Effect of Calcium Nitrate on the Performance of Slag Blended Cement

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Abstract.

Portland cement has been replaced with 50% ground, granulated blastfurnace slag (ggbs) of two types. The influence of 2 and 4% calcium nitrate accelerator on early hydration of such binders was investigated by isothermal calorimetry as well as X-ray diffraction and thermogravimetry. The strength development of mortar based on these binder blends has been followed up to 28 days and the influence of calcium nitrate discussed.

One ggbs lower in SiO_2, Al_2O_3 and MgO yielded somewhat lower strength (about 90%) than the other. Addition of calcium nitrate led to lower strength at 1 day, but higher strength from 3 days onwards. The blends with the two ggbs achieved similar strength at 7 and 28 days when blended with 4% calcium nitrate.

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.

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 CO_2 emission. Ground, granulated blastfurnace slag (ggbs) is such a SCM. However, large clinker replacements result in low early strength and an accelerator is often needed to keep up construction productivity. Calcium nitrate is a known setting accelerator for Portland cement [2], while latent hydraulic blastfurnace slag is known to be accelerated by compounds generating high pH [3]. Since addition of calcium salts should lower the initial pH in Portland cement by precipitating hydroxides to calcium hydroxide, it was uncertain how calcium nitrate would benefit the performance of Portland cement partly replaced by blastfurnace slags.

Experimental

Materials. The cement was 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 LKAB and O'Brien. The element compositions of the cement and the slags are given in Table 1. 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.

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 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 1 – Chemical composition of Portland cement and blastfurnace slags.

Oxide	Cem I	O'Brien ggbs (S1)	LKAB ggbs (S2)
CaO	62.00	42.0	39.6
SiO_2	20.77	35.7	37.3
Al_2O_3	3.51	8.33	13.0
MgO	1.97	6.47	9.0
TiO_2	0.21	0.78	0.7
Na_2O	0.29	0.48	-
K_2O	0.43	0.59	-
Fe_2O_3	4.46	0.77	0.6
MnO	-	-	0.5
SO_3	2.59	-	0.23
S^{2-}	-	-	0.86
Cl^-	0.02	0.09	0.06

Table 2 – Paste mixes for isothermal calorimetry.

ggbs – CN dosage	ggbs	Cement	Water	2% CN	4% CN
O'Brien - 0% CN	2.5	2.5	2.25		
LKAB - 0% CN	2.5	2.5	2.25		
O'Brien - 2% CN	2.5	2.5		2.35	
LKAB - 2% CN	2.5	2.5		2.35	
O'Brien - 4% CN	2.5	2.5			2.45
LKAB - 4% CN	2.5	2.5			2.45

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-Kα) X-Ray source. A 0.2 mm divergence slit was used, and measurements were taken from 5-60° 2θ with a step size of 0.2° 2θ 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 analyzed 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.

Table 3 – Recipe for the mortar samples with w/b = 0.45.

CEM I	O'Brien ggbs	LKAB 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
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

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 demolded after 1 day curing. The prism mass was noted after de-molding 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. 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.

Results and discussion

The hydration development of pastes with O'Brien ggbs (S1) and LKAB ggbs (S2) are plotted as a function of CN dosage in terms of hydration rate (mW/g binder) in Fig. 1, and in terms of cumulative heat development (J/g powder) 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 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.
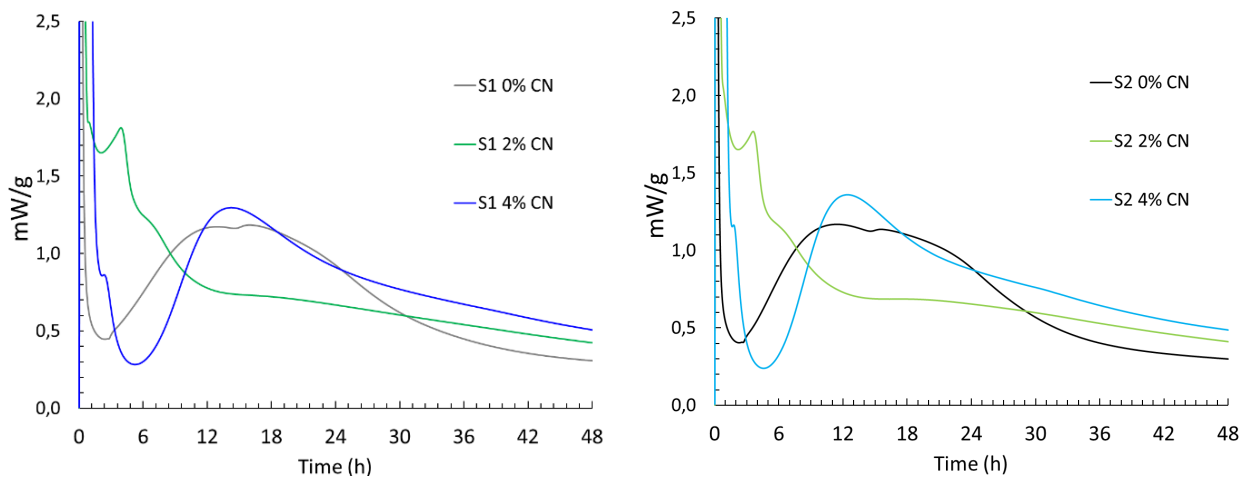

