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Reakcje azotanu wapnia z superplastyfikatorami

INTERACTION OF CALCIUM NITRATE AND SUPER-PLASTICIZERS

Streszczenie

Obecne wymagania w odniesieniu do betonu koncentrują się głównie na jego roli w procesie zrównoważonego rozwoju i poprawie urabialności. Sposobem na osiągniecie tych celów jest stosowanie domieszek chemicznych do betonu. Domieszki są stosowane, aby przyspieszyć reakcje zachodzące w mieszance betonowej, zmniejszyć ilość wody i cementu - ogólnie obniżyć nakłady związane z jego wyprodukowaniem. Typową domieszką jest azotan wapnia – od wielu lat dobrze znany i zbadany pod tym względem środek chemiczny. Inną grupą, dobrze przebadanych domieszek uplastyczniających i redukujących ilość wody w mieszance betonowej są polikarboksylany. Jednakże, nie ma zbyt wielu badań wzajemnych reakcji zachodzących pomiędzy tymi dwoma domieszkami do betonu. Celem artykułu jest zwięzła prezentacja tego zagadnienia.

Abstract

Today's requirements for concrete are focusing on increase of sustainability and workability. A way to address those aspects is the used of admixtures. Admixtures are used to accelerate the concrete reactions, to reduce water and cement amount needed and overall to reduce effort to actually produce the concrete. A typical admixture used to accelerate concrete is calcium nitrate which has been investigated over many years. A typical group of highly water reducing and plasticizing admixtures are polycarboxylate ether, which have been investigated plenty as well. However there has hardly been an investigation on their interaction. In this study an attempt is made to describe interactions of calcium nitrate and polycarboxylate ether briefly.

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1. Introduction

A key to modern concrete, especially self-compacting concrete, is the use of water reducers and super plasticizers, as they allow minimizing cement content and improving workability. Polycarboxylate ether (PCE) based products have gained a prominent role among the super-plasticizers. The typical climate environment of a super plasticizer modified concrete is mild temperature. However PCEs are not the only admixtures used. In particular accelerators can be of interest to shorten setting time and also reduce curing temperature level.

A major improvement regarding sustainability comes from today's cement types. Those incorporate increasingly amounts of supplementary cementitious materials (SCMs). SCMs like fly ash, lime stone or ground granulated blast furnace slag are helpful to reduce the CO_2 footprint, improve durability and reduce material cost. Consequently a variety of blended cements from CEM II/A to CEM III/B are available and in use in Europe and corresponding mixes are also available when ASTM standard applies. The downside of SCM is the overall reduced reactivity, based on the fact that those materials in itself are usually not reactive. The SCM need to be activated in a secondary reaction and this is generally achieved by the rise of pH value due to the cement hydration process. Thus the wanted effect of reduction of CO_2 footprint comes usually at the price of reduced performance. Admixtures can help to regain production performance and maintain the environmental benefit.

Calcium Nitrate ($Ca(NO_3)_2$, CN) is a well-known and common setting accelerator for concrete. Especially its use for Portland and blended Portland cements has been investigated during recent years. The use of a setting accelerator like calcium nitrate enables to cast concrete in a wide temperature range, especially in cold environments.

So far little has been reported about the interaction of calcium nitrate and super- plasticizer. There is however an indication in literature about a synergy in between calcium nitrates and some PCEs, especially at cold climate conditions.

This study summarizes the outcome of several projects addressing this interaction. In total the impact of calcium nitrate on 9 commercial PCEs has been evaluated based on changes in setting behavior and workability. In order to make the results useful for practical users the names of the PCEs are stated. The main point is to indicate the characteristics of the interactions of the PCEs. And keeping the PCEs anonymously would make the outcome less useful for practical use.

2. Methods and materials

The target of this investigation is to elaborate the interaction of CN and various commercial PCEs with the aim to give leads on good combinations. And beyond that it should help to prevent to make unsatisfying choices of combination.

Three projects have been conducted during the year 2016 on Yara's behalf which focus on the interaction of calcium nitrate and a selection of commercial PCEs, as indicated in Table 1.

Table 1. Overview over the studies

Institute	System	Investigation parameters
SINTEF (Norway)	Cement paste and mortar	Rheology, compressive strength, setting time
TUM (Germany)	Cement paste and mortar	Rheology, compressive strength, setting time
UCLA (USA)	Micro glass balls	Rheology, setting time

Only one report has been finalized at the time of preparing this paper is [1].

