Hardening accelerator based on new chemicals, efficient at low temperature in blended cement

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Abstract

The usage of blended cements and also demands for high productivity in building industry even during wintertime increase the need for more efficient hardening accelerator. The industry faces the problem of traditional accelerators not working at low temperatures or a problematic reduction of slump retention due to early setting of matrix.

To address this challenge, the performance of hardening accelerators, as well as in combination with a setting accelerator have been highlighted for their effectiveness in cements blended with slag and fly ash (CEM-II) here. The accelerators were shown to work extremely well at both low 5°C and room temperature, whereby compressive strengths of concrete casted during early hydration were found to be up to 150% higher than without the use of accelerators at low temperature 5°C and 24h. Additionally, the compressive strengths at 28 days were not negatively affected, but increased. No detrimental effect on the concrete slump flow was found, making them ideal for improving the hydration of blended cements.

Extended use of blended cement and reduced heating of the fresh concrete will from an environmentally perspective reduce energy consumption and carbon print from the industry. From an economical perspective a new efficient and well documented accelerator can increase the productivity on site in winter, cost reduction, better quality and increased security in building process.

Originality
New developed accelerator show huge increase in early strength development at low temperature, and will be an important contribution to the development of future casting techniques in areas with low temperature.

Keywords*: Hardening accelerator, casting in low temperature, early strength, blended cement.*

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1. Introduction:

Rapid industrialization is one of the aspects with the highest impact in the economy of our society in terms of addressing the lack of natural raw materials, reducing energy resources and global warming due to emissions of greenhouse gases. All industries worldwide attempts to combat and minimizes these global problems. Among which, concrete is one of the most widely used construction materials where 13-15 % of it is based on cement (Worrell E., et al, 2001). It is primarily the large emissions of CO_2 during the manufacturing of cement that makes concrete labelled with the negative environmental consequences. On a global basis, approximately one ton of CO_2 is released for every ton of cement produce**d** or approximately 300 kg CO_2 per m³ concrete. Both in Norway and internationally, research on how to reduce CO_2 emissions is the main issues. One of the solutions is by reducing the content of ordinary Portland cement (OPC) in concrete by means of using mineral admixtures such as fly ash, silica fume, granulated blast furnace slag, rice-husk ash, metakoalin, etc. (Malhofra V. M., 1999). There are two different kinds of mineral admixtures; one is slow reactive mineral admixture like fly ash, blast furnace slag, etc. while the other consists of highly reactive mineral admixture such as silica fume, metakaolin, etc. It is well known that using such minerals, particularly the former group of mineral in concrete will have a significant influence on the early strength, workability and permeability, etc. Therefore, chemical admixtures are commonly added to rectify this challenge (Hoang K. D.,2012, Justnes H., 2005, Aggoun S., et al, 2008, Xu S., et al, 2009).

One of these additions include the usage of accelerator that can increase the early strength of blended cement containing slow reactive minerals without any negative effect on the rheological properties of the fresh concrete. Many of the accelerators in the market work very well at temperature above 10 °C, but few of them are giving good results at lower temperatures. One of the main problems in Nordic country is that the temperature during winter time is very low for a long time of period. Therefore, the needs of an accelerator that can work well also at low temperatures are a task. Some of the advantages of using accelerators in concrete are, earlier treatment of the surface, earlier removal of molds, reduction of the required period of curing and protection, etc.

In this study three different blended cements from three different suppliers were examined. The early compressive strengths have been conducted both without and with using two different accelerators at two different temperatures. The slump of concrete was measured by using the cone test method.

2. Materials

2.1 Hydraulic binders

In this study, three types of cement have been tested. Norcem Standard Cement FA (CEM II/ A-V 42.5R) acc. to EN 197-1. It is a modified Portland cement containing approximately 20 % pozzolanic fly ash. Cementa Bascement (CEM II/A-V 52.5 N) acc. to EN 197-1, which is a Portland cement with also fly ash. Cemex Environmental cement (CEM II/B-S 52.5 N) acc. to EN 197-1, which is Portland cement with slag. The chemical compositions and physical characteristics of all the three cements are shown in Table 1.