Fig. 1 – Rate of heat of hydration (mW/g powder) for pastes based on O'Brien ggbs (S1) to the left and LKAB ggbs to the right as function of calcium nitrate (CN) dosage.
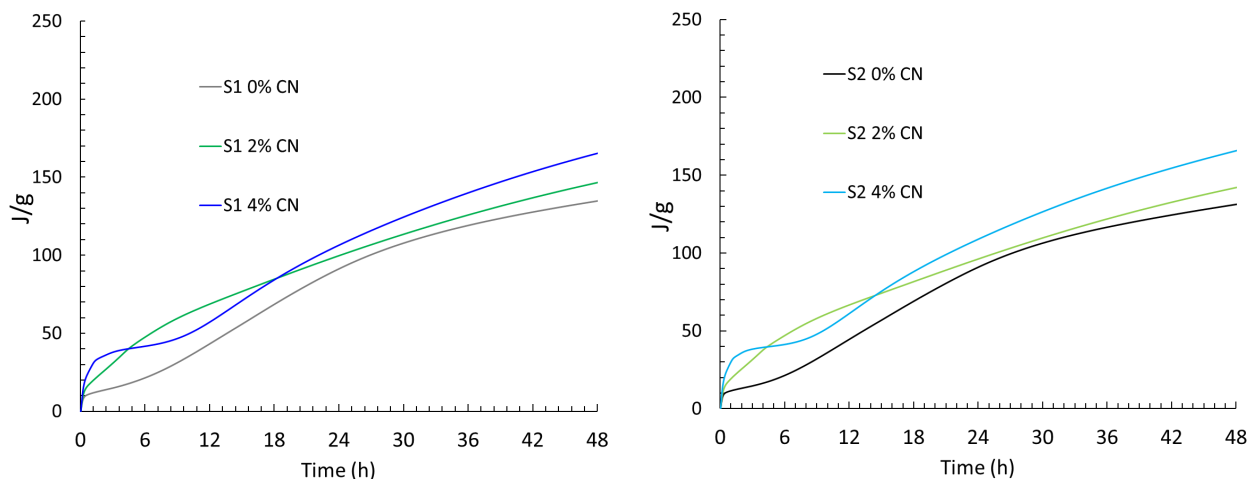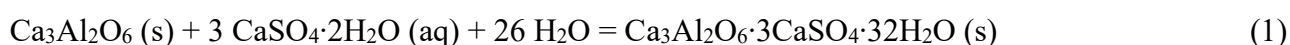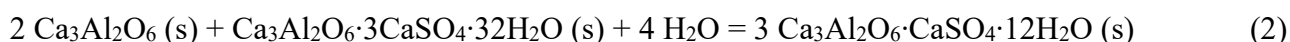

Fig. 2 – Cumulative heat of hydration (J/g powder) for pastes based on O'Brien ggbs (S1) to the left and LKAB ggbs to the right as function of calcium nitrate (CN) dosage.

The rate of heat of hydration plotted in Fig. 1 shows for the reference (0% CN) in both cases a bimodal curve. The start of the first broad peak is associated with the onset of the hydration of the main mineral alite (Ca_3SiO_5). This mineral dissolves incongruently releasing Ca^{2+} 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 initial setting time usually measured by a Vicat needle is just after the hydration rate acceleration and the final setting time just before the curve start to bend off. 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.

