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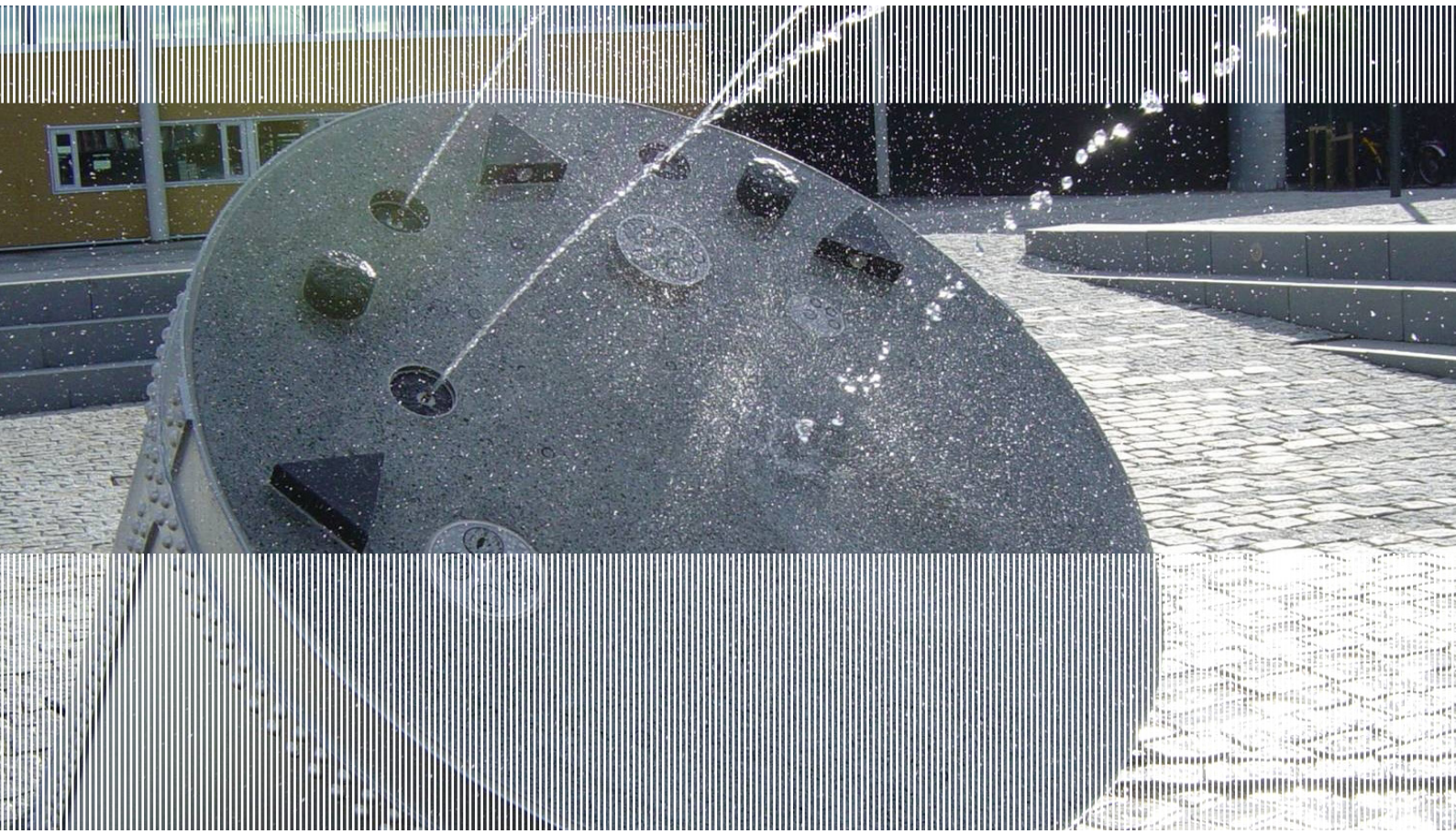
COIN project report 71 – 2015



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FA 1 Environmentally friendly concrete

SP 1.1 Low carbon-footprint binder systems

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Preface

This study has been carried out within COIN - Concrete Innovation Centre - one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfil this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently eight projects in three focus areas:

- Environmentally friendly concrete
- Economically competitive construction
- Aesthetic and technical performance

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %).

For more information, see www.coinweb.no

Tor Arne Hammer
Centre Manager

Summary

A former developed hardening accelerator for fly ash blended cement should be replaced with another formulation free from thiocyanate and preferentially with equal or better performance in terms of compressive strength. The 3rd component in the ternary accelerator consisting of 5 parts glycerol, 10 parts diethanol amine and 15 parts sodium thiocyanate (NaSCN) should be replaced since it is believed to cause rust stains on steel moulds.

Based on isothermal calorimetry and compressive strength measurements on mortar, the best candidate in terms of performance is sodium thiosulphate ($Na_2S_2O_3$) as it also fulfil the requirements to a hardening accelerator at a 0.35% dosage by weight of cement for fly ash blended cement. However, since thiosulphate like thiocyanate is known to form complexes with iron, it is possible that also this component will lead to rust stains on steel as well.

If rust stains still are a problem, it is proposed to change to sodium nitrite ($NaNO_2$) as the 3rd component in the ternary accelerator since this combination barely fulfilled the criteria as hardening accelerator (fell a bit short at 20°C) and is known to be a corrosion inhibitor. If toxicity is a problem, a third alternative is sodium nitrate ($NaNO_3$) that also barely made it but fell short at 20°C.

It is recommended to further work with sodium nitrate and/or sodium nitrite to see if the ternary accelerator could also fulfil the 20°C criterion if the ratio between the components is changed or the dosage relative to cement is increased from the tested 0.35% to for instance 0.50%.