Table 1 Physical properties and chemical compositions of cements %.

Oxide	CEM II/A-V 42.5 R	CEM II/A-V 52.5 N	CEM II/B-S 52.5 N
SiO_2	25.55	23.5	24
Al_2O_3	8.38	6.4	6.5
Fe_2O_3	4.03	3.4	2.0
CaO	51.99	56.3	57
MgO	2.51	2.6	5.3
SO_3	3.69	3.5	3.0
K_2O	1.19	1.2	0.65
Na_2O	0.57	0.3	0.3
Na_2O ekv.	1.4	1.1	0.73
C_3A	-	5.4	5.3
Fly ash	20	12.3	-
Blaine fineness (m^2/kg)	450	445	470
Density (kg/m^3)	2990	3014	3080

2.2 Aggregates

The natural aggregates 0/8 mm, and 8/16 mm used were supplied by NorStone As (Norway). The fine aggregate has a specific gravity of 2.68 kg/dm^3 and water absorption of 0.3 %, while the coarse aggregate has a specific gravity of 2.69 kg/dm^3 and water absorption of 0.4 %. The moisture content of the aggregates was measured on the same day as they were used. The grading curves are shown in Figure 1.

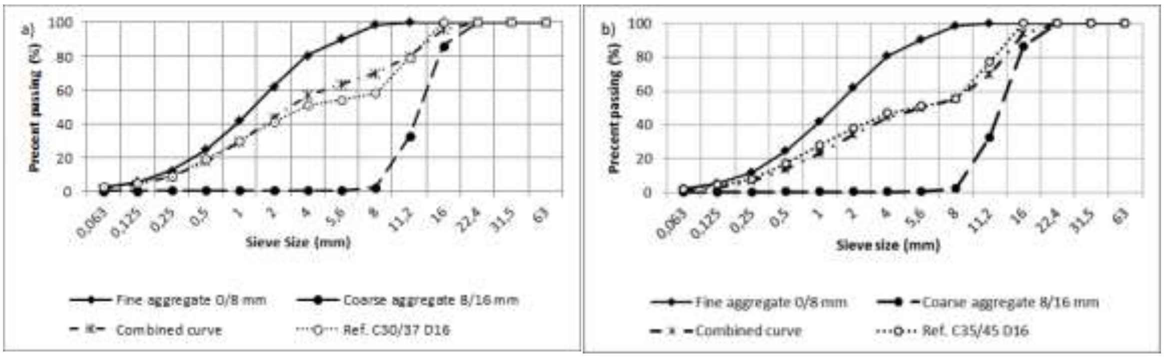

Figure 1 Grading curves of mixtures of fine and coarse aggregates, reference, and a combined curve for a) C30/37 D_{16} concrete, b) C35/45 D_{16} concrete.

2.3 Accelerators

Compressive strength, as well as other structural properties of concrete, depends largely on the degree to which cement hydrates. The main task of this paper is to highlight hardening accelerators for blended cements which was formulated by using chemicals based on the requirement state in EN-934-2. According to standard EN-934-2, a hardening accelerator is defined as: "a chemical that increase at least 120 % of 24 hours compressive strength at 20 °C and at least 130% of 48 hours compressive strength at 5 °C of control mix. In addition, the 28 days compressive strength of the testing samples at both temperatures is not less than 90% of the reference"

Mapefast HA and Mapefast SA are both commercial products produced by Mapei AS. They are hardening and set accelerators for concrete and mortar, respectively and the MSDS can be found in the references. Extensive research has been performed on these admixtures, both in order to determine their behavior and effectiveness on the strength of the concrete. The amount used is given in percentage of superplasticizer relative to cement content.

3. Mixing procedure and mix proportions

A 50 liters Zyklos (ZK 50 HE) mixer from Mischtechnik with a tiltable mixing pan of type "3-D Forced Flow Mixer" is used in (re)mixing the concrete batches, before a rheological measurement is conducted. The concrete volume that was used in this investigation is 25 liters. The mixing procedure for each concrete batch is shown in Table 2, and the mixture proportions of the concrete batches of all three cements are presented in Table 3.