$Ca_3Al_2O_6$ (often simply called "aluminate" phase) is the fastest reacting cement mineral, but its initial reaction is halted by gypsum forming ettringite on its surface:

$$Ca_3Al_2O_6 \text{ (s)} + 3 \text{ } CaSO_4 \cdot 2H_2O \text{ (aq)} + 26 \text{ } H_2O = Ca_3Al_2O_6 \cdot 3CaSO_4 \cdot 32H_2O \text{ (s)} \tag{1}$$

When alite has reacted a while, more surface of $Ca_3Al_2O_6$ 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 monosulphoaluminate hydrate caused by renewed hydration of the cement mineral $Ca_3Al_2O_6$:

$$2 \text{ } Ca_3Al_2O_6 \text{ (s)} + Ca_3Al_2O_6 \cdot 3CaSO_4 \cdot 32H_2O \text{ (s)} + 4 \text{ } H_2O = 3 \text{ } Ca_3Al_2O_6 \cdot CaSO_4 \cdot 12H_2O \text{ (s)} \tag{2}$$

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 exothermal and is the reason for the generally observed shoulder on the main 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, and besides that the slags are not all that different (see 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 $Ca_3Al_2O_6$:

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 exothermal reaction in Eq. 3. Calcium nitrate has been shown to function as a setting retarder for Portland cement clinker without gypsum [4].

$$Ca_3Al_2O_6 \text{ (s)} + Ca(NO_3)_2 \text{ (aq)} + 12 \text{ } H_2O = Ca_3Al_2O_6 \cdot Ca(NO_3)_2 \cdot 12H_2O \text{ (s)} \tag{3}$$
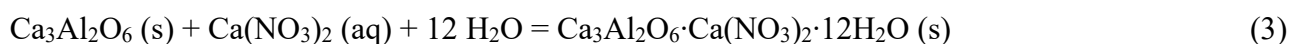
It is in general believed that cumulative heat is correlated to compressive strength. The mixes with calcium nitrate have higher cumulative heat at for instance 12 h, closer to the reference at 24 h (1 day) whereafter it deviates from the reference with higher values at 48 h (2 days). It is also observed earlier [5] 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. The cumulative heat values for all pastes at 12, 24 and 48 h are given in Table 4 for O'Brien ggbs and in Table 5 for LKAB ggbs as function of CN dosage.

Table 4 - Cumulative heat (J/g) of pastes with O'Brien ggbs as function of CN dosage at different times. Values in brackets are relative to reference without CN.

O'Brien slag	12 h	24 h	48 h
0% CN	43.2 (100%)	91.2 (100%)	134.8 (100%)
2% CN	68.9 (159%)	99.8 (109%)	146.5 (109%)
4% CN	57.1 (132%)	106.5 (117%)	165.2 (123%)

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

LKAB slag	12 h	24 h	48 h
0% CN	44.2 (100%)	90.8 (100 %)	131.3 (100%)
2% CN	66.4 (150%)	96.1 (106%)	142.0 (108%)
4% CN	61.4 (139%)	108.9 (120%)	165.7 (126%)

The masses of the mortar prisms after demolding are listed in Table 6. The compressive strength of mortars as a function of curing time is listed in Table 7, while the flexural strengths are given in Table 8. The masses do not deviate much and hence it is not necessary to correct measured strength by variations in air content.

Table 6 – Masses of mortar prisms upon demolding.

| Slag - CN dosage	Mass (g)
O'Brien-0% CN	583±2
O'Brien-2% CN	585±2
O'Brien-4% CN	586±5
LKAB-0% CN	586±2
LKAB-2% CN	587±1
LKAB-4% CN	585±2

Table 7 – Compressive strength development of mortars with ggbs blended cement and calcium nitrate.

Slag - CN dosage	1 day	3 days	7 days	28 days
O'Brien-0% CN	7.5±0.2 MPa	21.7±0.3 MPa	37.0±0.6 MPa	57.9±0.9 MPa
O'Brien-2% CN	6.0±0.1 MPa	24.3±0.3 MPa	43.5±1.2 MPa	59.4±2.4 MPa
O'Brien-4% CN	6.5±0.0 MPa	24.2±0.8 MPa	44.9±0.2 MPa	60.7±1.9 MPa
LKAB-0% CN	6.9±0.1 MPa	18.5±0.2 MPa	31.9±0.7 MPa	52.4±0.4 MPa
LKAB-2% CN	5.2±0.1 MPa	20.9±0.3 MPa	39.9±0.8 MPa	57.5±4.3 MPa
LKAB-4% CN	5.8±0.1 MPa	22.6±0.6 MPa	45.0±0.5 MPa	62.4±2.6 MPa

Table 8 – Flexural strength development of mortars with ggbs blended cement and calcium nitrate.

