

Performance of Calcium Nitrate as Accelerator for Cement Blended with Blast Furnace Slag

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Synopsis: The objective is to elucidate the effect of calcium nitrate CN on cement replaced with 50% blastfurnace slag (ggbS). The influence of 2 and 4% CN accelerator on hydration development of these binders were investigated by isothermal calorimetry, X-ray diffraction and thermogravimetry. The strength development of mortar with two different ggbS blended binders cured at 20°C was followed and the influence of CN discussed. Concrete with 50% of a third ggbS, 0, 2 and 4% CN and w/c = 0.46 was cured at +5°C and compressive strength development measured. CN led to lower mortar strength at 1 day at 20°C, but higher strength from 3 days onwards. Mortar with two different ggbS achieved the same strength at 7 and 28 days when added 4% CN. However, CN increased the 1-day strength of concrete cured at +5°C. Since ggbS is accelerated by high pH, the somewhat lower 1-day strength in mixes with CN is probably caused by the immediate precipitation of hydroxyl ions by calcium to portlandite leading to a lowering of the pH. CN led to more ettringite formation and AFm phases at 1-day sealed curing and the calcium hydroxide content was reduced. Reasons for calcium hydroxide reduction are discussed.

Keywords: Accelerator, blastfurnace slag, calcium nitrate, calcium hydroxide, compressive strength, ettringite, isothermal calorimetry, thermogravimetry, X-ray diffraction.

INTRODUCTION

The fastest way to make cement more sustainable [1] is to replace clinker with substantial amounts of a supplementary cementitious material (SCM) with less CO₂ emission. Ground, granulated blastfurnace slag (ggbs) as a by-product from iron production is such a SCM. Ggbs is a so called latent hydraulic SCM [2] that only need to be activated by high alkalinity from portland cement [3] or alkaline admixtures. Large clinker replacements result in low early strength in general and an accelerator is often needed to keep up construction productivity, in particular at lower temperatures (e.g. +5°C). An alternative is to use heated concrete or insulated formwork. Accelerators have been around for quite some time [4, 5], with calcium chloride being the best accelerator both shortening setting time and increasing strength. However, due to the risk of initiating steel corrosion, chloride containing accelerators has been restricted for steel reinforced concrete structures. Justnes showed already in 1995 [6] that calcium nitrate worked well as set accelerator for portland cement at low temperatures. Later the mechanism of calcium nitrate was studied [7], which also was recently confirmed [8]. Calcium nitrate is not a hardening accelerator increasing the 1-day strength at 20°C, but it has been shown that it can increase the longer-term strength [9]. Increased strength at very early age (< 1 day) is only a side-effect of set acceleration by the cement starting hydration earlier than without set accelerator. Since addition of calcium salts should lower the initial pH in portland cement by precipitating more soluble hydroxides to calcium hydroxide, it was uncertain how calcium nitrate would benefit the performance of portland cement partly replaced by blastfurnace slags. Thus, the objective of this paper is to study the effect of calcium nitrate on cement/ggbs blends.

EXPERIMENTAL

Materials

The cements OPC1 and OPC2 were of the type CEM I according to NS-EN 197-1 and produced by Norcem, Brevik, Norway. The granulated, ground blastfurnace slags (ggbs) were delivered by Yara but originating from O'Brien (S1) in Ireland, LKAB (S2) in Sweden and Merit (S3) in Sweden. The element compositions of the cement and the slags are given in Table 1. The fineness (Blaine) of OPC1 and OPC2 was 359 and 388 m²/kg, respectively. A simple Bogue calculation based on CaO, SiO₂, Al₂O₃ and Fe₂O₃ values in Table 1 yielded 64.6% C₃S, 10.8% C₂S, 1.8 %C₃A and 13.5% C₄AF for OPC1 and 60.5% C₃S, 14.9% C₂S, 5.8 %C₃A and 11.4% C₄AF for OPC2. The calcium nitrate (CN) was in the form of 50% solution without any foreign ions and is a product of Yara, Porsgrunn, Norway. The sand was norm sand for mortar testing (DIN EN 196-1). The water was de-ionized water.

Table 1 – Chemical composition of portland cement and blastfurnace slags according to suppliers.

Oxide	OPC1	OPC2	S1	S2	S3
CaO	62.00	63.21	42.0	39.6	31.8
SiO ₂	20.77	21.12	35.7	37.3	33.5
Al ₂ O ₃	3.51	4.60	8.33	13.0	13.0
MgO	1.97	1.71	6.47	9.0	15.2
TiO ₂	0.21	0.31	0.78	0.7	2.33
Na ₂ O	0.29	0.40	0.48	-	0.66
K ₂ O	0.43	0.35	0.59	-	-
Fe ₂ O ₃	4.46	3.77	0.77	0.6	-
FeO	-	-	-	-	0.52
MnO	-	-	-	0.5	0.33
SO ₃	2.59	3.39	-	0.23	-
S ²⁻	-	-	-	0.86	1.67
Cl ⁻	0.02	0.07	0.09	0.06	-

- Not analysed or reported by supplier.

Methods

Isothermal calorimetry — Isothermal calorimetry of cement pastes was performed with a TAM Air instrument set to 20°C. Mixing of the pastes was performed outside the calorimeter. Materials were weighed in directly into

plastic ampoules (2.5 g cement + 2.5 g slag). A solution was prepared with the aimed dosage of CN by weight of binder. A water to binder ratio of 0.45 was used. After injecting the correct amount of water with CN, the pastes were mixed with a Vortex SA6 mixer for 1 min at 4500 rpm. The recipes of the paste mixes are given in Table 2.

Table 2 – Paste mixes for isothermal calorimetry where ggbs represents all three slags: S1, S2 and S3.

ggbs – CN dosage	ggbs	CEM I	Water	2% CN	4% CN
ggbs - 0% CN	2.5 g	2.5 g	2.25 g		
ggbs - 2% CN	2.5 g	2.5 g		2.35 g	
ggbs - 4% CN	2.5 g	2.5 g			2.45 g

X-ray diffraction — Qualitative X-ray diffraction (XRD) was performed on a Bruker D8 Focus instrument equipped with a Lynx Eye detector and a standard copper (Cu-K α) X-Ray source. A 0.2 mm divergence slit was used, and measurements were taken from 5-60° 2 θ with a step size of 0.2° 2 θ and 0.8s time per step. Before analysis the hydration of the pastes was stopped after 1 day by double solvent exchange with iso-propanol and diethyl ether. The dried pastes were milled down by hand and prepared for XRD by front/side loading the powder into the sample holder. The same mixing procedure as for isothermal calorimetry was used.