A number of metal silicate hydrate (MeSH) suspensions were tested as accelerators at a dosage of 0.25%, but none performed as well as the ternary accelerators. The most promising MeSH was the one where Me was magnesium. It fulfilled the 5°C criterion of >30% strength increase relative to reference at 2 days with good margin, but fell short for the 20°C criterion of >20% strength increase relative to reference. If the magnesium silicate suspension is to be tested further it is recommended to use sodium silicate as a base rather than potassium silicate, and to perhaps test higher dosages (e.g. 0.5%) relative to cement.

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1 Introduction

1.1 Objectives

A former developed hardening accelerator for fly ash blended cement should be replaced with another formulation free from thiocyanate and preferentially with equal or better performance in terms of compressive strength.

1.2 Background

In the quest for making cement with lower CO_2 emission, one of the easiest measures on a short time horizon is to replace part of the cement clinker with supplementary cementing materials (SCMs) such as fly ash (FA) from coal fired energy plants. For the time being FA is considered waste and has zero CO_2 emission attached to it. One drawback of replacing too much of the cement clinker with SCMs in general is that the early strength will be lower than cement with 100% clinker, in particular at lower temperature, which may hamper productivity.

One way of counteracting the lower early strength is to grind the blended cement finer, and another is to develop a hardening accelerator that will increase the early strength. The European standard (EN 934-2 of 2009) for concrete admixtures has the following demands for a hardening accelerator;
1) >120% compressive strength compared to reference without accelerator at 24 h and 20°C
2) >130% compressive strength compared to reference without accelerator at 48 h and 5°C
3) in both cases compressive strength >90% of reference after 28 days

The standard EN 934-2 prescribes this to be tested on concrete, but for simplicity in the development it was in this case tested on mortar prisms.

During the PhD study of Kien Dinh Hoang [1] in the focus area 1.1 within COIN, a ternary accelerator based on 0.05 parts glycerol (GLY), 0.10 parts diethanol amine (DEA) and 0.2 parts sodium thiocyanate, NaSCN, was developed that fulfilled the criteria set by EN 934-2 for hardening accelerators. Only a dosage of 0.35% of cement mass was required to reach the target for cement where 30% clinker was replaced with FA as seen from Fig. 1. The formulation was patented [2] by MAPEI, the admixture company partner in COIN.

MAPEI then produced a large quantum and tested it out on their customers in concrete in real applications. The initial results were positive, but after some time people were noticing rust spots on their steel moulds and claimed it must be due to the accelerator. This is hard to believe with a dosage of 0.5% of cement mass. However, the customers "painted" some pure accelerator on steel and got rust spots as shown in Figure 2 and used this as an argument. It is well-known that thiocyanate ions form strong complexes with iron, so this was no surprise, albeit unrealistic compared to the use as accelerator in concrete.

Nevertheless, it was then decided to try to find an alternative to sodium thiocyanate in the ternary accelerator formulation, or alternatively find a new accelerator all together without thiocyanate. The present report documents these findings.

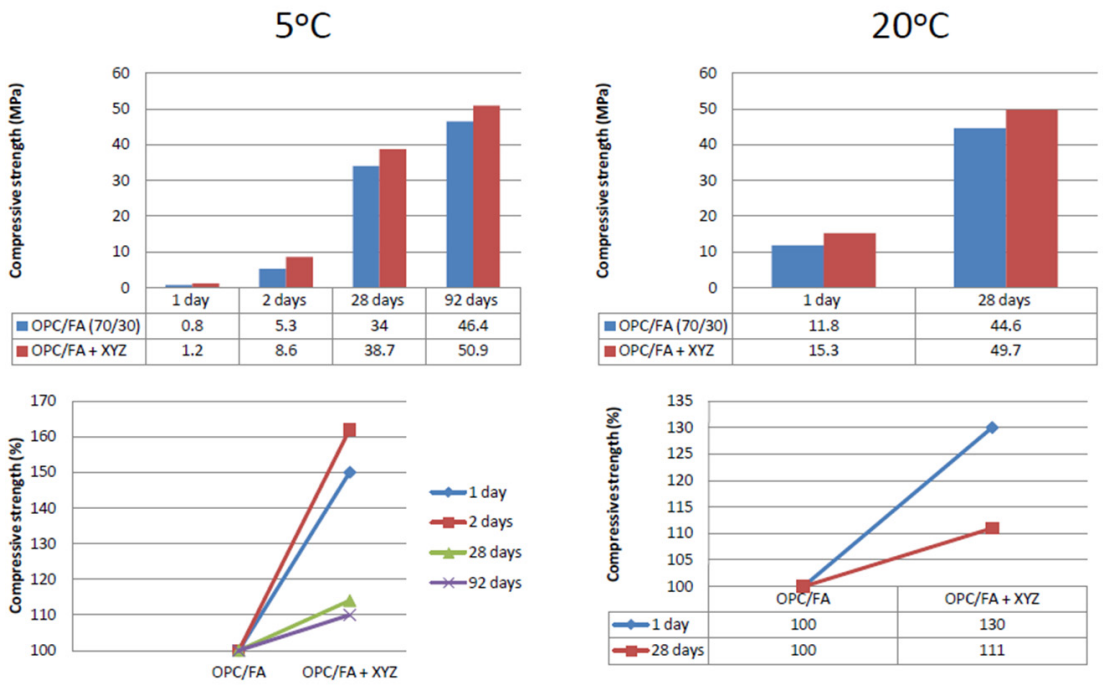

Fig. 1 The compressive strength development of mortar where 30% ordinary portland cement (OPC) is replaced with fly ash (FA) without and with 0.35% of the ternary accelerator (xyz) at 5 (upper left figure) and 20°C (upper right figure), and with the relative change compared to reference in the lower part of the figure.