Slag - CN dosage	1 day	7 days
O'Brien-0% CN	1.8±0.1 MPa	7.0±0.2 MPa
O'Brien-2% CN	1.5±0.2 MPa	6.3±0.4 MPa
O'Brien-4% CN	1.6±0.1 MPa	7.1±0.2 MPa
LKAB-0% CN	1.6±0.1 MPa	5.7±0.3 MPa
LKAB-2% CN	1.4±0.2 MPa	6.3±0.4 MPa
LKAB-4% CN	1.6±0.0 MPa	6.9±0.6 MPa

It is interesting to notice that despite higher cumulative heat at 1 day when calcium nitrate (CN) is added, the measured 1-day 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:

$$Ca(NO_3)_2 \text{ (aq)} + 2 \text{ NaOH (aq)} = Ca(OH)_2 \text{ (s)} + 2 \text{ NaNO}_3 \text{ (aq)} \tag{4}$$
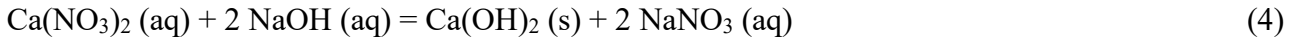
The reaction in Eq. 4 is exothermal and will generate some heat, but it will also lower the pH of the water phase. High pH is usually needed to accelerate slag reaction and Eq. 4 may therefore be the reason why 1-day strength is lower with CN, even though it is not increasingly reduced with increasing dosage. The reason is probably that since the CEM I is a low alkali cement (0.57% Na_2O equivalent), 2% CN is sufficient to precipitate all released hydroxide attached to alkalis.

The compressive strength of the mortar with LKAB slag is lower than with O'Brien slag when CN is not added, and the values are 92, 85, 86 and 91 % of the O'Brien slag 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 LKAB and O'Brien slag mixes at 7 days, and even higher for LKAB 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. In Tables 4 and 5 it is clear 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 XRD-diffractograms for the three paste mixes with O'Brien and LKAB slag after 1-day sealed curing are plotted in Fig. 3 for the diffraction angle range 8.5-11.0° 2θ covering the formation of ettringite (AF_t) and AF_m-phases. Increasing dosages of calcium nitrate leads to increasing amounts of ettringite; $Ca_3Al_2O_6 \cdot 3CaSO_4 \cdot 32H_2O$. This can happen on the expense of calcium monosulfo-aluminate hydrate; $Ca_3Al_2O_6 \cdot CaSO_4 \cdot 12H_2O$:

$$2 Ca(NO_3)_2 \text{ (aq)} + 3 Ca_3Al_2O_6 \cdot CaSO_4 \cdot 12H_2O \text{ (s)} + 20 H_2O =$$

$$Ca_3Al_2O_6 \cdot 3CaSO_4 \cdot 32H_2O \text{ (s)} + 2 Ca_3Al_2O_6 \cdot Ca(NO_3)_2 \cdot 12H_2O \text{ (s)} \tag{5}$$
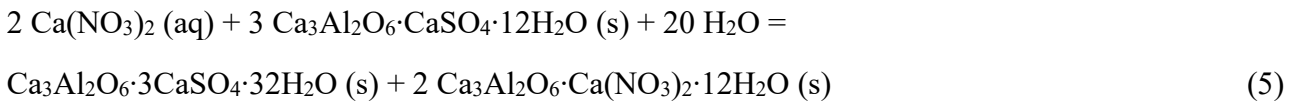
The AF_m-phase $Ca_3Al_2O_6 \cdot CaSO_4 \cdot 12H_2O$ is a layered compound where the sulphate ion lies between the layers and can easily be replaced by other ions depending on the stability of the resulting AFm-phase. One can refer to it as AF_m-SO_4 and the nitrate version formed in Eq. 5 as AF_m-NO_3. AF_m-NO_3 is more stable than AFm-SO_4 [6]. 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. [7]. They confirmed the formation of AFm-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 sulphate as it is released by slag hydration through different intermediates of sulfur oxy-anions and even other nitrogen oxides. For instance:

$$4NO_3^- + S^{2-} = 4\ NO_2^- + SO_4^{2-} \tag{6}$$

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% sulphate, and the system would have 2% sulphate from the cement in these paste blends (see Table 1 for exact values of constituents).

