Study on Calcium Nitrate impact on Carbonation of Concrete

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Abstract

Calcium Nitrate is a well-established concrete admixture since the 1980s and mostly used as setting accelerator. Additional effects have been documented such as compressive strength enhancement and several studies indicate reinforcement corrosion mitigation. Due to the impact on the distribution of the porosity it was suspected that Calcium Nitrate might influence the carbonation process, too. Accelerated tests and non-accelerated tests have been conducted to study the impact on several cement types. The results indicate that the carbonation depth of a concrete can be reduced by up to 40% depending on the cement type and test method.

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I. INTRODUCTION

Technical Calcium Nitrate (CN) is a well-established concrete admixture known since the 1980s. [1] described the effect of setting acceleration by CN among the first. Today CN is used as setting accelerator in line with for instance industry standard requirements [2, 3].

Additional side effects have been documented. Several studies [4, 5, 6] indicate reinforcement corrosion mitigation (for instance, where nitrate and nitrite show similar performance. Additionally compressive strength enhancement was identified [7], and the reason was suspected to be a modification in the porosity. The same mechanism seems to explain a synergy of calcium nitrate and an air entrainer regarding freeze-thaw-resistance [8].

The modification of the porosity might have additional benefits. For instance it seemed reasonable to evaluate the impact on the carbonation process. Carbonation is the result of a transport process of carbon dioxide (CO_2) as gas and aqueous acid and obviously should be affected by the porosity characteristics.

Accelerated tests (elevated CO_2 exposure, 56 days) and non-accelerated tests (182 days) have been conducted to study the impact of calcium nitrate on concrete made with different cement types.

II. Methods and Materials

The carbonation has been measured according to two methods:

- Accelerated tests according to [9]: Exposure of samples from day 28 on in 2% CO_2 atmosphere. Measurement of carbonation depth after 56 days.
- Not-Accelerated tests: Exposure of samples from day 7 on in the controlled atmosphere (20°C / 65% relative humidity) with ordinary CO_2 exposure. Measurement of carbonation depth after 182 days.

Three types of cement have been used: CEM I 42.5 R (Schwenk, Germany), CEM II/A-LL 42.5 R (Schwenk, Germany) and CEM II/A-V 42.5 R (Norcem, Norway). The cement amount was chosen to be 350 kg/m3 concrete and the w/c ratio has been chosen to be 0.5 in order to obtain an ordinary concrete.

As admixture a 50% solution of calcium nitrate technical grade has been used (Yara, Norway). The calcium nitrate dosage was chosen in different steps from 0 M.-% to 4 M.-% by weight of cement (bwoc.).

For all mixtures two beam shaped samples (10/10/50 cm) and six cube shaped samples (15/15/15 cm) have been prepared. The samples have been cured for 7 days under water and further until testing at 20°C / 65% relative humidity.