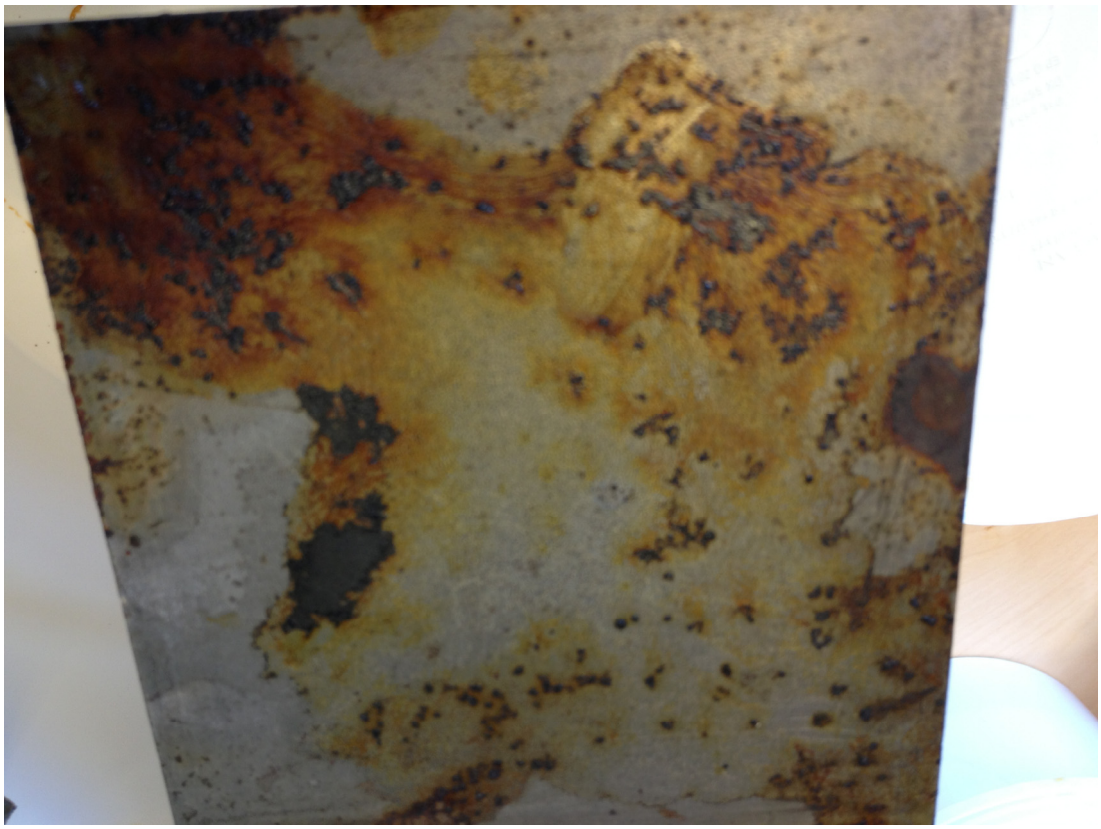

Fig. 2 The appearance of steel "painted" with ternary accelerator solution containing sodium thiocyanate after 100 days in ambient conditions.

2 Experimental

2.1 Preparation of ternary accelerator solutions

A number of chemicals were used that all were of laboratory grade. Distilled water was used to dissolve the chemicals and blend them as accelerator formulations.

The basic formulation of Kien Dinh Hoang is called TerAcc and is based on 5 parts glycerol, 10 parts diethanol amine (DEA) and 15 parts sodium thiocyanate (NaSCN) dissolved in water.

All the other substances tried out to replace sodium thiocyanate were dosed on an equimolar basis compared to NaSCN. The compounds were calcium formate; $Ca(HCOO)_2$, calcium nitrate; $Ca(NO_3)_2$, calcium nitrite; $Ca(NO_2)_2$, calcium lactate pentahydrate; $Ca(CH_3CH(OH)COO)_2 \cdot 5H_2O$, lactic acid; $CH_3CH(OH)COOH$, sodium nitrate; $NaNO_3$, sodium nitrite; $NaNO_2$ and sodium thiosulphate; $Na_2S_2O_3$.

2.2 Preparation of metal silicate hydrate (MeSH) accelerator suspensions

2.2.1 Using sodium silicate "water glass" as reactant

The principle of making the MeSH accelerators is to make a solution of water glass and then add a solution of metal (Me) nitrate that will ion exchange sodium for the metal making an insoluble silicate as a precipitate and sodium nitrate remaining in the solution. The sodium nitrate is not removed from the solution before using it as an accelerator. The metal nitrate was added gradually over a few minutes to the solution during stirring and allowed to digest over a few days. Thereafter it was added a few % of a polycarboxylate type superplasticizer to disperse the small silicate particles and prevent them from flocculation.

The MgSH accelerator was made by adding 71.6 g water to 100 g of a 33% sodium water glass (with 8% Na_2O and 27% SiO_2) solution prepared beforehand. Another solution was made by dissolving 8.25 g magnesium nitrate hexahydrate, $Mg(NO_3)_2 \cdot 6H_2O$, in 16.5 g water. This second solution was added to the first solution during stirring with a magnet stirrer over a few minutes. Immediate precipitation could be observed as a suspension. It was allowed to stir for 3 days to equilibrate (required time not known). It was then added 2 ml of a PCE superplasticizer and stirred for another 2 hours prior to use. The suspension had then a milky-white colour. The total solids in the solution were then calculated to 23.8 % and the content of soluble sodium nitrate 3.5 %. Note that the amount of "MgO" added was 0.0322 mol, which is short of replacing the 0.0426 mol "Na_2O", so a fraction of water glass remains.