The XRD-diffractograms for the three paste mixes with O'Brien and LKAB slag after 1-day sealed curing are plotted in Fig. 4 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.
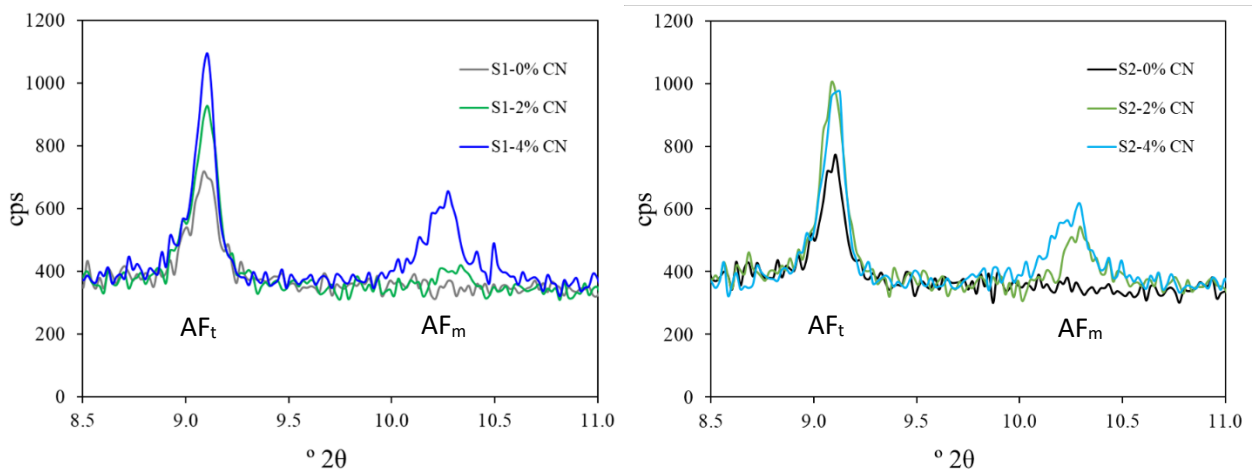

Fig. 3 – X-ray diffractogram sequence covering AF_t and AF_m phases for mixes with O'Brien ggbs (left) and LKAB ggbs (right).
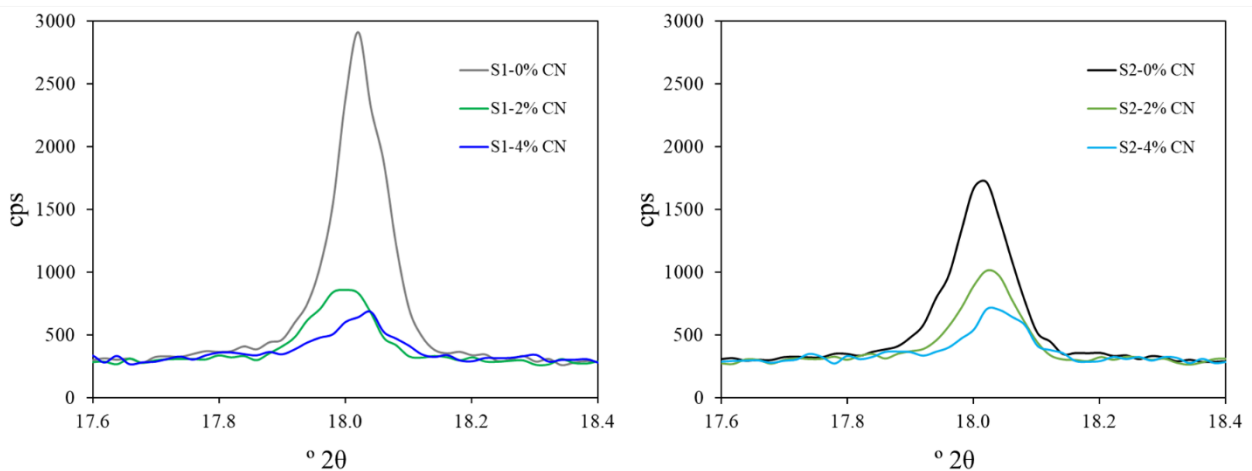

Fig. 4 – X-ray diffractogram sequence covering the peak of calcium hydroxide for mixes with O'Brien ggbs (left) and LKAB ggbs (right).