Within [1] three commercial PCEs (Mapei Dynamon SXN, Mapei Dynamon SRN and BASF Glenium Sky 615; all at 0,15% bwoc. dosage) have been tested in combination with CN (Yara NitCal 50; 1% bwoc. CN respectively 2% bwoc. NitCal 50). All three PCEs are designed for slightly different purpose and therefore it was interesting to see how they interact with CN.

The rheology has been evaluated by slump test and by rheometer test (Physica MCR 300 rheometer, Anton Paar, Graz/Austria), setting time has been measured with a Vicat apparatus and compressive strength has been measured on mortar cubes. The compositions of the paste and mortars investigated in the study at SINTEF are given in table 2 and 3.

The other two institutes used similar setups. The results will be presented during the conference.

Table 2. Recipe for paste preparation (according to SINTEF, 2016)

No.	Sample name	w/c	Water [g]	Cement [g]	PCE Type	PCE [g]	CN [g]
1	Reference (no admix-ture)	0.45	180.00	400	-	-	0
2	1% CN	0.45	176.00	400	-	-	8
3	0.15% Glen	0.45	177.54	400	Glen	3.06	0
4	0.15% Glen + 1%CN	0.45	173.54	400	Glen	3.06	8
5	0.15% SXN	0.45	177.36	400	SXN	3.24	0
6	0.15% SXN + 1%CN	0.45	173.36	400	SXN	3.24	8
7	0.15% SRN	0.45	177.52	400	SRN	3.08	0
8	0.15% SRN + 1%CN	0.45	173.52	400	SRN	3.08	8

Table 3. Recipe for mortar preparation (according to SINTEF, 2016)

No.	Sample name	w/c	Water [g]	Sand [g]	Cement [g]	PCE Type	PCE [g]	CN [g]
1	Reference	0.45	202.50	1350	450	-	-	0
2	1% CN	0.45	198.00	1350	450	-	-	9
3	0.15% Glen	0.45	199.73	1350	450	Glen	3.44	0
4	0.15% Glen + 1%CN	0.45	195.23	1350	450	Glen	3.44	9
5	0.15% SXN	0.45	199.53	1350	450	SXN	3.65	0
6	0.15% SXN + 1%CN	0.45	195.03	1350	450	SXN	3.65	9
7	0.15% SRN	0.45	199.71	1350	450	SRN	3.46	0
8	0.15% SRN + 1%CN	0.45	195.21	1350	450	SRN	3.46	9

3. Results

The results are given in detail in the reports. In this paper only some examples are re-presented from study [1].

The SINTEF study [1] shows that the spread of both concretes with the Mapei PCEs (SXN and SRN) is increased whereas the mix with BASF PCE (GLEN) does not seem to benefit. In detail, the reference sample has a spread of approximately 120 mm, whereas all PCE treated samples have a spread of 200 mm. The CN addition gives an extra 20-30 mm of spread. The spread however does not increase for the reference when CN is added. The results by SINTEF are given in figure 1.

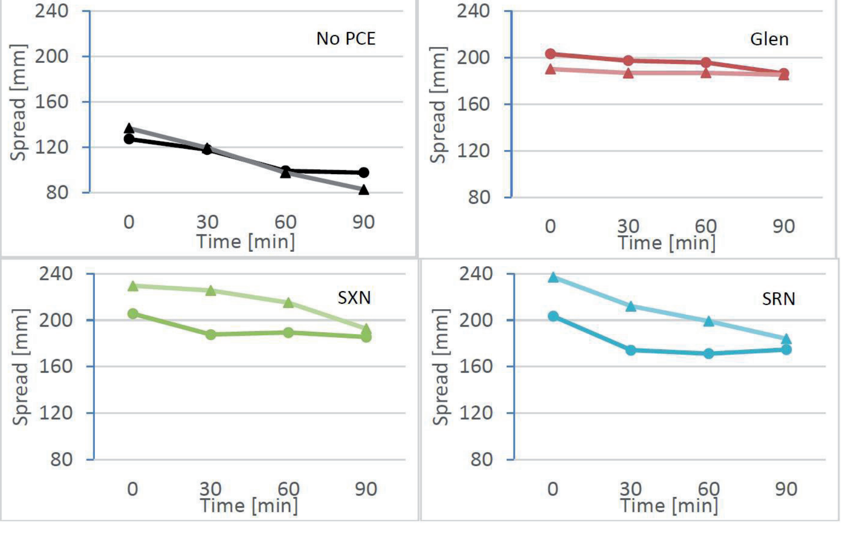


Figure 1: Spread of cement paste with and without 1%CN according to [1]; reference with PCE is marked with circles and mixture with PCE and CN is marked with triangles