Table 2 Mixing procedure for the concretes

Time (min)	Procedure
00:00 - 02:00	Mixing of aggregate and 50 % of water
02:00 - 04:00	Mixer stop
04:00 - 04:30	Addition of cement and mixing
04:30	Addition of admixtures with the rest of water
04:30 - 07:00	Mixing
07:00 - 09:00	Mixer stop

Table 3 Mixture proportions of the concrete batches for the three cement types. CEM II/A-V 42.5 R, CEM II/A-V 52.5 N, and CEM II/B-S 42.5 N.

Concrete class	Name			Mix. 1 Referance	Mix. 2	Mix. 3	Mix. 4
C30/37	Cement		kg/m^3	422	422	422	422
	NorStone 0/8 mm		kg/m^3	945	945	945	945
	NorStone 8/16 mm		kg/m^3	688	688	688	688
	w/c			0.55	0.55	0.55	0.55
	Dosage admixtures by cement weight	HA	(%)		1	2	1
		SA	(%)				1
C35/45	Cement		kg/m^3	540	540	540	540
	NorStone 0/8 mm		kg/m^3	897	897	897	897
	NorStone 8/16 mm		kg/m^3	623	623	623	623
	w/c			0.44	0.44	0.44	0.44
	Dosage admixtures by cement weight	HA	(%)		1	2	1
		SA	(%)				1

4. Measurements

It is well known that blended cement has low early strength, particular at low temperature. Therefore, three types of cements have been investigated in this study in combinations with various types and or amount of accelerators and the early compressive strength were conducted at both 5 °C and 20 °C.

The slump of the concrete has been measured according to European standard EN 12350-2 by using Abram`s Cone apparatus which consists of a mold in the shape of a truncated metal cone, open at both ends. The internal diameter of the slump cone is 200 mm at the base, 100 mm diameter at the top and has a height of 300 mm. The cone is placed on a hard non-absorbent surface. This cone is filled with fresh concrete in three layers, each approx. one-third of the height of the mold when compacted. Each layer should be compacted with 25 strokes of the tamping rod. At the end of the last layer, concrete is struck off flush to the top of the mold. Thereafter, the mold is lifted vertically upwards and the concrete subsides. This subsidence is termed as slump. The slump flow is determined as the average of the diameter in the X and Y direction.
The compressive strength of concrete of test specimens were measured according to the European standard EN 12390-3. Measurements were performed at 8h, 10h, 12h, 24h and 28 days respectively. The first four measurements were conducted to monitor the rate of increment in compressive strength, particularly at 20°C where variation in compressive strength during the early hours is believed to be greater. 28 days measurements was done to determine the late strength in relation to control as concrete samples with conventional accelerators were known to display a slightly lower compressive strength than control samples (without accelerators) after curing for 28 days.

5. Results and discussions

5.1 Effect of chemicals on compressive strength development of blended cement at low temperature 5 °C:

To scrutinize the influence of chemicals on the hardening process of the concrete, the compressive strength has been measured for concrete class C35/45 and C30/37, with a water to cement ratio equal to 0.44 and 0.55, respectively. The effect of the addition of several accelerators at a concentration of 1 % and 2 % of the cement weight has been scrutinized. The results of the early compressive strength are collected in Figure 2.

It is evident from Figure 2 that after 24 hours; all three concretes prepared with the three cements exhibit an extreme increment in the early compressive strength 100-230 % as compared to the reference sample. For the cements containing fly ash, the increase in the early strength is more pronounced at 2 % of the HA than the others (Figure 2a,b).

The effect of different dosages of HA or different accelerator chemicals are insignificant for the blended cement with slag (Figure 2c). This indicated that 1% HA is sufficient to accelerate the hydration of CEM II/B-S 52.5 N (35 % slag and 65 % clinker) at low temperatures.

The same scenario is obtained for the concrete C30/37 with water to cement ratio equal to 0.55 (Figure 3). The early compressive strength after 24 hours increases with all three cements. It may be noted that the enhancement in strength for concrete containing CEM II/A-V 52.5 N C30/37 is higher than for C35/45, (234 % with 2 % HA in C35/45 versus 462% with the same amount of HA in C30/37). This could be caused by the fact that CEM II/A-V 52.5 N gives lower early compressive strength at higher water to cement ratio than CEM II/A-V 42.5 R. The optimum dosage of the accelerator is also 2% of the cement weight for all three cements.