Thermogravimetry — Thermogravimetric analysis (TGA) was performed with a Mettler Toledo TGA/SDTA 851. Samples were analysed with a heating rate of 10°C/min between 40 and 950°C. All measurements were performed in nitrogen atmosphere with a flow rate of 50 ml/min. Same samples as for XRD were used.

Strength development — The recipes for the mortars are listed in Table 3. Two sets of 3 prisms of dimensions 160x40x40 mm were made for each of the 6 mixes. Mortars were cured (up to 28 days) at 90% RH and 20°C and prisms demoulded after 1 day curing. The prism mass was noted after de-moulding to check for compaction errors or variations in air content. Flexural strength was measured in a 3-point bending test after 1- and 7-days curing for 3 parallels. Each test of flexural strength resulted in 6 end-pieces. These were used to test compressive strength on 40 mm cubes equivalent for 3 parallels after 1-, 3-, 7- and 28-days curing. CN is dosed as 50% solution to 2 and 4% dry CN of cement/slag mass, respectively, while inherent water is subtracted from the added water to obtain w/b = 0.45 for all mixes

The recipes for the concrete made with ggbs S3 and cured at +5°C are shown in Table 4. The super-plasticizer (SP) used for the concrete mixes was Mapei Dynamon SX-23 with 23% solids content. The aggregate was granite from Årdal, Norway. The concrete recipes resulted in w/(c+ggbs) = 0.46 and 0, 2 and 4% dry calcium nitrate (CN) of the sum of cement and ggbs. The concrete was mixed at +20°C and cast in 100 mm cubic steel that immediately after was partly submersed in water in a +5°C room.

Table 3 – Recipe for the mortar samples with w/b = 0.45 where ggbs represents blast furnace slags S1 and S2.

CEM I	ggbs	50% CN	Water	Norm sand
225 g	225 g	-	202.5 g	1350 g
225 g	225 g	18 g	193.5 g	1350 g
225 g	225 g	36 g	184.5 g	1350 g

Table 4 – Concrete recipes (kg/m³) with ggbs S3 resulting in w/b = 0.46.

Constituent	0% CN	2% CN	4% CN
CEM I	175.2	171.2	167.5
ggbs	175.2	171.2	167.5
Total water	161.2	157.7	154.4
Granite sand (0-8 mm)	1247.1	1253.5	1253.5
Granite gravel (8-16 mm)	622.9	616.8	616.8
SP	3.5	3.4	3.3
CN (50% water)	0.0	13.7	26.8

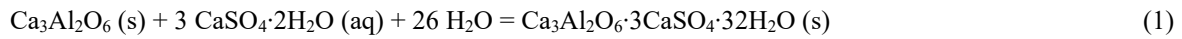
RESULTS AND DISCUSSION

The hydration development of pastes with ggbs S1, S2 and S3 are plotted as a function of CN dosage in terms of hydration rate (mW/g OPC+ggbs) in Fig. 1, and in terms of cumulative heat development (J/g OPC+ggbs) in Fig. 2. Note that the mix was blended outside the calorimeter and the filled sample holder dropped into the instrument.

The first strong peak out of scale is due to the sample being slightly warmer than the background due to mixing energy etc. and the curves in Fig. 1 should not be interpreted in terms of hydration within the first 45 minutes.

The rate of heat of hydration plotted in Fig. 1 shows for the reference (0% CN) in all cases a bimodal curve. The maximum heat in the main hydration peak for the reference (0% CN) and S3 is much higher than for S1 and S2. This is because OPC2 used for S3 has a higher C₃A content (5.8% vs. 1.8% according to Bogue estimation) and higher specific surface (388 vs. 359 m²/kg) than OPC1 used for S1 and S2. The start of the first broad peak is associated with the onset of the hydration of the main mineral alite (Ca₃SiO₅). This mineral dissolves incongruently releasing Ca²⁺ and OH⁻ ions to the pore solution and leaving a silicate rich layer behind. The concentration of calcium and hydroxide ions can build up to level where it is supersaturated relative to calcium hydroxide, and when calcium hydroxide finally start to crystallize, there is a burst in renewed alite hydration leading to the first broad peak. The general setting acceleration of alite by calcium nitrate can be understood by the increase of calcium ion concentration introduced to the mixing water and thereby less alite hydration (shorter time) needed to reach super-saturation with respect to calcium hydroxide and on-set of its crystallization.

Ca₃Al₂O₆ (often simply called "aluminate" phase) is the fastest reacting cement mineral, but its initial reaction is halted by gypsum forming ettringite on its surface:



When alite has reacted a while, more surface of Ca₃Al₂O₆ in the multi-mineral cement grain will be exposed and after a while there will be more aluminate reacted than there is gypsum to stabilize ettringite. The second peak (or shoulder on the broad peak) for the reference is due to decomposition of initial formed ettringite to calcium monosulfoaluminate hydrate caused by renewed hydration of the cement mineral Ca₃Al₂O₆:

