular Chemistry (CMaC), Ghent University, Krijgslaan 281, Building S4-bis, 9000 Ghent, Belgium – email: sandra.vanvlierberghe@ugent.be

Abstract
Ultra-high performance concrete (UHPC) with low w/c-ratio is very prone to the formation of cracks due to autogenous shrinkage. These cracks can lead to a decreased durability of the concrete, resulting in higher maintenance and/or repair costs in the future. Superabsorbent polymers (SAPs) can be added to cementitious materials to provide internal curing and as a result reduce or even mitigate this autogenous shrinkage. In this paper, two different types of SAPs were added to cement paste to see their influence on mitigating autogenous shrinkage. One SAP is a commercially available SAP whereas the other SAP is especially developed within the framework of the LORCENIS project by the company ChemStream, with the aim to mitigate autogenous shrinkage and induce self-healing of cracks. The SAPs from ChemStream were based on a copolymerization of sodium vinyl sulfonate (SVS) with 2-acryloylamino-2-methyl-propane-1-sulfonate (NaAMPS) and contained 1.0 mol% N,N'-methylenebisacrylamide (MBA) with respect to the monomer as cross-linker. The commercial SAP from BASF was based on poly(acrylamide-co-acrylic acid). In case SAPs were used, an additional fixed amount of water was added to mitigate autogenous shrinkage. The amount of SAPs used was determined based on their swelling capacity in cement filtrate and in order to obtain the same workability as the reference mixture. The amount of SAPs needed was in the range of 0.2-0.26 m% of the cement weight. To see whether the size of the SAPs plays a role in the efficiency of mitigating autogenous shrinkage, two average particle sizes, namely 40 and 100 µm, were tested. With the used amount of SAPs, a reduction or even complete counteraction of autogenous shrinkage was observed for the cement pastes.

Keywords: Superabsorbent polymers (SAPs), autogenous shrinkage, corrugated tubes, internal curing

1. Introduction
Ultra-high performance concrete (UHPC) is prone to autogenous shrinkage due to the low W/C-ratio (0.35 or lower) and as a result, the formation of cracks is inevitable. Due to a lack of free water the internal relative humidity (RH) will drop, resulting in self-desiccation when no external water source is present (RH < 100%) [1]. This may result in micro- and macro cracks which impair the strength, durability and aesthetics. Next to this, these cracks can create preferential pathways for water and gases, possibly containing harmful substances. These substances could induce steel corrosion, frost attack, chemical attack and internal expansive reactions resulting in a decreased

durability and structural integrity of the concrete structure [1]. Shrinkage of cementitious materials is divided in two stages: early age and later age shrinkage. Early age shrinkage, i.e. during the first 24 hours after mixing, is of great importance since at that age, the material has not yet gained substantial strength against crack formation. This results in micro-cracks which can widen over time due to later age shrinkage, i.e. beyond 24 hours after mixing [2], [3]. Autogenous shrinkage is a type of shrinkage which could have a negative effect on the cementitious material at early age [4]. Therefore, mitigating this type of shrinkage is of great importance. Internal curing can be applied to mitigate autogenous shrinkage. The basis of this method is the release of water in the cementitious matrix during cement hydration when the RH starts to drop and self-desiccation initiates. Superabsorbent polymers (SAPs) can be used as internal curing agents. Superabsorbent polymers are able to absorb up to 500 times their own weight in aqueous solutions, resulting in a swollen hydrogel. They are able to hold the liquid in their polymer network without dissolving [1].
In this paper, the effectiveness of different types and sizes of SAPs in mitigating autogenous shrinkage in cement paste is investigated.