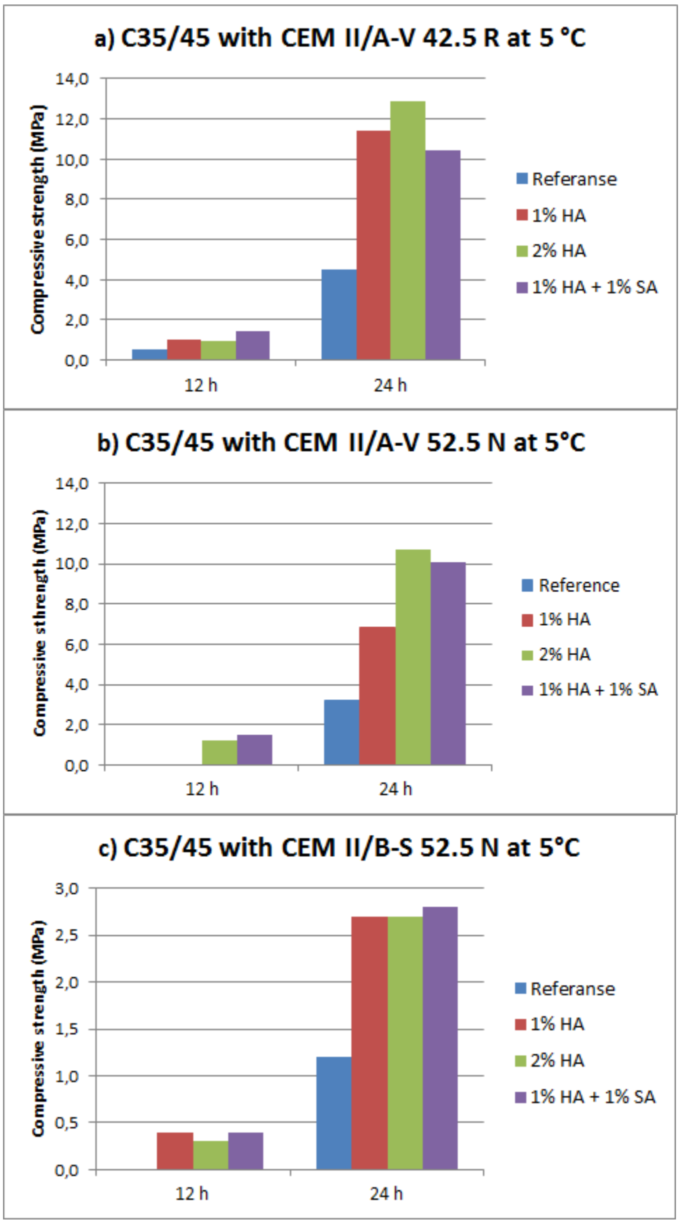

Figure 2 Early compressive strength of C35/45 concrete with the indicated cements with different amount and or types of accelerators at 5 °C.