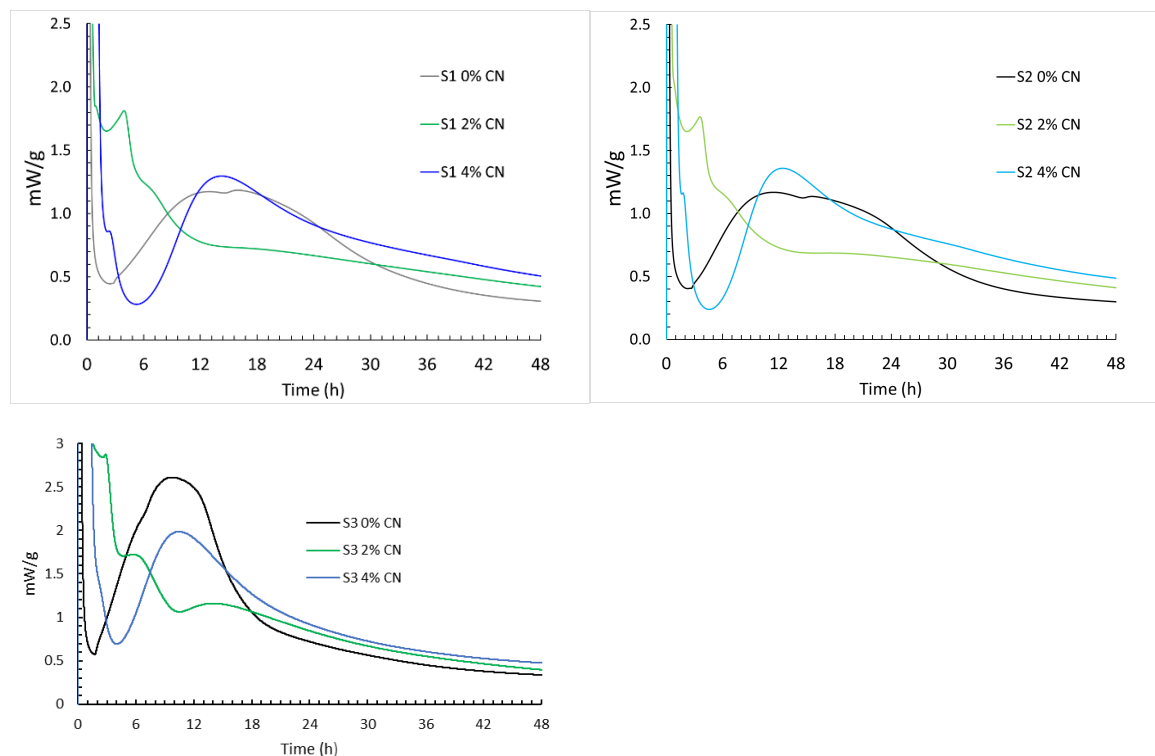
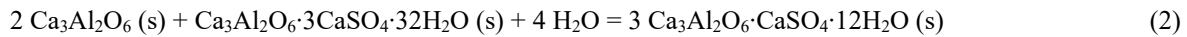


Fig. 1 – Rate of heat of hydration (mW/g powder) for pastes based on 50% cement replacement by ggbs S1, S2 and S3 as function of calcium nitrate (CN) dosage. Note that the OPC2 used with S3 was different from OPC1 used with S1 and S2 (composition details in Table 1).

The heat from this initial ettringite formation in Eq. 1 is included in the observed intense peak the first minute along with adsorption of water when water is added directly to dry cement in the calorimeter, but is also responsible for the sample being warmer than ambient when mixed outside the calorimeter in addition to the mixing energy. The reaction in Eq. 2 is also exothermic and is the reason for the generally observed shoulder on the main bimodal hydration peak.

The effect of calcium nitrate on the rate of hydration heat curves in Fig. 1 is quite similar and independent of the slag type. This is as expected since cement reacts much faster than the slag and will dominate the curve.

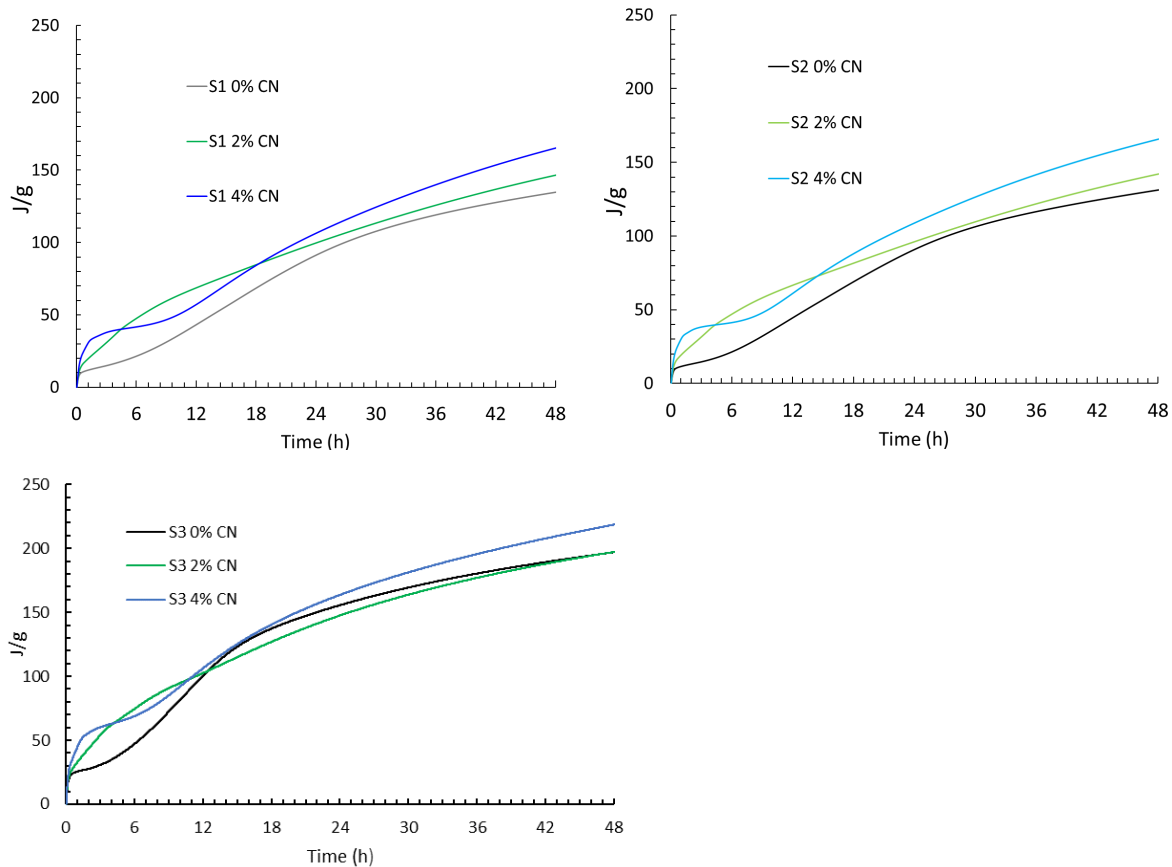
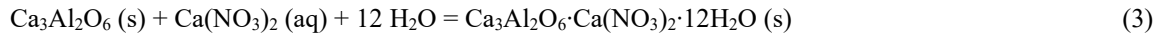


Fig. 2 – Cumulative heat of hydration (J/g powder) for pastes based on 50% cement replacement by ggbs S1, S2 and S3 as function of calcium nitrate (CN) dosage. Note that the OPC2 used with S3 was different from OPC1 used with S1 and S2 (composition details in Table 1).