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.

For the highest dosage of CN it is also possible that an AF_m-heminitrate can be formed with formula; $Ca_3Al_2O_6 \cdot \frac{1}{2}Ca(OH)_2 \cdot \frac{1}{2}Ca(NO_3)_2 \cdot 12H_2O$. This would reduce the amount of calcium hydroxide, but it is not known if such a compound exists. However, it is not unlikely since AF_m-hemicarbonate; $Ca_3Al_2O_6 \cdot \frac{1}{2}Ca(OH)_2 \cdot \frac{1}{2}CaCO_3 \cdot 12H_2O$, do exist. A reflection from a possible AF_m-heminitrate compound would only be marginally displaced from the AFm-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 $Ca(NO_3)_2 \cdot 3Ca(OH)_2 \cdot 12H_2O$ in analogy to the well-known compound $CaCl_2 \cdot 3Ca(OH)_2 \cdot 12H_2O$ [8]. 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 $CaO \cdot Ca(NO_3)_2 \cdot 3H_2O$ can form at 25°C [9, 10]. 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. This will only be an explanation if calcium nitrate accelerated slag hydration.

A test with thermogravimetry for the paste mixes sealed cured for 1 day was carried out to quantify the total amount of calcium hydroxide. The thermogravimetry (TG) results and derivative of TG-curves (DTG) for the O'Brien slag mixes are shown in Fig. 5, while the curves for the mixes with LKAB slag are plotted in Fig. 6. Both figures show the same trend independently of the slag-type. The decomposition peak of calcium hydroxide in the DTG-curve (peak at 480°C) is reduced when calcium nitrate is included, and new peaks appear. This is a strong indication that calcium nitrate indeed forms other compounds with calcium hydroxide as discussed in the preceding text and that the reduction in intensity of the calcium hydroxide reflection in the X-ray diffractograms is real and not an artifact of preferred orientation of crystalline platelets.