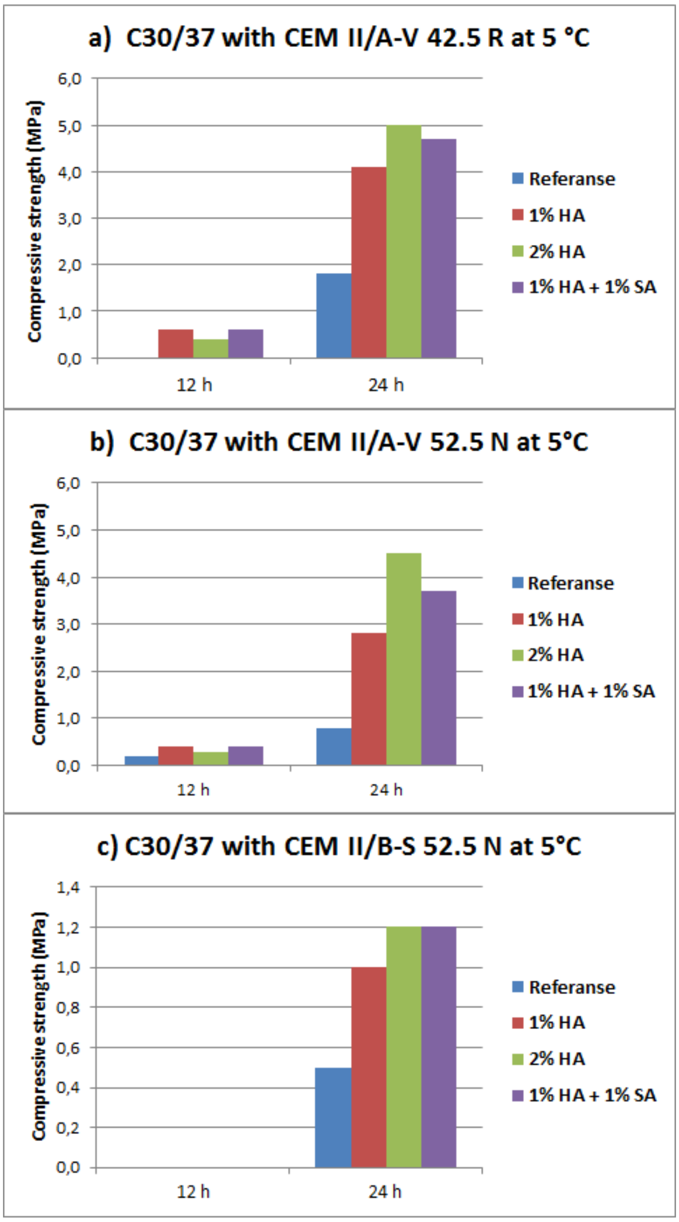

Figure 3 Early compressive strength of C30/37 concrete with the indicated cements with different amount and or types of accelerators at 5 °C.

For more comparison, the 28 days compressive strength of the concrete were determined. It is commonly known that increased early hydration often led to a decrease in 28 days strength. Figure 4 shows the compressive strength of C35/45 and C30/37 after 28 days at 5 °C with and without different amount and types of accelerators. Instead of the common observation where a decrease of up to 10% in strength after addition of accelerator, an enhancement of the compressive strengths with 1 % HA was observed. In comparison, the improvement is more pronounced for CEM II/A-V 52.5 N and CEM II/B-S 52.5 N than CEM II/A-V 42.5 R in both concrete classes. This illustrate that slag may be more susceptible to the accelerating effect from the accelerators. Figure 4a showing a significant drop of the strength for C35/45 concrete with 2 % HA for all three cements.

For concrete with higher water to cement ratio, an increase in the strength is observed for all cement types and the accelerator amounts or types have not negatively affected the compressive strength.

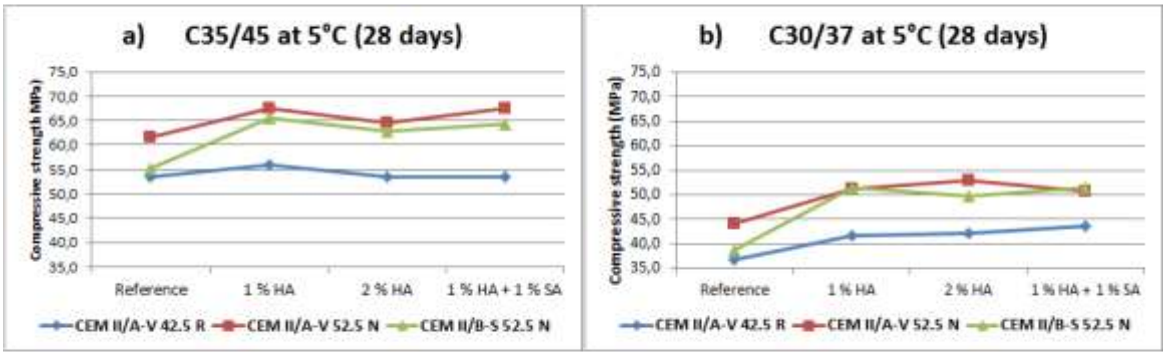

Figure 4 The compressive strength of C35/45 and C30/37 concrete with the indicated cements with different amount and or types of accelerators after 28 days at 5 °C.