The SINTEF study shows that the dynamic yield stress is reduced when combining CN and a PCE. The reference however does not show a significant change in dynamic yield stress due to CN addition. A similar result is obtained for the flow resistance, where the combined systems show the lower resistance combined to systems without CN. The results by SINTEF are given in figure 2.

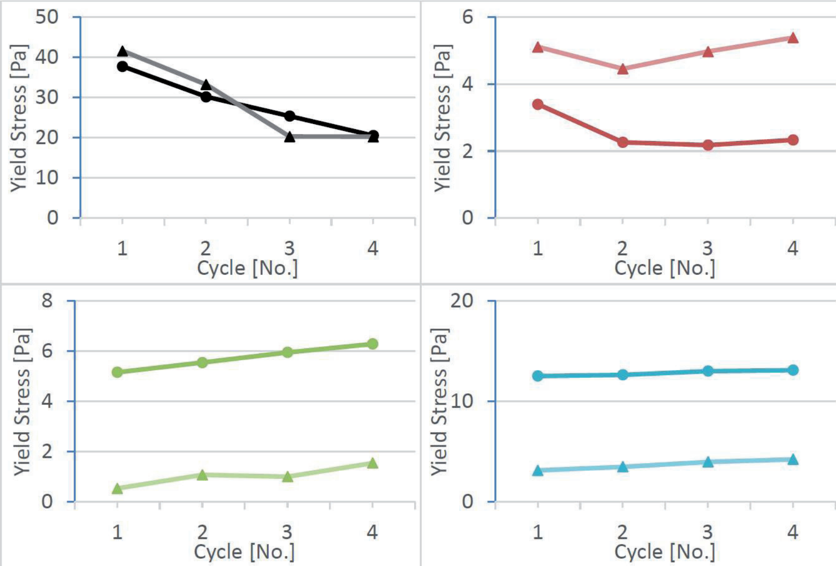
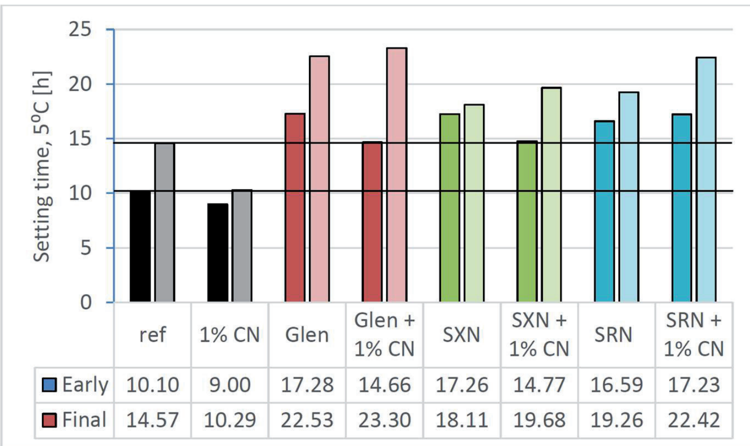


Figure 2: Yield stress of cement paste with and without 1%CN according to [1]; reference with PCE is marked with circles and mixture with PCE and CN is marked with triangles

The setting time is reduced for the BASF PCE (GLEN) as well as the Mapei SXN but not the SRN. And generally all PCE treated samples have a significantly longer setting time (several hours) compared to the reference. The results by SINTEF are given in figure 3.



	ref	1% CN	Glen	Glen + 1% CN	SXN	SXN + 1% CN	SRN	SRN + 1% CN
Early	10.10	9.00	17.28	14.66	17.26	14.77	16.59	17.23
Final	14.57	10.29	22.53	23.30	18.11	19.68	19.26	22.42

Figure 3: Setting time of pastes with and without 1%CN according to [1]

The compressive strength is increased by adding CN to all samples. It can be observed that the 1 day strength is generally lower when a PCE is used compared to the references. Differences however are only in the range of few MPa. The results by SINTEF are given in figure 4.