2. Materials and methods

In this paper, two different SAPs were tested to investigate their influence on the mitigation of shrinkage: one SAP produced by the company CHEMSTREAM (abbreviated as CS) and one commercially available SAP from the company BASF. The SAPs from ChemStream were based on a copolymerization of sodium vinyl sulfonate (SVS) with 2-acryloylamino-2-methyl-propane-1-sulfonate (NaAMPS) and contained 1.0 mol% N,N'-methylenebisacrylamide (MBA) with respect to the monomer as cross-linker. The commercial SAP from BASF was based on poly(acrylamide-co-acrylic acid), but no information on the amount nor type of the used cross-linker is available. The SAPs from ChemStream were ground with a centrifugal mill to mean particle sizes d_{50} of 40 and 100 μm (indicated in the code). The cement paste consisted of CEM I 52.5N (Holcim), superplasticizer Glenium 51 (35% active material) from BASF with a dosage of 0.42 m% (compared to cement) and one of the two types of SAPs. A W/C ratio of 0.3 was used. In case SAPs were used, an additional fixed amount of water based on literature (W/C = 0.054) [5] was added to mitigate autogenous shrinkage. The amount of SAPs used was determined based on their swelling capacity in cement filtrate as a starting value, which was adapted to obtain the same workability as for the reference mixture (i.e. 30 cm flow after 10 minutes). The final composition of the cement pastes is shown in Table 1. It can be seen that for the SAPs from ChemStream the final amount of SAPs is the same for both particle sizes (40 and 100 μm). For the commercial SAPs from BASF a smaller amount is needed, as their swelling capacity is somewhat higher, as will be discussed in the results section.

Table 1: Overview of the final composition of the various cement pastes.

	REF 0.3	CS_05_40 and 100	BASF_100
CEM I 52.5 N	750 g	750 g	750 g
Water	225 g	225 g	225 g
Extra water	-	40.5 g (W/C 0.054)	40.5 g (W/C 0.054)
Glenium 51	0.42 m% cement	0.42 m% cement	0.42 m% cement
SAP	-	1.93 g (0.257 m% cement)	1.5 g (0.2 m% cement)

The flow of each type of cement paste was measured 10 minutes after water contact (to allow the SAPs to swell completely) on a spread flow table, according to the standard NBN EN 1015-3. The value of two mutually perpendicular diameters of the mortar spread was measured to the nearest 10 mm. The average of these two diameters is called the flow.
The swelling capacity of the SAPs in cement filtrate was determined by the filtration method described in the RILEM TC-RSC recommendation [6]. The cement filtrate was prepared by mixing 10 g of CEM I 52.5N and 100 ml of demi-water for 24 h. Afterwards, the slurry was filtered to remove the cement particles and the collected solution was used in the experiments. The measurements were performed in triplicate at different time intervals , namely 10 min, 1 h, and 24 h after contact with the liquid. The amount of fluid that can be absorbed by 1 g of SAPs can be calculated by Formula 1:

$$\text{Swelling ratio [g fluid/g unpurified SAP]} = \frac{w_{\text{fluid added}} - w_{\text{fluid not absorbed}}}{w_{\text{dry SAP}}} \quad (1)$$

with

$w_{\text{fluid added}}$ [g]: the amount of fluid before filtration;
$w_{\text{fluid not absorbed}}$ [g]: the amount of fluid that was not absorbed by the SAPs;
$w_{\text{dry SAP}}$ [g]: the amount of dry, unpurified SAPs.

The autogenous shrinkage was monitored according to the guidelines in ASTM C 1689-09. A flexible corrugated mould and a dilatometer, namely an automatic Linear Variable Differential Transducer (LVDT) with a range of 5 mm and a accuracy of 5 µm, were the basis of this test. The shape of the mould allows the sample to shrink or expand freely without restraint during hardening. Above that, the mould avoids moisture loss as much as possible. From the measurements, the autogenous strain can be calculated using Formula (2). The measurements were started at the time of final setting. This property was determined by the Vicat needle test using an automatic Vicat apparatus following the recommendations in NBN EN 196-3.

$$\varepsilon_{\text{autogenous}} = \frac{L(t)-L(t_{fs})}{L(t_{fs})}10^6 = \frac{l(t)-l(t_{fs})}{L(t_{fs})}10^6 \quad (2)$$

With

$\varepsilon_{\text{autogenous}}$ [µm/m]: the autogenous strain at time t;
$L(t_{fs})$ [mm]: the length of the specimen at final setting;
L(t) [mm]: the length of the specimen at time t after final setting;
$l(t_{fs})$ [mm]: the LVDT reading at final setting;
l(t) [mm]: the LVDT reading at time t after final setting.