The NiSH accelerator was made by adding 67.8 g water to 94.75 g of the 33% sodium water glass (with 8% Na_2O and 27% SiO_2) solution. Another solution was made by dissolving 8.86 g nickel nitrate hexahydrate, $Ni(NO_3)_2 \cdot 6H_2O$, in 15.63 g water. This second solution was added to the first solution during stirring with a magnet stirrer over a few minutes. Immediate precipitation could be observed, but as a livering and not suspension. It was allowed to stir for 3 days and then it looked more like a suspension after equilibration (required time not known). It was then added 2 ml of a PCE superplasticizer and stirred for another 2 hours prior to use. The suspension had then a light mint-green colour. The total solids in the solution were then calculated to 24.6% and the content of sodium nitrate 3.5 %. Equimolar (0.0305 mol) of "NiO" was added to content of "Na_2O" in the suspension.

2.2.2 Using potassium silicate as reactant

Procedure for Me = Mg (magnesium) in MeSH with the basis of potassium silicate:

Take water glass consisting of 11.2% K_2O and 23.8% SiO_2 or 35% total solids with K_2O/SiO_2 molar ratio of 0.300. Make 100 g 10.5% solution of water glass (29 g potassium silicate solution and 71.5 g water).

Precipitate with magnesium nitrate hexahydrate during stirring.

Need to know the molar masses for calculation:
Molar mass of K_2O; 94.20 g/mol
Molar mass of SiO_2; 60.09 g/mol
Molar mass of $Mg(NO_3)_2 \cdot 6H_2O$; 256.41 g/mol
Molar mass of $Mg(NO_3)_2$; 148.41 g/mol

So 100 g of 10.5% water glass contains 100 g*0,105*11.2/35.0 = 3.36 g K_2O or 0.0357 mol K_2O.

If one want to precipitate MgSH with the same Mg/Si ratio as 2K/Si ratio of 0.300, you would need $0.0357 \cdot 256.41 = 9.15$ g $Mg(NO_3)_2 \cdot 6H_2O$ or if one goes for Mg/Si = 0.900 one would need 27.46 g.

27.46 g hexahydrate means 15.89 g anhydrous + 11.57 g crystal water. Adding 64.43 g water gives 20.9% solution of anhydrous magnesium nitrate. 1 ml PCE superplasticizer (Dynamon SX-130) was added to the potassium silicate solution, stirred, and then the magnesium nitrate solution was added to that during vigorous stirring in 1 minute. The suspension was left for maturing with stirring for 3 days. The total solids of the suspension is then (10.5+15.9)/(100+76) = **15%**

2.3 Calorimetry

For the liquid ternary accelerators, 5 g of cement was weighed into glass ampoules. Water with dissolved accelerator was sucked up in syringes that will attach to the glass vial together with motorized stirrer. This was sealed and placed in the TAM air isothermal calorimeter for thermal equilibration to 20°C. Thereafter the liquid was injected and the internal stirrer activated for 1 min stirring while recording heat flow of the resulting paste.

Since the MeSH accelerators were suspensions, pastes where made outside the calorimeter in a high shear mixer. The suspension was dispersed in the water and the water content of the suspension included in total water. The cement was added to water and mixed at high shear rate for 1 min, left resting for 5 min and mixed again for 1 min. About 8g of the pastes prepared were weighed accurately into a glass vial, sealed with a lid and placed in the isothermal TAM Air calorimeter (TA Instrument, New Castle/USA). Measurements were performed up to 24h from the point of first contact between dry powder and water against a calibrated reference of inert alumina powder of similar mass. The time of placement was recorded and all subsequent hydration profiles were calculated and tabulated after 1h due to excessive heat transfer arising from initial preparation.

2.4 Strength test

Mortar mixes were made consisting of 450 g Norcem Standard FA cement, 1350 g norm sand (sand : reactive powder = 3:1) and water to make a water-to-reactive powder ratio of 0.50. This makes about one liter of fresh mortar sufficient to fill 3 pieces of 40x40x160 mm RILEM steel moulds. One set of mortar prisms were demoulded after 1 day at 20°C and another set demoulded after 2 days at 5°C. Then the flexural strength was tested in a 3 point bending mode on each set of three parallel prisms and the compressive strength on the 6 resulting end-pieces.

3 RESULTS AND DISCUSSION

3.1 Ternary liquid accelerators

In the work on replacing sodium thiocyanate (NaSCN) with another component in the ternary accelerator, isothermal calorimetry was used to measure the rate of hydration heat and the cumulative hydration heat as a function of time at 20°C. The cumulative hydration heat is assumed to correspond more or less directly to the degree of hydration of cement. The calorimeter curves for a number of accelerator combinations are shown in Figs. 1 and 2. The legend TerAcc stand for the old ternary accelerator comprised of 5 parts glycerol, 10 parts diethanolamine and 15 parts NaSCN dosed as 0.35% by weight of cement (bwoc). DiAcc represents the accelerator without 3rd component and dosed at 0.25% bwoc to get an idea of the performance without the inorganic part.