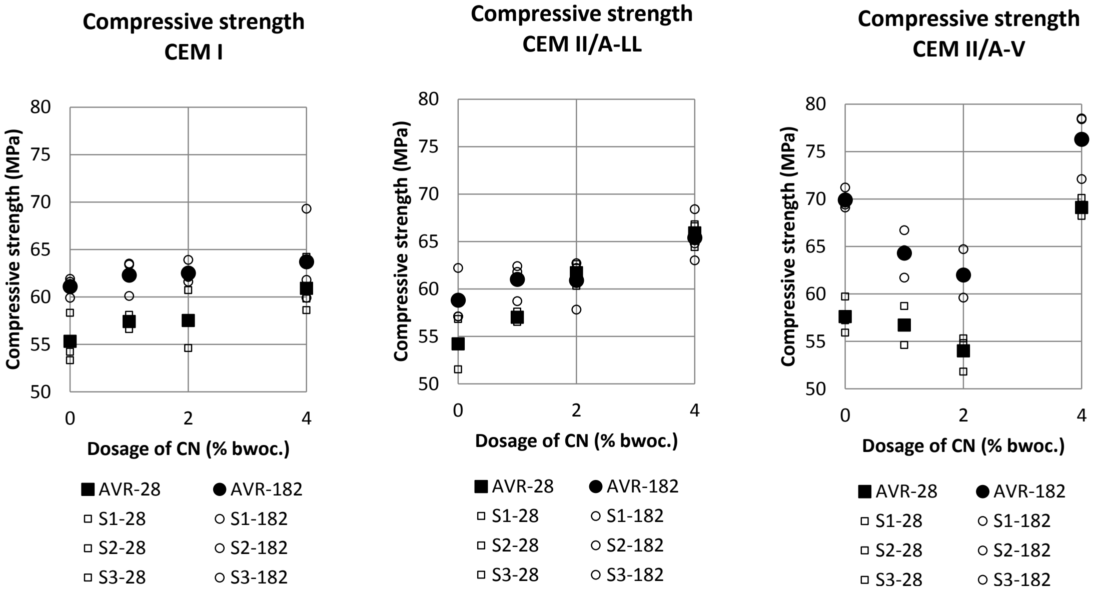
Compressive strength was measured according to [10] after 28 days and 182 days. For these tests three parallel samples were used.

III. RESULTS

A. Compressive strength

The results of the compressive strength tests are given in [Figure 1].

The compressive strength increases with linear dependency on the CN addition for CEM I. At 4% CN dosage the 28 day strength is about the same as the 182 day strength without



Compressive strength CEM I

Compressive strength CEM II/A-LL

Compressive strength CEM II/A-V

Figure 1: Compressive strength after 28 days and 182 days of each sample (S1-S3) and the average of the samples for the three cement types

CN dosage. Generally the CN addition increases the long term strength of the CEM I containing concrete.

The compressive strength increases with linear dependency on the CN addition for CEM II/A-LL. At 2% CN dosage the 28 day strength is higher than the 182 day strength without CN dosage. At 4% CN dosage the maximum strength seems to be reached after 28 days, as the 182 day results are at least not higher. Generally the CN addition increases the long term strength of the CEM II/A-LL containing concrete.

For CEM II/A-V the dependency was clearly non-linear. Low dosage has led to a slight reduction in strength whereas the high dosage of 4% CN bwoc. has led to a strength gain. This pattern seems to be valid for both 28 and 182 days strength.

B. Carbonation depth

The carbonation depth results are plotted in [Figure 2].

There is a correlation in between dosage level and carbonation in accelerated tests for CEM I and CEM II/A-V. In standard tests there are however only minor changes noticeable.

The measurement results for the CEM II/A-LL do not provide a conclusive trend. There the standard method suggests potentially an increase in carbonation whereas the accelerated method does not.

IV. DISCUSSION

The compressive strength tests are in line with literature on the topic. For instance [11]showed similar patterns. There CEM I, CEM III, CEM IV and CEM II/A-LL seemed to benefit regarding compressive strength and setting time. The results presented here confirm the finding by [12], that fly ash cements responds with both early setting and increased compressive strength only at the high dosage level of 4% bwoc., but not at a 2% level. However it can be concluded that CN has mostly a positive impact on compressive strength development.

The novel part of this study was the investigation of the impact of CN on carbonation itself.

Carbonation is a concrete deterioration mechanism based on CO_2 availability and high level of humidity at the same time. The CO_2 concentration in ambient air is commonly about 350 ppm. In case of sufficient humidity a concrete in an outdoor environment is therefore generally at risk. And in some applications the risk might be even higher: For instance in greenhouse farming the CO_2 concentration can be elevated up to 1.300 ppm to obtain better yields [13]. Therefore a greenhouse environment with elevated humidity, temperature and three to four times the natural CO_2 concentration might be even more prone to carbonation.