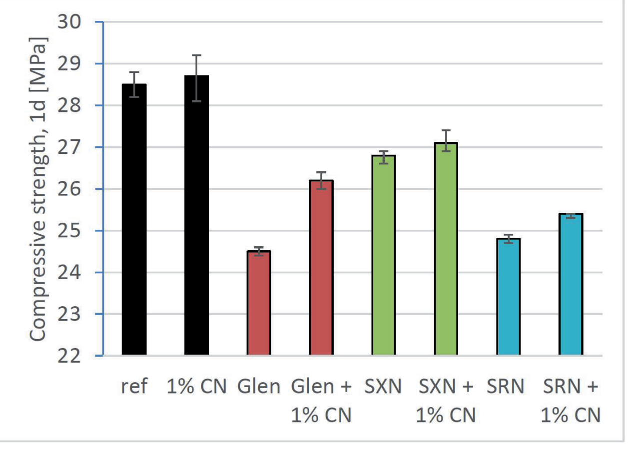


Figure 4: 1 day compressive strength of mortar samples with and without 1%CN according to [1]

4. Discussion

PCE based super plasticisers become more and more dominant in the global market. They are the cornerstone of modern concrete as they enable to reduce water demand and cement content of concrete as well as maintain long term concrete properties. In addition they are supposed to be not retarding and thus should not have a negative impact on the early age properties.

Traditionally PCEs have been a premium segment product with high prices. Therefore attempts have been made to mimic the performance by combining standard plasticizers, like Lignosulphonate, and an accelerator, for instance demonstrate by [2]. PCEs have become more affordable and today mixtures of CN and standard plasticizers are not as interesting any more.

Already the study [3] showed that CN and super plasticizers might have a synergy as well. Therefore there was a motivation to extend that approach.

CN is established as setting accelerators for ready mix concrete. It is used especially when a non-corrosive, non-hazardous accelerator is needed, that also can (unlike sodium nitrate) maintain long term compressive strength.

Studies like [4] and [5] described the use of CN as setting accelerator at different temperatures and in different regions. Also [6] documented setting time reduction. Overall CEM II/A-V and CEM III type cements seem to benefit, whereas CEM II/A-LL benefits to lesser degree.

Furthermore [7] found that CN reduces the drying shrinkage of concrete by early surface hydration and by that in addition reduces surface cracking.

When it comes to durability, various studies ([8], [9], [10]) documented the corrosion inhibitor effect. Additionally [11] investigated the increase of long term compressive strength. According to [12] there is also a positive effect on the freeze-thaw-resistance, when CN and an air entrainer are used in combination. The CN might by itself give benefits on the durability and enable to make more efficient use of the PCE.

The results of the first available study [1] (out of the three) indicate that combining CN and a PCE can have benefits, but this depends on the PCE type. Generally the rheology can be improved by combining these two admixtures and also the setting and compressive strength development appears to be improved. However it becomes obvious that 2 out of 3 PCEs seemed to benefit for each aspect. The two Mapei products SXN and SRN benefitted on the rheology but the BASF GLEN product did not. Regarding setting and strength only one of the Mapei products and the BASF product benefitted. The results also demonstrate that there is an interaction of CN and the PCEs, as some effects do not occur at the addition of CN only.

The results show the importance of evaluating the interaction of PCE and CN prior application. Determining the best combination might help to produce an even better concrete, with improved workability and long term properties.

Furthermore, the literature indicates that the dosage level of CN should be chosen with respect to the cement type. Together with the here presented findings this leads to the conclusion that future work needs to address the combined system of CN, PCE and cement type to define the best mixture for an economically beneficial and at the same time durable concrete.

5. Conclusion

The here presented information regarding the interaction of CN and PCE suggests that both admixture types interact. In general PCE seem to have a retarding effect as well as a reducing the compressive strength. Both effects can be counteracted with CN as an accelerator. All three selected PCEs behaved differently. Therefore pre testing appears to be necessary to evaluate the suitable candidate. This might be valid for each PCE and not only the ones tested here. More results will be obtained and presented once the further two studies are accomplished.

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