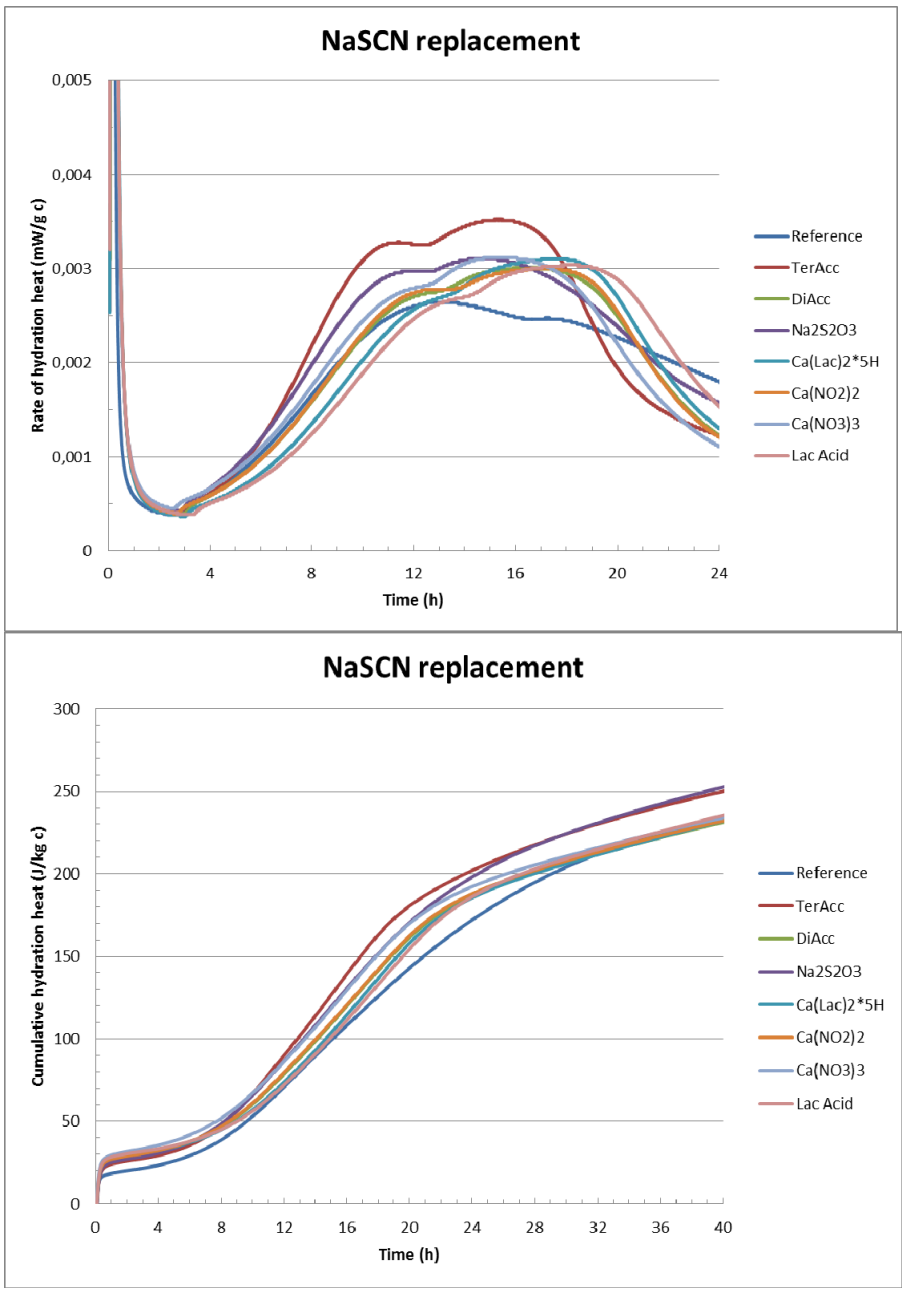

Fig. 1 - The rate of hydration heat at 20°C for 24 h (upper graph) and cumulative hydration heat (lower graph) for 40 h, both isothermally at 20°C for Std FA cement (w/c = 0.50) with a number of accelerators.