5.2 Effect of chemicals on compressive strength development of blended cement at low temperature 20 °C:

The compressive strengths of the concrete samples were measured at 20°C next. It is clear that the early compressive strength of concrete with accelerators were much higher than the concrete without accelerators. The results showing an increase in the compressive strength by 200- 300 % for CEM II/A-V just after 8 hours. For the cement with fly ash, the compressive strength was over 5 MPa after only 8 hours while for the cement with slag more time is needed (10 hours).

Figure 5 illustrate the early compressive strength of C35/45 concrete with water to cement ratio equal to 0.44 with different amount and types of accelerator. Figure 5a showing that the optimal dosage of HA is 1 % of the cement weight for the cement CEM II/A-V 42.5 R, while for the cement CEM II/A-V 52.5 N is 2 % HA. This could be caused by the amount of the clinker in the cement, the CEM II/A-V 42.5 R containing 80 % clinker while the CEM II/A-V 52.5 N containing 88 % clinker, (Figure 5b).

For the cement with slag, results showed an optimal performance at an accelerator dosage of 1 % HA according to our studies (Figure 5c). This cement contains 65% clinker only and further investigation should be done to confirm the real optimal dosage for this kind of cement.

After 10 hours, the strength of concrete was enhanced by around 150-200 % for all three cements compared to that of the reference.

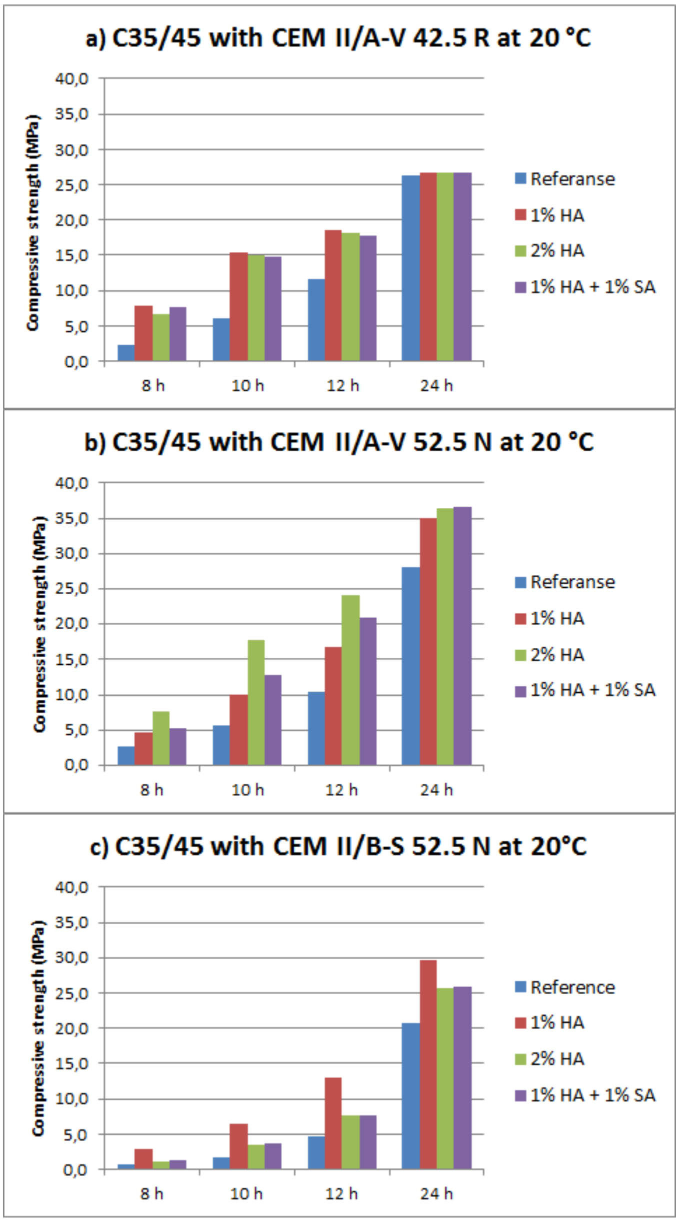

Figure 5 Early compressive strength of C35/45 concrete with the indicated cements with different amount and or types of accelerators at 20 °C.