For the 2% CN there is a sharp, early peak and the broad peak is also moved to shorter time, while at 4% CN dosage there is an even earlier sharp peak (more like a shoulder) and a broad peak later than the reference. Hence 4% CN seems to be too much leading to a retardation of the alite reaction, while 2% CN accelerates hydration and setting, but distributes the reaction over longer time. Both effects will result in lower 1-day compressive strength as shown later.

The sharp peak may be due to an early aluminate reaction. There are two different ways in which CN might interact with $\text{Ca}_3\text{Al}_2\text{O}_6$:

- 1) Due to the increased concentration of calcium introduced into the mixing water, the solubility of gypsum can be depressed by the common ion effect and lead to less/slower ettringite formation making the reaction in Eq. 2 happen earlier.
- 2) Since calcium nitrate is much more soluble than gypsum it may react directly with the aluminate and form AF_m -nitrate. This may block for an ettringite formation until nitrate is consumed and the peak observed is the exothermic reaction in Eq. 3. Calcium nitrate has been shown to function as a setting retarder for portland cement clinker without gypsum [10].



$\text{Ca}_3\text{Al}_2\text{O}_6 \cdot \text{Ca}(\text{NO}_3)_2 \cdot 12\text{H}_2\text{O}$ (AF_m-nitrate) is more stable [11] than $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ (AF_m-sulfate) and its formation will limit reaction (2) so more ettringite will be stabilized.

The cumulative heat values for all pastes at 12, 24 and 48 h are given in Table 5 for ggbs S1, S2 and S3 as function of CN dosage. It is common to believe that cumulative heat is correlated to compressive strength. The mixes with calcium nitrate have in general higher cumulative heat at for instance 12 h, closer to the reference at 24 h (1 day) whereafter it deviates from the reference with higher values at 48 h (2 days). However, the effects are small for OPC2/S3. It is also observed earlier [9] that CN as accelerator is mostly a *setting* accelerator with higher strength very early (8-12 h) because the cement hydration starts earlier, being close to the reference at 1 day and again higher than the reference at 2 days onwards. The lack of response at 1 day is why calcium nitrate is not considered to be a *hardening* accelerator.

Table 5 — Cumulative heat (J/g) of pastes with ggbs S1 as function of CN dosage at different times. Values in brackets are relative to reference without CN.

ggbs - CN	12 h	24 h	48 h
S1 - 0% CN	43.2 (100%)	91.2 (100%)	134.8 (100%)
S1 - 2% CN	68.9 (159%)	99.8 (109%)	146.5 (109%)
S1 - 4% CN	57.1 (132%)	106.5 (117%)	165.2 (123%)
S2 - 0% CN	44.2 (100%)	90.8 (100 %)	131.3 (100%)
S2 - 2% CN	66.4 (150%)	96.1 (106%)	142.0 (108%)
S2 - 4% CN	61.4 (139%)	108.9 (120%)	165.7 (126%)
S3 - 0% CN	100.2 (100%)	155.6 (100 %)	196.9 (100%)
S3 - 2% CN	102.5 (102%)	147.5 (95%)	197.2 (100%)
S3 - 4% CN	106.2 (106%)	163.6 (105%)	218.5 (111%)

The compressive and flexural strength of mortars as a function of curing time are plotted in Figs. 3 and 4, respectively, as average values for three parallels with error bars representing individual standard deviations for ggbs S1 and S2. The masses of the mortar prisms upon demoulding were all constant with 586 ± 3 g. Hence, it is not necessary to correct measured strength due to variations in air content or compaction flaws, as 1 vol% extra macro void (air or flaw) would have reduced compressive strength by about 5%. The average compressive strength of concrete (2 parallel cubes) as function of curing time is shown as bar diagram in Fig. 5 with error bars representing individual standard deviations.

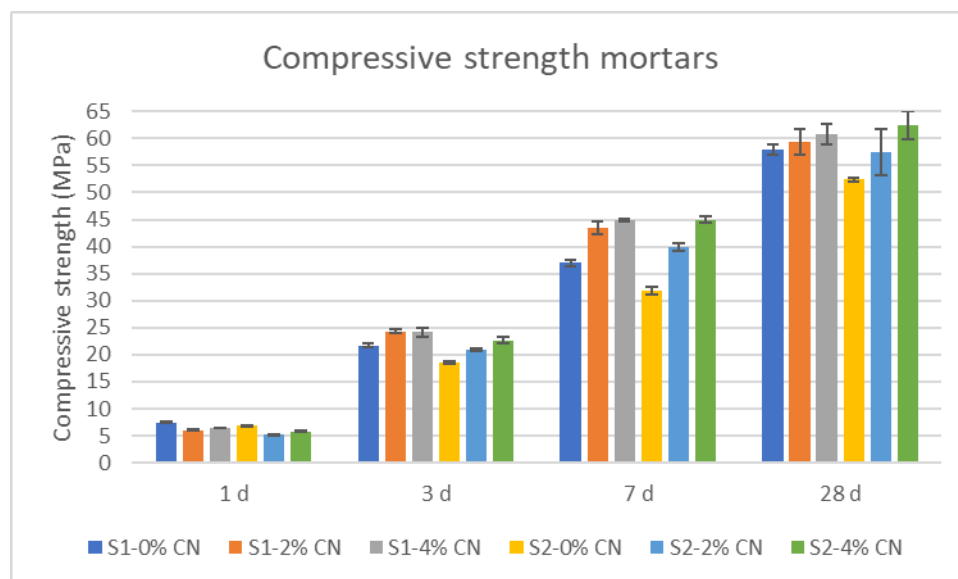


Fig. 3 – Compressive strength of mortars as a function of curing time, ggbs type (S1 and S2) and calcium nitrate (CN) dosage.