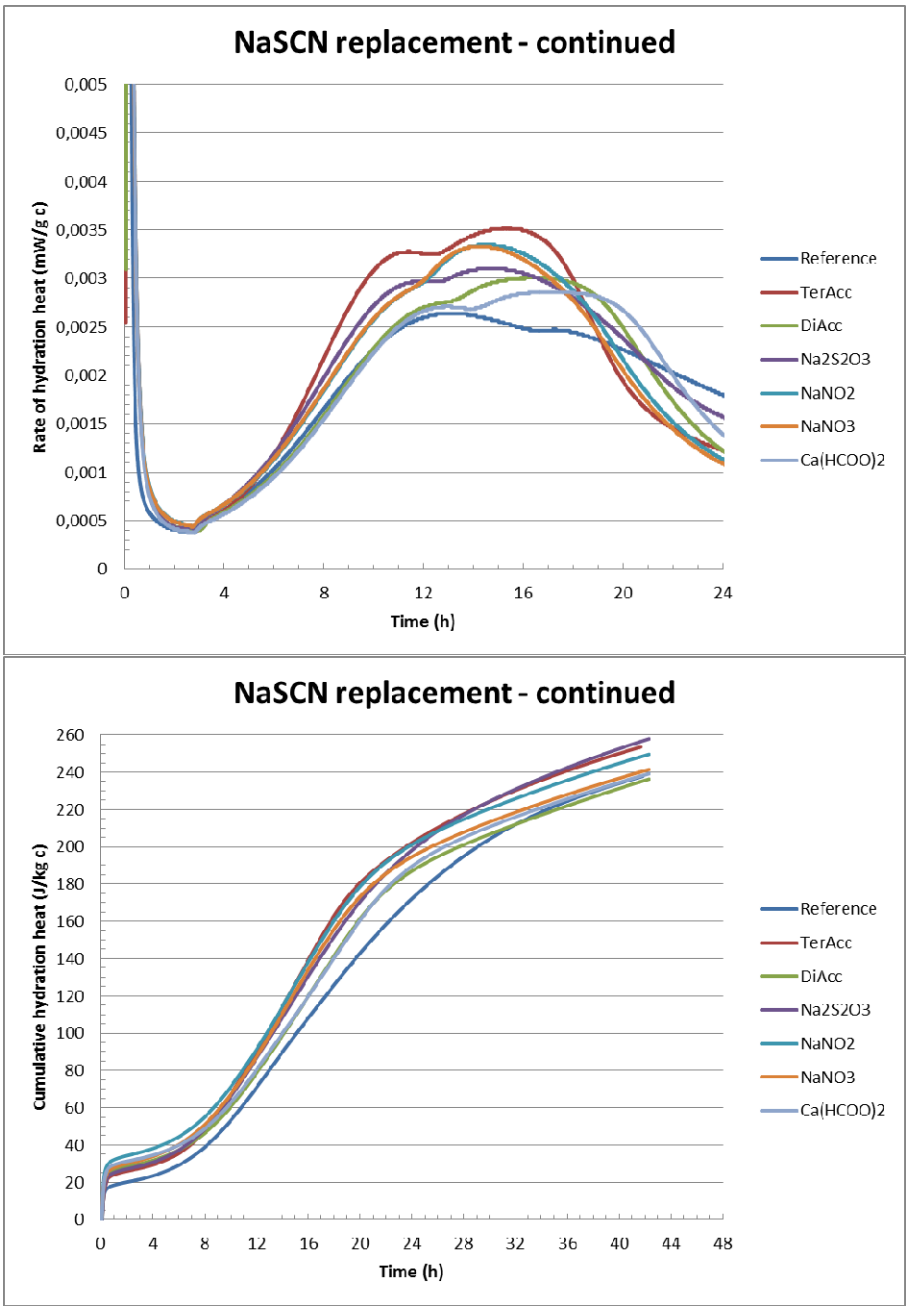

Fig. 2 - The rate of hydration heat at 20°C for 24 h (upper graph) and cumulative hydration heat (lower graph) for 42 h, both isothermally at 20°C for Std FA cement (w/c = 0.50) with a number of accelerators.

The rate of hydration curves has the characteristic double peak shape, where the first peak starts with the acceleration of the alite (C_3S) and the initial setting time is believed to be just after the rise of this peak. The second peak, or shoulder, is believed to be associated with the conversion of ettringite to monosulphate and its magnitude can be increased by for instance activation of the ferrite phase (C_4AF) giving more aluminate to the system.

The first conclusion from the upper graphs is that TerAcc gives a steeper curve for the first peak than DiAcc, meaning that NaSCN leads to an *acceleration* of the C3S hydration once it starts, but not the setting time as all curves more or less start at the same time. Secondly, the second peak is more intense, but perhaps not more in total area. The increased height of the peak means that the hydration rate at this point is higher. From the lower graphs it is quite clear that the cumulative heat at 24 h is substantially higher (and thereby degree of

hydration) for TerAcc than for DiAcc, so the inorganic part plays a role. Both TerAcc and DiAcc lead to higher cumulative heat than the reference at 24 h, as do all admixture combinations.

The accelerator combination with $Na_2S_2O_3$ has a lower early acceleration than NaSCN, but the cumulative heat at 24 h was nearly the same. However, thiosulphate is like thiocyanate known to make strong complexes with iron, so it is possible that similar rust spots may appear if the pure accelerator is painted on steel.

From the graphs in Fig. 1, calcium nitrite, $Ca(NO_2)_2$, and calcium nitrate, $Ca(NO_3)_2$, was second best, but both lower in acceleration and cumulative energy compared to $Na_2S_2O_3$. Both lactic (Lac) acid and calcium lactate pentahydrate, denoted $Ca(Lac)_2$*5H, performed worse and will not be further pursued. Besides, calcium lactate has limited solubility making formulation solutions without particles difficult.

From the graphs in Fig. 2 it appears that both sodium nitrate, $NaNO_3$, and sodium nitrite, $NaNO_2$, are candidates for replacing NaSCN, as they lead to nearly the same acceleration as $Na_2S_2O_3$ and about the same cumulative heat at 24 h (sodium nitrate slightly less). At the same time it seems clear that calcium formate, $Ca(HCOO)_2$ is not worth pursuing further, but at the same time it is commonly used as accelerator in pre-packed products. Sodium nitrite can be advantages with respect to stains on steel since it is known to be a corrosion inhibitor.

Since the real test in the end is how the hardening accelerator affect compressive strength, the most promising combination were tested in mortar (w/c = 0.50) at a dosage of 0.35% bwoc, and the results are shown in Table 1.

Table 1: Compressive and flexural strength of mortars (w/c = 0.50) and 0.35% bwoc of different ternary accelerators after 1 day curing at 20°C and 2 days curing at 5°C.

3rd component in accelerator	Compressive strength (MPa)		Flexural strength (MPa)	
	1 day at 20°C	2 days at 5°C	1 day at 20°C	2 days at 5°C
- (reference)	18.1±0.5	10.3±0.2	3.9±0.2	2.3±0.1
NaSCN*	22.9±0.3	17.6±0.2	4.9±0.2	4.2±0.1
$Na_2S_2O_3$	22.1±0.2	17.6±0.3	4.8±0.3	3.4±0.1
$NaNO_2$	20.5±0.4	17.1±0.3	4.7±0.1	4.0±0.4
$NaNO_3$	20.6±0.4	16.4±0.4	4.5±0.3	3.8±0.1
$Ca(NO_3)_2$	19.8±0.2	15.3±0.4	4.7±0.3	3.5±0.2
$Ca(HCOO)_2$	19.8±0.4	13.3±0.3	4.5±0.3	3.3±0.1

*The 3rd component in the ternary accelerator by Kien Dinh Hoang [1]

In order to generate >120% compressive strength of reference after 1 day at 20°C and >130% compressive strength after 2 days at 5°C, the accelerators should lead to compressive strength > 21.7 MPa and > 13.4 MPa, respectively.

All the tested ternary accelerators, with the exception of when calcium formate, $Ca(HCOO)_2$, is used as 3rd component fulfil the 5°C criterion with good margin.

However, only the ternary accelerators with sodium thiocyanate (NaSCN) and sodium thiosulphate ($Na_2S_2O_3$) as 3rd component fulfil the 20°C criterion. NaSCN was the one to be replaced and $Na_2S_2O_3$ is also known to form complexes with iron. So perhaps that one also would make rust stains if painted in concentrated form directly on steel.