Carbonation is primarily a migration process. CO_2 enters the concrete element through the voids and dissolves in the pore water. There carbon acid (H_2CO_3) is formed and accumulates over time. This leads to reduction of the pH value of the pore water. Eventually the pore water changes from alkaline to neutral or even acidic conditions. This acidic frontier moves through the concrete and will reach the reinforcement. At that stage the embedded reinforcement steel stops self-passivation. The resulting corrosion will lead to failure of the reinforced concrete. More details about carbonation can be found for instance at [14].

Carbonation is a comparatively slow process. The migration

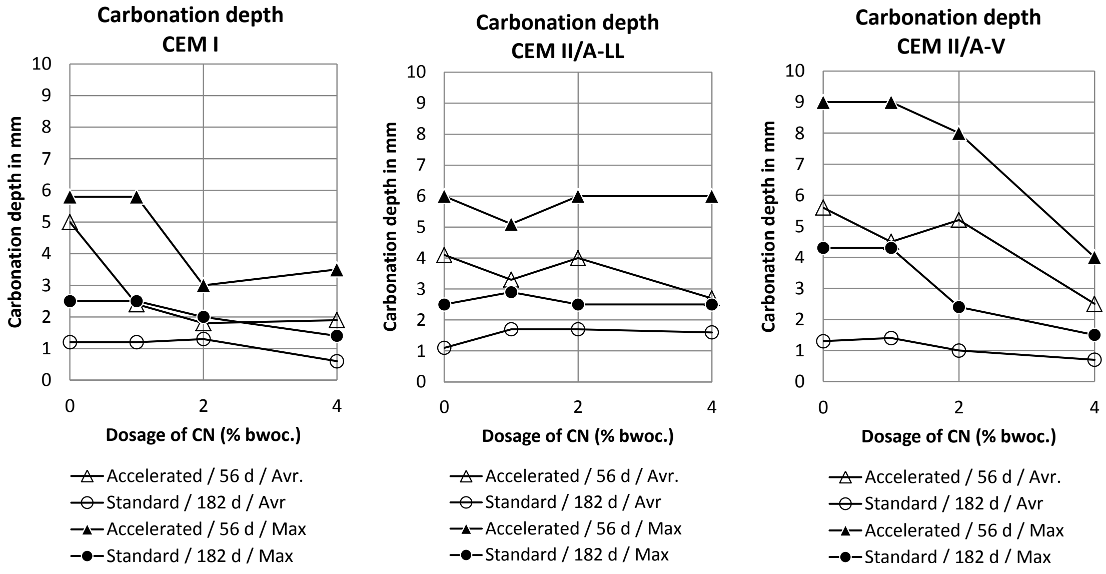


Figure 2: Carbonation depth for accelerated and standard method with average and maximum penetration depth for the three cement types

velocity of the acidic frontier can be assumed with 1 mm / year [15], but might also progress faster depending on the concrete quality and exposure class The traditional strategy to mitigate carbonation is to increase the specific or absolute resistance towards CO2 ingress by maximum limit for the w/c ratio, minimum limit of the cement content and an elevated minimum limit of concrete coverage. With growing expectations on durability those measures might be accompanied by chemical admixtures improving the carbonation resistance.

The change of carbonation depth due to CN addition is illustrated in [Figure 3].

The changes of the carbonation depth are evident for CEM I and CEM II/A-V. Especially the high dosage of 4% CN bwoc. seems to result in a reduction of the carbonation depth for the CEM I in the range of 40% to 60%. And a significant reduction was observed for 2% CN dosage as well. However at a dosage level of 1% CN bwoc. the effect is minor. For CEM II/A-V the dosage level needs to be higher compared to CEM I in order to obtain a comparable reduction in carbonation. Again for 1% CN dosage the effect is minor.

For CEM II/A-LL the test gives inconclusive results. Depending on the measurement method and dosage level either a slight increase or decrease of carbonation rates can be found. The explanation cannot be given so far. The samples prepared with CEM I and CEM II/A-LL (both from the same producer) show similar carbonation depth for the reference samples (0% CN dosage) independent of the test method. This seems to be in line with literature [16] which indicates that limestone may have no or a reducing effect on carbonation. However, in opposite to the CEM I containing samples there is no significant effect of CN on carbonation of the CEM II/A-LL containing samples.