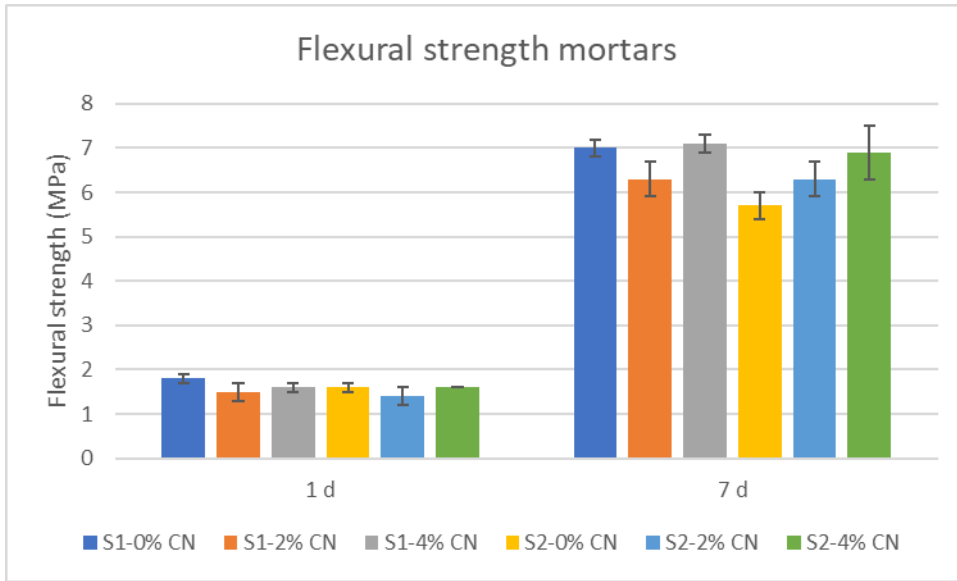


Fig. 4 – Flexural strength of mortars as a function of curing time, ggbs type (S1 and S2) and calcium nitrate (CN) dosage.

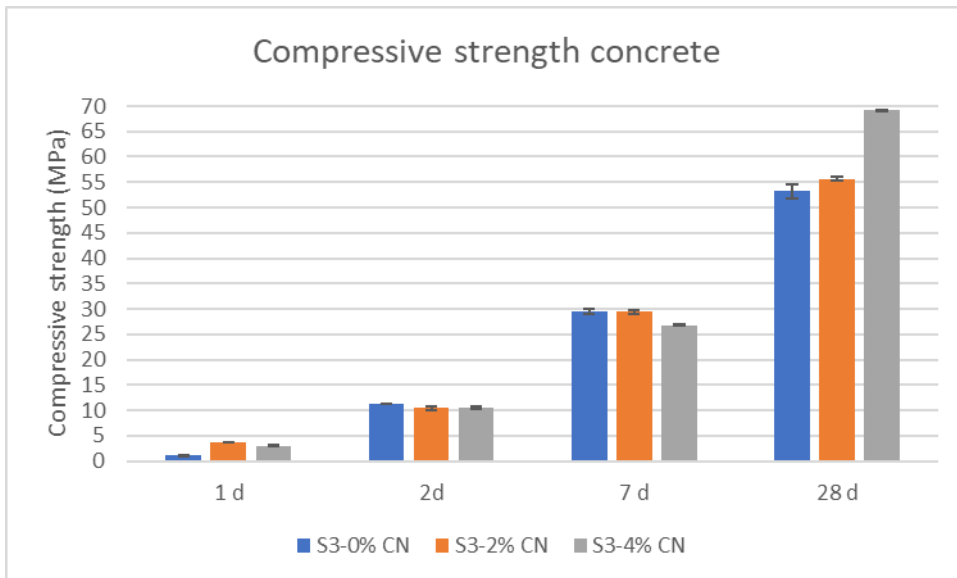
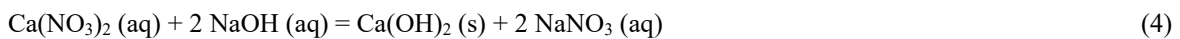


Fig. 5 – Compressive strength of concrete as a function of curing time, ggbs type (S1 and S2) and calcium nitrate (CN) dosage.

It is interesting to notice that despite higher cumulative heat at 1 day when calcium nitrate (CN) is added (especially 4% CN), the measured 1-day mortar strength is lower. CN must create reactions generating heat early on that is not resulting in more bound water and thereby lower porosity and higher strength. Such a reaction could be precipitation of alkali hydroxides dissolved from the cement to calcium hydroxide by the extra calcium ions added to the water phase:



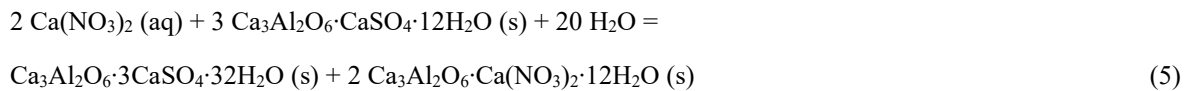
The reaction in Eq. 4 is exothermic and will generate some heat, but it will also lower the pH of the water phase. High pH is usually needed to accelerate slag reaction and Eq. 4 may therefore be the reason why 1-day strength is lower with CN, even though it is not increasingly reduced with increasing dosage. The reason is probably that since OPC1 and OPC2 are low alkali cements ($\approx 0.6\%$ Na_2O equivalent), 2% CN is sufficient to precipitate all released hydroxide attached to alkalis. It can be calculated that if all the alkalis were dissolved in the initial mixing water, it will result in 0.215 M NaOH equivalent and $\text{pH} = 13.3$. In the case of 2% CN dosage there will be 0.271 M calcium nitrate in the initial mixing water with the capacity of precipitating 0.542 M NaOH-equivalents. This

is twice the amount of maximum NaOH equivalents theoretically present. The excess calcium (0.1635 M) present in the mixing water after precipitation will suppress the solubility of calcium hydroxide and reduce its pH. Using $5.5 \cdot 10^{-6}$ as the solubility product of $\text{Ca}(\text{OH})_2$ gives a pH of 12.34 (simplified calculation ignoring CaOH^+ species [12]), but including an extra 0.1635 M Ca^{2+} in the water will reduce the pH to 11.78 due to the “common ion” effect. For 4% CN the surplus calcium concentration will be $0.164 + 0.271 = 0.435$ M Ca^{2+} reducing the initial pH further to 11.55.

The compressive strength of the mortar with S2 ggbs is lower than with S1 ggbs when CN is not added, and the values are 92, 85, 86 and 91 % of the S1 ggbs mix after 1-, 3-, 7- and 28-days curing. The addition of CN accelerates the strength development after 1 day and 4% CN leads to equal strength for the S2 ggbs and S1 ggbs mixes at 7 days, and even higher for S2 ggbs at 28 days (or equal considering the standard deviation). It can be seen from the cumulative heat curves in Fig. 2 that the mixes with slag and CN start to deviate from the reference curve without CN towards higher values from about 35 hours onwards. Table 5 show that the percentual cumulative heat relative to the mix without CN is higher at 2 days than at 1 day (one exception being equal).