Sodium nitrite as 3rd component makes the best ternary accelerator after the two other and nearly fulfils both criteria. Furthermore, sodium nitrite is known as corrosion inhibitor for

steel, so this may be a ternary accelerator worth looking further into. Perhaps can a change in component ratios make the blend fulfil both criteria as a true hardening accelerator.

3.2 Accelerators based on metal silicate hydrate suspensions

The isothermal calorimeter curves at 20°C for accelerators based on metal silicate hydrate (MeSH) suspensions are plotted in Fig. 3 as both rate of hydration heat (upper graph) and cumulative hydration heat (lower graph) for the first 24 h. The curves are compared to TerAcc at its regular dosage (0.35% bwoc) and at the dosage used for the MeSH (0.25% bwoc). The legend in the graphs are given as the metal used (Me) and its molar ratio to Si for those based on potassium (K) silicate and they are also compared directly with K-silicate alone. Legend old Me refers to those based on sodium silicate. It is evident from the calorimeter curves that none of the MeSH tested perform as well as TerAcc, even at the comparable dosage of 0.25% bwoc.

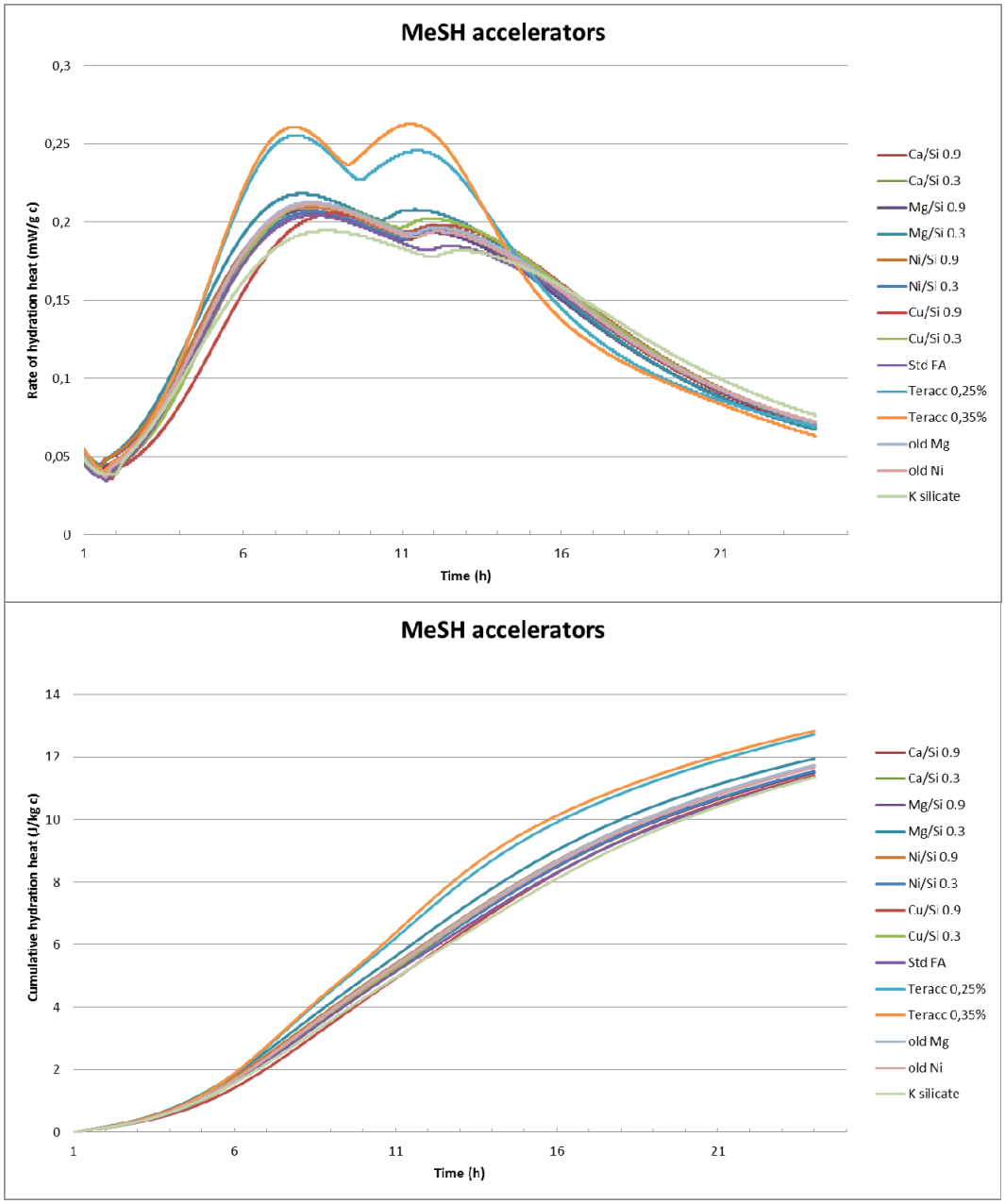

Fig. 3 - The rate of hydration heat at 20°C for 24 h (upper graph) and cumulative hydration heat (lower graph) for 24 h, both isothermally at 20°C for Std FA cement (w/c = 0.50) with a number of accelerators.

The compressive and flexural strength of mortar cured for 1 day at 20°C and for 2 days at 5°C are given in Table 2 and 3 added 0.25% bwoc MeSH accelerators based on sodium silicate and potassium silicate, respectively. Note that the strength of reference mortars without accelerator is slightly different as the cement is taken from different batches, but it is the same within each test series.

Table 2 - The effect of 0.25% MeSH accelerators based on sodium silicate on strength of mortars with fly ash blended cement (w/c = 0.50).