3. Results and discussion

Table 2 shows the results from the filtration tests of the tested SAPs over time (10 min, 1 and 24 h) in cement filtrate. It can be seen that the CS_05 SAPs have a somewhat lower swelling capacity compared to the commercial SAP from BASF. It can be observed that most of the swelling of CS_05 occurred within the first 10 minutes. The liquid uptake increased only slightly after 1 and 24 h. However, the swelling kinetics of the commercial SAP (BASF) were different. There was an increase in swelling up to 28 g/g during the first hour, but after 24 h the swelling ratio decreased to approximately 22 g/g. This could indicate that the BASF hydrogel is degrading due to the high pH of the liquid cement solution. Results have also shown that the SAP particle size (d_{50} 40 or 100 µm) does not have a significant influence on the swelling ratio.

The determination of the amount of SAP needed to absorb the additional amount of water (W/C = 0.054) added to the cement pastes to mitigate autogenous shrinkage was based on equal workability in order to reduce the impact of the SAPs on the mechanical properties since in this way the amount of extra water is completely absorbed by the SAPs. The workability of the fresh cement pastes was measured by the flow test and the starting value of this process was taken equal to the swelling capacity of the SAPs in cement filtrate solution after 10 min resulting from the filtration test. In Table 2 also the additional amount of water based on the flow test for equal workability for the different cement pastes is shown.

Table 2: Additional amount of water based on the filtration test and the workability.

[g/g SAP]	Based on filtration test			Based on workability
	After 10 min	After 1 hour	After 24 h	Slumpflow 30 ± 2 cm after 10 min
CS_05_100	21.0 ± 1.4	22.1 ± 0.5	22.2 ± 1.3	21
CS_05_40	18.7 ± 1.4	19.6 ± 0.6	21.5 ± 2.2	21
BASF_100	26.4 ± 1.7	28.1 ± 0.6	22.3 ± 2.3	27

As can be seen, the extra amount of water after 10 minutes from the filtration test and the water based on the same workability is more or less the same. In the next experiments described within this paper, the amount of SAPs is based on the results from the flow tests, meaning 21 g/g SAP for CS_05 (for d_{50} 40 and 100 µm) and 27 g/g SAP for the commercial SAP from BASF.

The time of final setting of the reference cement paste and the cement pastes containing the SAP particles is shown in Table 3. The final setting times are slightly higher for the mixtures with SAPs. No differences in the setting times can be found when comparing the different SAPs. Moreover, the particle size of the SAPs did not show any influence on this property.

Table 3: Final setting time for the different cement pastes with automated Vicat.

	Setting time [hours]
REF 0.30	9.25
CS_05_100	12.75
CS_05_40	12.75
BASF_100	11.75

The evolution of the average of three corrugated tubes from the autogenous shrinkage test as a function of time for the different cement pastes over 5 days is shown in Figure 1. The negative values correspond with shrinkage while the positive values are related with expansion, compared to the initial length of the sample at final setting. The starting point of the strain-time curves is the time of final setting determined by the Vicat needle test from Table 3.