The increased compressive strength of concrete at 1 day at +5°C by CN is expected since CN is known [9] to be more effective as a set accelerator at low temperatures, while the hydration of the reference has barely started. The strength at the later ages is close to the reference, apart from 4% CN at 28 days. The reason for this is unknown, but it may be worth noting that S3 ggbs is particular low in CaO (Table 1) and perhaps the extra calcium can help stabilizing compounds in need of extra calcium as the slag reaction proceed.

The XRD-diffractograms for the three paste mixes with S1 and S2 ggbs after 1-day sealed curing are plotted in Fig. 6 for the diffraction angle range $8.5\text{-}11.0^\circ$ 2θ covering the formation of ettringite (AF_t) and AF_m -phases. Increasing dosages of calcium nitrate leads to increasing amounts of ettringite; $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. This can happen on the expense of calcium monosulfo-aluminate hydrate; $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$:



The AF_m -phase $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ is a layered compound where the sulfate ion lies between the layers and can easily be replaced by other ions depending on the stability of the resulting AF_m -phase. One can refer to it as $\text{AF}_m\text{-SO}_4$ and the nitrate version formed in Eq. 5 as $\text{AF}_m\text{-NO}_3$. $\text{AF}_m\text{-NO}_3$ is more stable than $\text{AF}_m\text{-SO}_4$ [11]. The observation of increased ettringite formation (peak at 9.1° 2θ) and formation of AF_m -nitrate (peak at 10.3° 2θ) after 1-day sealed curing is independent of the slag type.

The mechanism of calcium nitrate as accelerator for portland cement is recently discussed by Dorn et al. [8]. They confirmed the formation of AF_m -nitrate and increased amount of ettringite, as well as that CN accelerated alite due to increased calcium concentration in the pore water.

Blastfurnace slag also contains some sulfide. Nitrate is a strong oxidizing agent, and it cannot be ruled out that nitrate in solution (concentrated up as water is consumed by hydration) can oxidize sulfide to sulfate as it is released by slag hydration through different intermediates of sulfur oxy-anions and even other nitrogen oxides.

For instance:



The resulting sulfate from Eq. 6 (or similar) can then lead to more ettringite formed, also as the slag contributes with more calcium and aluminate to the system. Blastfurnace slags typically contain about 1% sulfide measured as S. A complete reaction of 50% slag replacing cement could then contribute with about 0.5% S corresponding to 1.5% sulfate if oxidized. Not a small number as a portland cement could contain 3.5% SO_3 corresponding to about 4% sulfate, and the system would have 2% sulfate from the cement in these paste blends (see Table 1 for exact values of constituents).

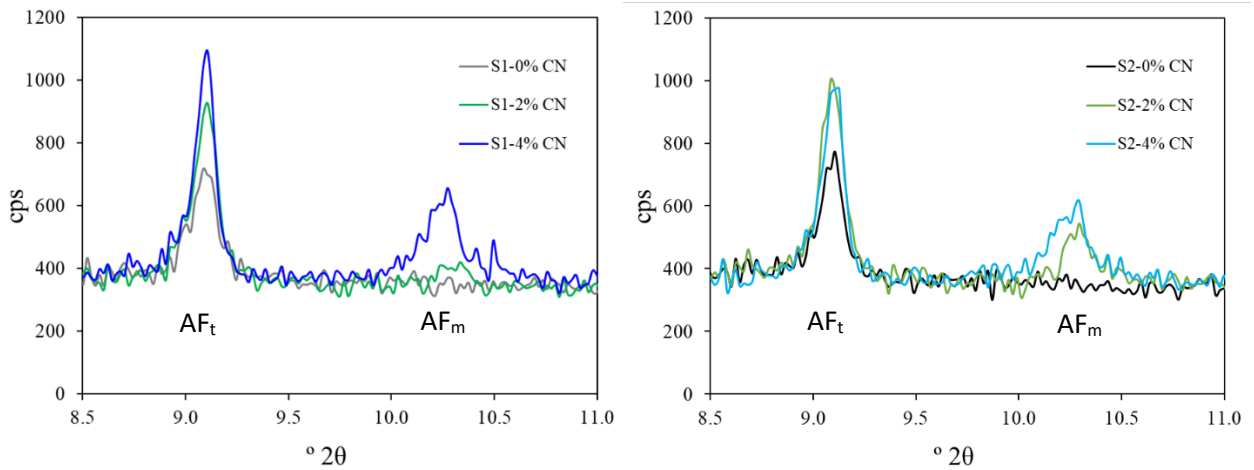


Fig. 6 – X-ray diffractogram sequence covering AF_t and AF_m phases for mixes with S1 ggbs (left) and S2 ggbs (right).

The XRD-diffractograms for the three paste mixes with S1 and S2 slag after 1-day sealed curing are plotted in Fig. 7 for the diffraction angle range 17.6-18.4° 2θ covering the formation of crystalline calcium hydroxide (peak at about 18° 2θ). The calcium hydroxide peak is significantly reduced in intensity by the addition of 2% calcium nitrate and further reduced by 4% CN.

As a first assumption the amount of calcium hydroxide should be unaffected by calcium nitrate, or rather increased if more alite has reacted at 1 day when calcium nitrate is added. The peak at about 18° 2θ has hkl-indices <001> and is prone to be increased by preferred orientation of large platelets in the plane of the sample holder. However, the sample preparation technique is designed to avoid/limit preferred orientation. To be sure, other reflections with different indices from calcium hydroxide have been checked to see if they are reduced to the same extent. The strongest reflection for calcium hydroxide is the <101> reflection occurring at 34.1° 2θ. For both slags the intensity of this reflection is NOT affected by 2% CN but is lowered by 4% CN. If the solubility of calcium hydroxide is reduced by the common ion effect of high calcium concentration in the pore water, it is possible that smaller platelets less prone to preferred orientation are formed or even less crystalline calcium hydroxide not showing up in X-ray diffractograms for the highest CN dosage.