Me in MeSH (Na silicate)	Compressive strength (MPa)		Flexural strength (MPa)	
	1 day at 20°C	2 days at 5°C	1 day at 20°C	2 days at 5°C
- (reference)	17.7±0.3	9.0±0.1	3.8±0.2	2.0±0.1
Mg	20.3±0.3	13.1±0.2	4.1±0.2	2.8±0.1
Ni	19.8±0.4	13.7±0.4	4.1±0.3	3.0±0.0

The results in Table 2 shows that 0.25% bwoc MgSH based on sodium silicate does not fulfil the criterion for a hardening accelerator at 20°C with only 15% increase in compressive strength rather than >20%, but the 5°C criterion of >30% is fulfilled with an increase of 46%. The results for NiSH are similar. At the same time the dosage is very low, so perhaps the strength requirements could have been reached with a higher dosage relative to cement.

Table 3 - The effect of 0.25% MeSH accelerators based on potassium silicate on strength of mortars with fly ash blended cement (w/c = 0.50).

Me in MeSH (K silicate)	Compressive strength (MPa)		Flexural strength (MPa)	
	1 day at 20°C	2 days at 5°C	1 day at 20°C	2 days at 5°C
- (reference)	18.1±0.5	10.3±0.2	3.9±0.2	2.3±0.1
Ca	17.9±0.3	12.1±0.3	3.8±0.2	2.6±0.0
Mg	18.8±0.3	13.2±0.2	4.0±0.2	2.8±0.3
Cu	17.3±0.7	11.8±0.2	4.0±0.2	2.4±0.2
Ni	18.5±0.2	11.8±0.2	4.2±0.1	2.6±0.1

The results in Table 3 shows that 0.25% bwoc MgSH based on potassium silicate is the best of the MeSH tested, but it does not fulfil the criterion for a hardening accelerator at 20°C with only 4% increase in compressive strength rather than >20%, but the 5°C criterion of >30% is barely (within standard deviation) fulfilled with an increase of 28%. At the same time the dosage is very low with 0.25% bwoc, so perhaps the strength requirements could have been reached with a higher dosage relative to cement.

In order to have a proper reference to accelerators based on metal silicate hydrate (MeSH) suspensions, other than mortars with Standard FA cement without accelerator, finally (September 2014) we got hold of MASTER X-SEED 100 which is based on a suspension of calcium silicate hydrate particles thought to act as nucleation sites ("seeds") for the formation of CSH from the cement hydration and thereby accelerate the hydration process (i.e. a dissolution / precipitation mechanism). The compressive and flexural strength are shown in Table 4 for reference mortar and mortar added 0.5% (recommended dosage) of MASTER X-SEED 100 by weight of cement (bwoc) after 1 day curing at 20°C and 2 days curing at 5°C.

Table 4 Strength of mortar with out and with 0.5% MASTER X-SEED 100

MASTER X-SEED 100	Compressive strength (MPa)		Flexural strength (MPa)	
	1 day at 20°C	2 days at 5°C	1 day at 20°C	2 days at 5°C
0% (reference)	16.1±0.4	7.7±0.3	3.4±0.3	1.8±0.1
0.5% bwoc	16.3±0.4	7.5±0.2	3.6±0.1	1.8±0.0

As can be seen from the table above, there was no significant improvement in strength for mortar with fly ash blended cement using this commercial accelerator. The test was done at equal w/c = 0.50 and the spread for the fresh mortar was 185 and 183 mm, respectively for reference mortar and mortar with 0.5% MASTER X-SEED 100. Note that the cement used for the testing of MASTER X-SEED 100 was a different delivery (internal marking Std FA9) than the Standard FA laboratory cement due to the difference in time for testing (about half a year).

4 CONCLUSIONS

The 3rd component in a ternary accelerator consisting of 5 parts glycerol, 10 parts diethanol amine and 15 parts sodium thiocyanate (NaSCN) should be replaced since it is believed to cause rust stains on steel moulds.

Based on isothermal calorimetry and compressive strength measurements on mortar, the best candidate in terms of performance is sodium thiosulphate ($Na_2S_2O_3$) as it also fulfil the requirements to a hardening accelerator at a 0.35% dosage by weight of cement for fly ash blended cement. However, since thiosulphate like thiocyanate is known to form complexes with iron, it is possible that also this component will lead to rust stains on steel as well.

If rust stains still are a problem, it is proposed to change to sodium nitrite ($NaNO_2$) as the 3rd component in the ternary accelerator since this combination barely fulfilled the criteria as hardening accelerator (fell a bit short at 20°C) and is known to be a corrosion inhibitor. If toxicity is a problem, a third alternative is sodium nitrate ($NaNO_3$) that also barely made it but fell short at 20°C.

It is recommended to further work with sodium nitrate and/or sodium nitrite to see if the ternary accelerator could also fulfil the 20°C criterion if the ratio between the components is changed or the dosage relative to cement is increased from the tested 0.35% to for instance 0.50%.

A number of metal silicate hydrate (MeSH) suspensions were tested as accelerators at a dosage of 0.25%, but none performed as well as the ternary accelerators. The most promising MeSH was the one where Me was magnesium. It fulfilled the 5°C criterion of >30% strength increase relative to reference at 2 days with good margin, but fell short for the 20°C criterion of >20% strength increase relative to reference. If the magnesium silicate suspension is to be tested further it is recommended to use sodium silicate as a base rather than potassium silicate, and to perhaps test higher dosages (e.g. 0.5%) relative to cement.

5 References

[1] Kien Dinh Hoang: "Hardening Accelerator for Fly Ash blended Cement", Doctoral Thesis at NTNU (Norwegian University of Science and Technology), Faculty of Engineering Science and Technology, Department of Structural Engineering, 2012:366, 195 pp.

[2] Hoang Kien Dinh [NO]; Geiker, Mette [DK]; Justnes, Harald [NO]; Rudberg, Espen [NO]; Myrdal, Roar [NO]: Hardening-Accelerator and a Method for Accelerating the Hardening of Hydraulic Binders and Mixtures Thereof,, WO2013066192 (A1) — 2013-05-10.

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