Looking at the graphs in Figs. 5 and 6, 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 and even split in two for the highest CN dosage. Thermal decomposition of a compound like formula $CaO \cdot Ca(NO_3)_2 \cdot 3H_2O$, or rather $Ca(OH)_2 \cdot Ca(NO_3)_2 \cdot 2H_2O$, is likely to result in calcium hydroxide with high surface that will decompose at lower temperature than usual.
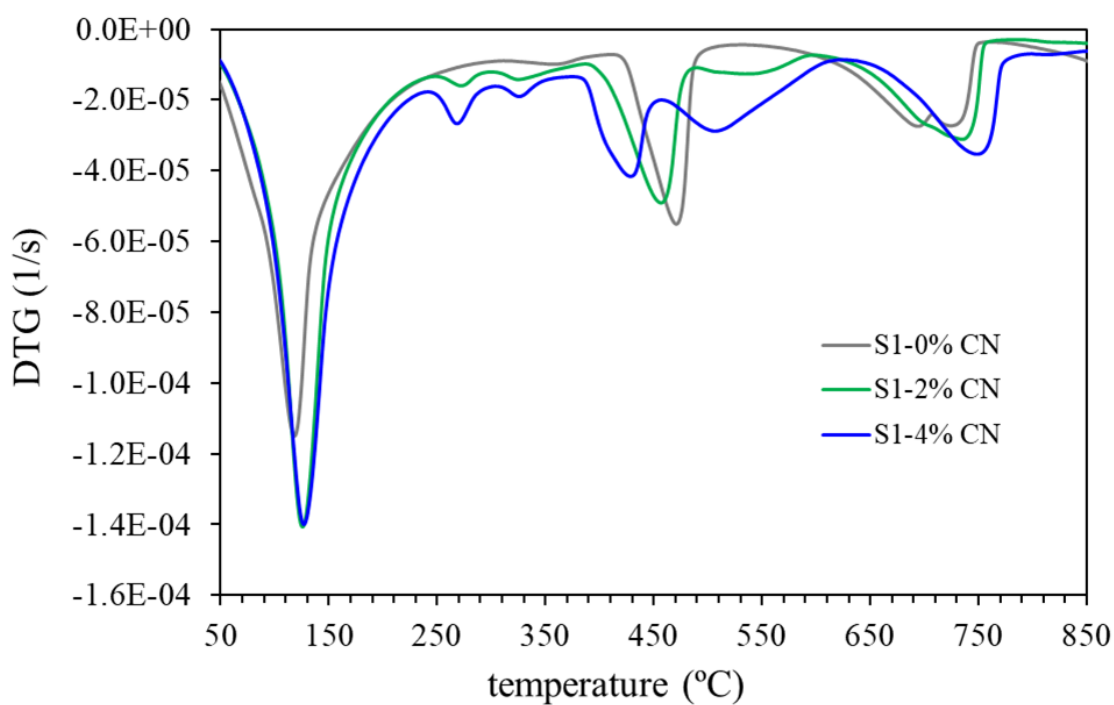
Fig. 5 – TG-curves (gradual weight loss curves) and DTG- curves (peaks) of reference mix with O'Brien slag without CN (black), with 2% CN (red) and with 4% CN (blue).
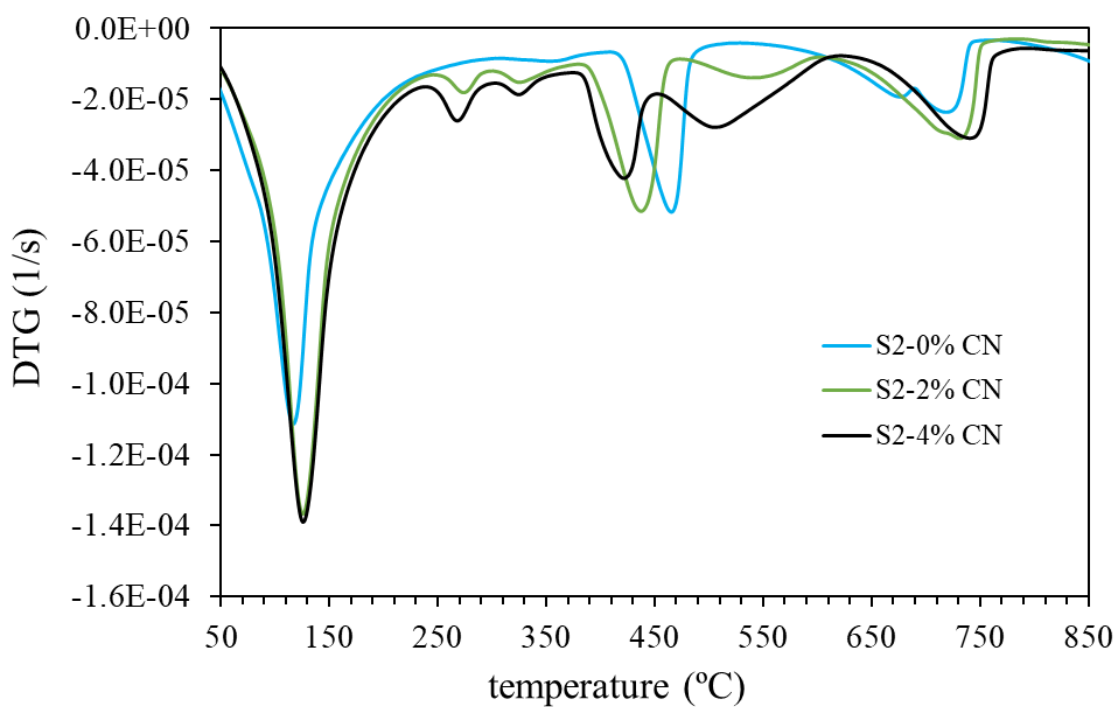

Fig. 6 – TG-curves (gradual weight loss curves) and DTG- curves (peaks) of reference mix with LKAB slag without CN (black), with 2% CN (red) and with 4% CN (blue).

Conclusions

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

The LKAB ggbs yield somewhat lower strength (about 90%) of the O'Brien ggbs.

Calcium nitrate led to lower strength at 1 day for the slag-blended cement, but higher strength from 3 days on-wards.

The LKAB slag blend had the same strength as O'Brien slag blend at 7 and 28 days when blended with 4% calcium nitrate.

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.

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