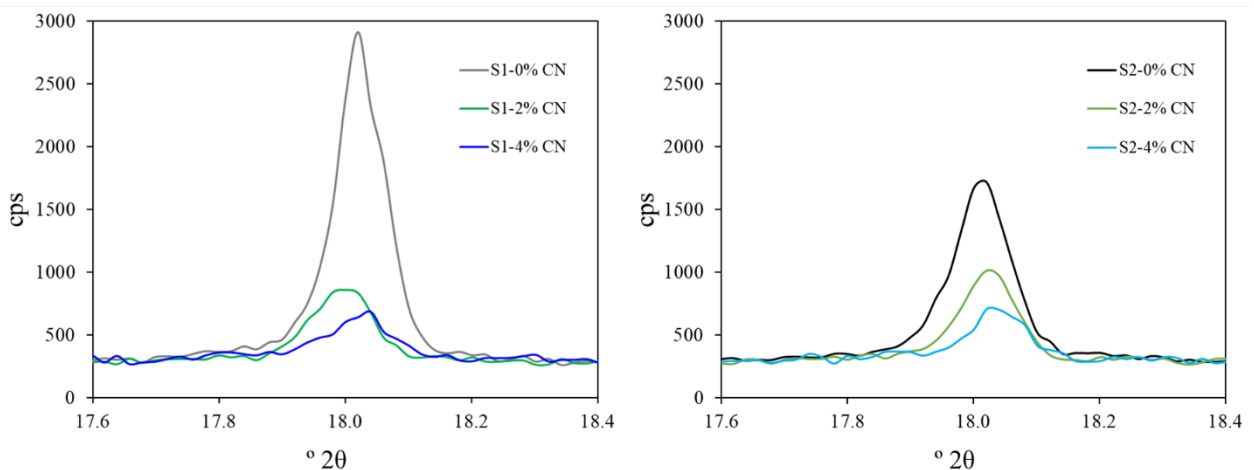


Fig. 7 – X-ray diffractogram sequence covering the peak of calcium hydroxide for mixes with S1 ggbs (left) and S2 ggbs (right).

For the highest dosage of CN it is also possible that an AF_m-heminitrate can be formed with formula; $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot \frac{1}{2}\text{Ca}(\text{OH})_2 \cdot \frac{1}{2}\text{Ca}(\text{NO}_3)_2 \cdot 12\text{H}_2\text{O}$. This would reduce the amount of calcium hydroxide, but it is not known if such a compound exists. However, since AF_m-hem碳酸盐; $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot \frac{1}{2}\text{Ca}(\text{OH})_2 \cdot \frac{1}{2}\text{CaCO}_3 \cdot 12\text{H}_2\text{O}$, do exist,

it is not unlikely. A reflection from a possible AF_m-heminitrate compound would only be marginally displaced from the AF_m-nitrate reflection as the distance between the layers in the crystal structure would only be modestly affected if any.

A third possibility exists of why the calcium hydroxide reflection is lowered for the highest concentration of CN. The formation of a compound with formula Ca(NO₃)₂·3Ca(OH)₂·12H₂O in analogy to the well-known compound CaCl₂·3Ca(OH)₂·12H₂O [13]. The chloride compound has strong reflections at about 10.8, 21.5 and 34.0° 2θ, and a nitrate analogue (if isostructural) should have reflections in the vicinity of these reflections. However, even at low concentrations of Ca(OH)₂ and high concentration of calcium nitrate (opposite of the current situation), compounds like CaO·Ca(NO₃)₂·3H₂O can form at 25°C [14, 15]. Note that CN concentration in pore water may concentrate up as the cement hydration consumes liquid water, even when only 2-4% of cement mass is added.

A fourth explanation is some pozzolanic reaction with the slag consuming calcium hydroxide. Blastfurnace slags are not considered pozzolanic in general, but rather being latent hydraulic additives that only need to be activated by cement or alkali hydroxides. However, it will depend on the Ca/(Si+Al) ratio of the slag composition, so minor consumption of calcium hydroxide to create stable hydration products cannot be ruled out. The authors postulate that the molar ratio

$$\text{CaO}/(\text{SiO}_2 + 3 \cdot \text{Al}_2\text{O}_3) \geq 1 \quad (7)$$

in order to NOT be pozzolanic assuming that C-S-H gel formed has molar Ca/Si = 1, that aluminate form crystalline compounds with molar Ca/Al = 1.5 and that the slag glass phase dissolve/react congruently. The molar ratio in Eq. (7) is 0.9352, 0.7038 and 0.6031 for ggbs S1, S2 and S3, respectively. This will, however, only be an explanation if calcium nitrate accelerated slag hydration at 1 day, which is unlikely in light of the pH reduction discussed in the preceding.

A test with thermogravimetry (TG) for the paste mixes sealed cured for 1 day was carried out to quantify the total amount of calcium hydroxide. The derivative of TG-curves (DTG) for the S1, S2 and S3 ggbs mixes are shown in Figs. 8, 9 and 10, respectively. All figures show the same trend independently of the slag-type: The increase in intensity of the first peak at 125°C is attributed to increased formation of ettringite, while the two peaks at 250 and 340°C is attributed to the decomposition of AF_m phases. Both these observations comply with the observations made by XRD. The main peak of calcium hydroxide decomposition at 480°C is displaced to lower temperature. Thermal decomposition of a compound with formula Ca₃Al₂O₆·½Ca(OH)₂·½Ca(NO₃)₂·12H₂O and even CaO·Ca(NO₃)₂·3H₂O (rather Ca(OH)₂·Ca(NO₃)₂·2H₂O) decomposing in the 250-350°C range are likely to result in calcium hydroxide with higher surface that will decompose at lower temperature than usual. However, the total amount of calcium hydroxide measured by TG may not be changed if a wider temperature range is encompassed, while XRD will show less calcium hydroxide since the compounds it has formed are intact.

The peak at 530-550°C absent in the reference and increasing in magnitude with increasing CN dosage is probably decomposition of calcium nitrate to calcium oxide and nitrous gases. Calcium nitrate decomposes generally in the range 550-600°C, but due to flow of nitrogen carrying away produced NO_x, temperature will be lowered. Small crystal sizes of CN from decomposed compounds containing calcium nitrate will also lower the decomposition temperature by TG.

The mass loss relative to sample mass from TG is listed for the three slag blended cement pastes as function of CN dosage in Table 6 for the temperature range relevant for calcium hydroxide. The relative mass loss in the 390-500 °C range for calcium hydroxide seems to increase with increasing dosage of calcium nitrate, but one cannot rule out that there are contributions from other compounds decomposing in the same temperature range.