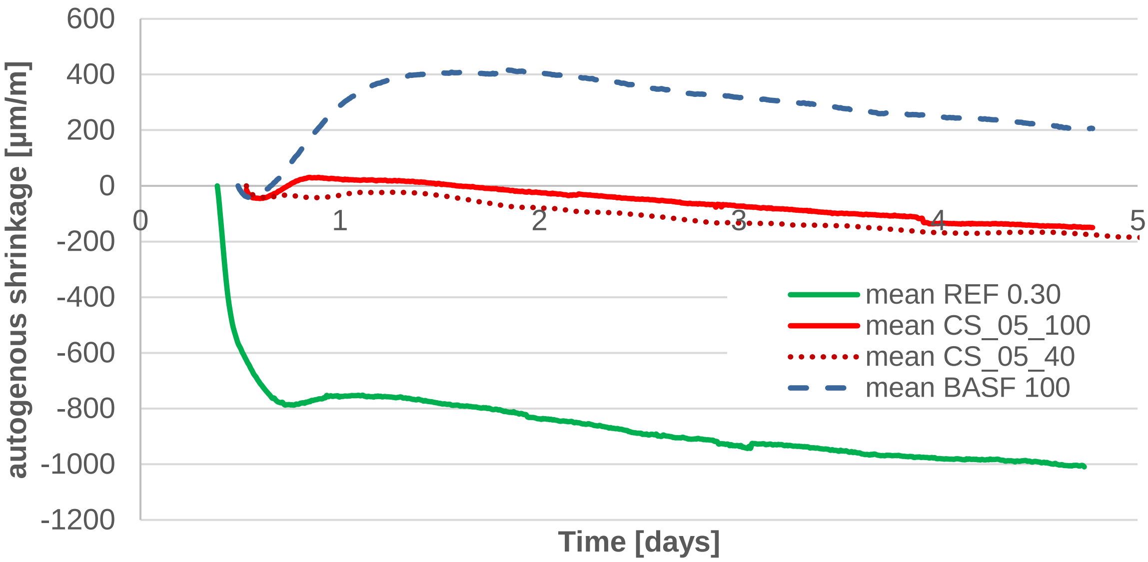

Figure 1: Average autogenous strain curve as a function of time for the various cement paste mixtures.

As can be seen, the curves consist of two stages, i.e. an acceleration and a deceleration period. The former starts immediately after the point of final setting and it is characterized by a fast development of shrinkage for the reference mixture due to autogenous shrinkage caused by the consumption of water during the hydration reaction.

The results showed that the addition of the SAPs led to a reduction of the autogenous shrinkage: the REF 0.3 has an autogenous shrinkage of 1000 µm/m after 5 days, whereas the cement paste containing ChemStream SAPs has a shrinkage of 200 µm/m at the same age. The mixture containing the commercial SAPs from BASF even shows an expansion of 200 µm/m after 5 days. However, it can be seen that the curve of this sample has not reached a steady state after 5 days and it is possible that overall shrinkage will occur at later age.

Since the SAPs from ChemStream were not able to completely mitigate autogenous shrinkage with the amount of SAPs added, future research will focus on finding the optimal amount of SAPs to completely mitigate autogenous shrinkage without compromising the compressive strength too much.

4. Conclusion

A reduction or even complete counteraction of autogenous shrinkage after 5 days is present for the cement pastes containing SAPs. A higher swelling capacity (BASF SAP) results in a higher reduction of the autogenous shrinkage. For this commercial SAP, expansion occurs during the first five days, but it is possible that overall shrinkage will occur at later age. Although the ChemStream SAPs were not able to completely mitigate autogenous shrinkage, promising results were obtained and it will be useful to further examine the behavior of cementitious materials containing the ChemStream

SAPs. The benefit of using ‘’in-house’’ developed SAPs (as the ones of ChemStream) compared to the use of commercially available SAPs is that the former offers the possibility of fine-tuning their properties in order to achieve a better or a desired performance. By for example varying the cross-linking degree of the ChemStream SAPs (and thus their swelling capacity), complete mitigation of autogenous shrinkage might be possible, and they may offer additional benefits for self-healing of cracks in concrete elements.

Acknowledgements
These results are part of a project that has received partial funding from the European Union's Horizon 2020 research and innovation program under grant agreement Nº685445 – LORCENIS and partial funding from the Research Foundation Flanders (FWO Vlaanderen) under project No.G.0A28.16.

References
[1] D. Snoeck, O.M. Jensen, N. De Belie, The influence of superabsorbent polymers on the autogenous shrinkage properties of cement pastes with supplementary cementitious materials, Cem. Concr. Res. 74 (2015) 59–67. doi:10.1016/j.cemconres.2015.03.020.
[2] E.E. Holt, Early age autogenous shrinkage of concrete, VTT Publ. (2001) 2–184.
[3] L. Wu, N. Farzadnia, C. Shi, Z. Zhang, H. Wang, Autogenous shrinkage of high performance concrete: A review, Constr. Build. Mater. 149 (2017). doi:10.1016/j.conbuildmat.2017.05.064.
[4] L. Barcelo, M. Moranville, B. Clavaud, Autogenous shrinkage of concrete : a balance between autogenous swelling and self-desiccation, Cem. Concr. Res. 35 (2005) 177–183. doi:10.1016/j.cemconres.2004.05.050.
[5] O.M. Jensen, P.F. Hansen, Water-entrained cement-based materials I. Principles and theoretical background, Cem. Concr. Res. 31 (2001) 647–654. doi:10.1016/S0008-8846(02)00737-8.
[6] D. Snoeck, C. Schröfl, V. Mechtcherine, Recommendation of RILEM TC 260-RSC : testing sorption by superabsorbent polymers (SAP) prior to implementation in cement-based materials, 8 (2018). doi:10.1617/s11527-018-1242-8.