Thus the presented results give evidence that the proposed modification of the porosity can have an impact of the carbonation of at least some types of concretes. The CEM I seems to benefit regarding carbonation resistance and strength development. The CEM II/A-LL seems to benefit from strength gain but not carbonation mitigation. The CEM II/A-V seems to benefit from carbonation mitigation but shows actually some strength loss at medium dosage levels.

According to previously mentioned literature [4, 5, 6] the recommended dosage level to obtain chloride corrosion inhibition is about 4% bwoc.. This study found a dosage level of 4% bwoc. as most effective for carbonation mitigation, too.

The study indicates that there is an impact of CN on carbonation. In order to gain deeper understanding more research may be done, for instance applying methods like CDF-test, porosity measurement, indentation or chloride ingress.

V. CONCLUSION

The here presented results indicate that CN may have an impact on carbonation process. The results indicate in particular that the carbonation depth of a concrete prepared with CEM I or CEM II/A-V (fly ash) can be reduced by up to 40% in average. This might be explained by the porosity change found in previous studies. However concretes produced with CEM II/A-LL (lime stone) do not benefit. The reason is for this is at the moment not known.

Overall it might be concluded that the mostly positive

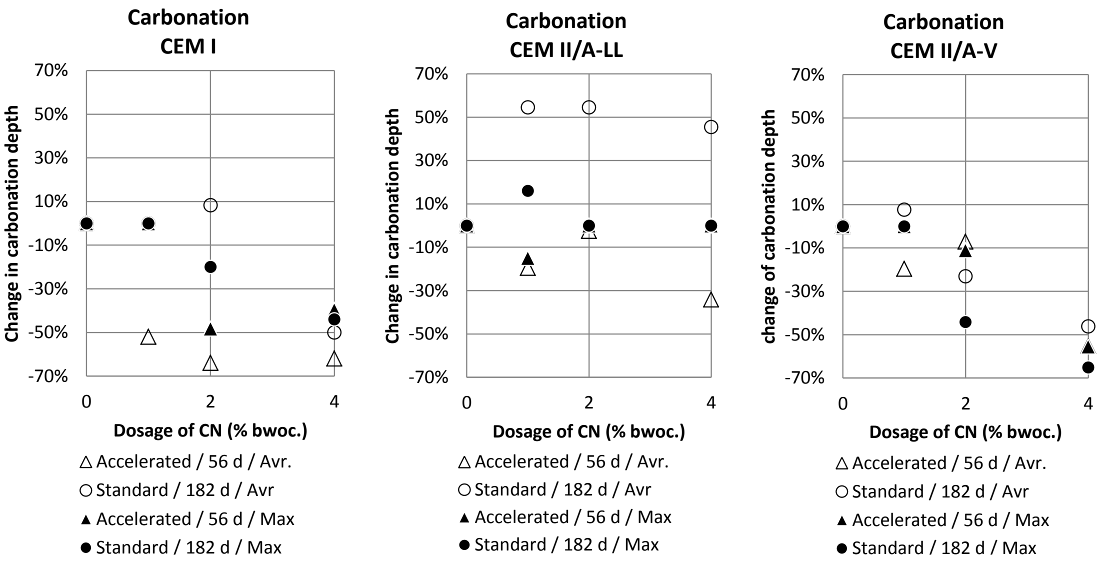


Figure 3: Change of carbonation depth for accelerated and standard method with average and maximum penetration depth for the three cement types

impact on carbonation is a beneficial side effect of using CN as setting accelerator. This effect seems to be significant above dosage levels of 2% CN bwoc.. Generally the compressive strength does not seem to be compromised, and in most cases might be increased.

According to literature the recommended dosage level is about 4% bwoc. to obtain chloride corrosion inhibition. This study found that at the same dosage level also the carbonation mitigation is significant.

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