Table 6 – Mass loss relative to sample mass from TG in the range 390 - 500°C

CN dosage	S1 ggbs	S2 ggbs	S3 ggbs
0%	1.525%	1.428%	1.912%
2%	1.686%	1.668%	2.413%
4%	1.871%	1.839%	2.516%

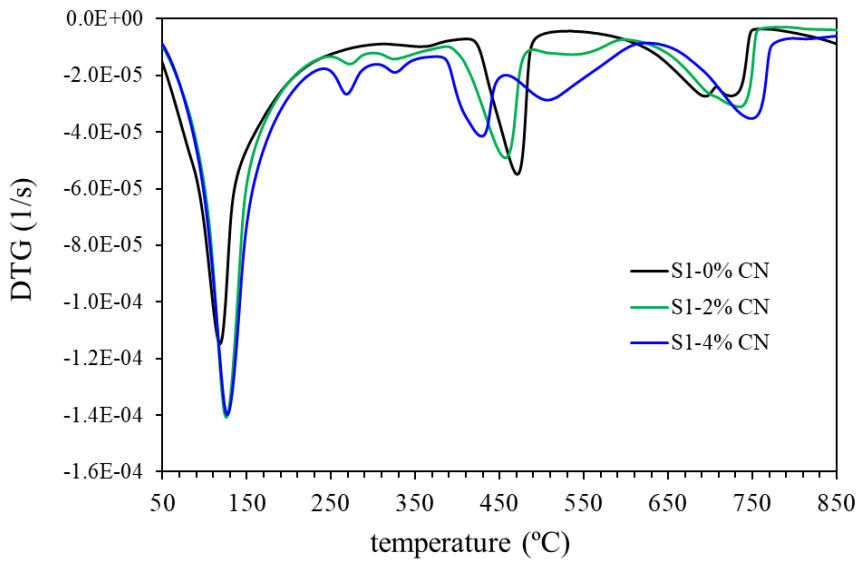


Fig. 8 –DTG- curves (peaks) of reference mix with S1 ggbs without CN (black), with 2% CN (green) and with 4% CN (blue).

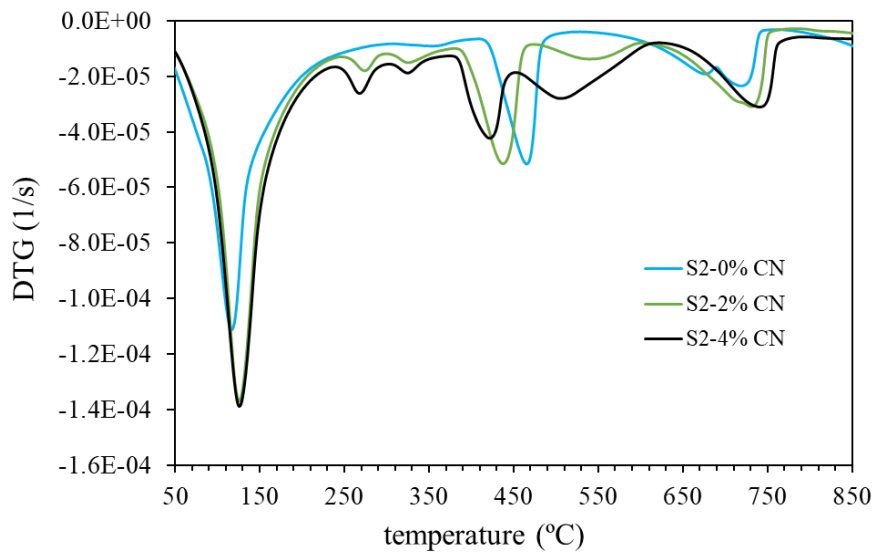


Fig. 9 –DTG- curves (peaks) of reference mix with S2 ggbs without CN (blue), with 2% CN (green) and with 4% CN (black).

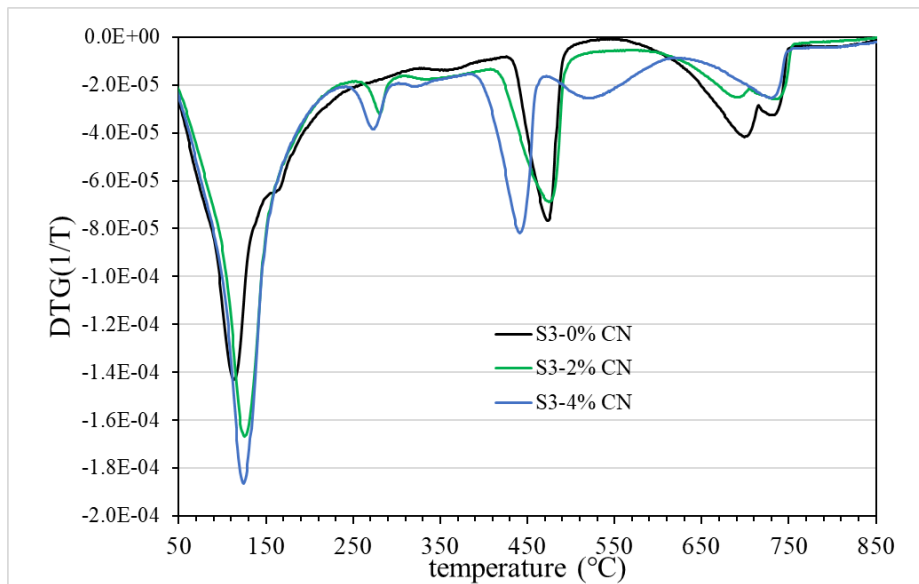


Fig. 10 –DTG- curves (peaks) of reference mix with S3 ggbs without CN (black), with 2% CN (green) and with 4% CN (blue).

CONCLUSION

The effect of calcium nitrate on cement blended with three types of blastfurnace slag (50/50) has been tested.

The S2 ggbs yield somewhat lower strength (about 90%) of the S1 ggbs in for mortars with $w/(c+ggbs) = 0.45$ cured at 20°C.

Calcium nitrate led to lower strength at 1 day for the slag-blended cement in mortars, but higher strength from 3 days on-wards. The reason for low 1 day strength is probably initial reduction of pH in pore water by surplus calcium.

The S2 ggbs blend had the same mortar strength as S1 ggbs blend at 7 and 28 days when blended with 4% calcium nitrate.

CN increased the 1-day strength of concrete with S3 ggbs cured at +5°C since CN is more effective as a set accelerator at cold temperatures and cement setting without is delayed. At other ages strength was unaffected, apart from 4% CN at 28 days where strength was increased by 15 MPa relative to reference for unknown reason.

Calcium nitrate led to more ettringite formation and AF_m phases (probably nitrate version) at 1-day sealed curing. However, the calcium hydroxide content was reduced. Potential explanations for calcium hydroxide reduction are discussed where formation of new compounds consuming calcium hydroxide seems most likely.

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