For C30/37 concrete, the addition of accelerators shows an increasing of the early strength around 100-150 %. Figure 6 shows the early strength of concrete with different blended cements and different amount and types of accelerators. It is obvious that concrete with higher amount of water needs longer time to reach strength of 5 MPa than concrete with lower water amount. Figure 6a,b display a strength above 5 MPa for blended cement with fly ash after 10 hours. For the cement with slag, more times is needed to obtain this strength. The results showing that after 24 hours, the strength of about 12-14 MPa is reached for CEM II/B-S.

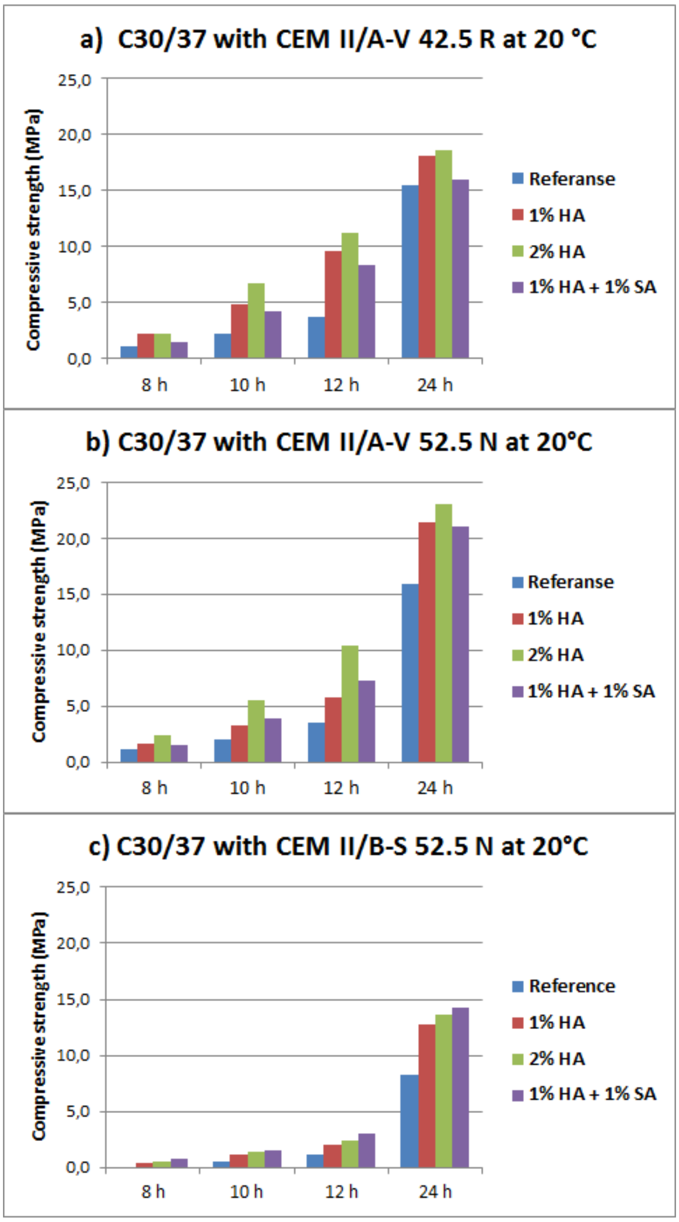

Figure 6 Early compressive strength of C30/37 concrete with the indicated cements with different amount and or types of accelerators at 20 °C.

Figure 7 shows the strength of concrete at the age of 28 days for all three blended cement for C35/45 and C30/37. The strength is increased by 1 % addition of accelerator for all blended cements and different concrete classes. It is evident from Figure 7a that addition of 2 % of accelerator HA for C35/45 will affect the strength of concrete in a negative way. A big drop is observed for all three cements at this concentration. The drop is not observed for concrete with higher water amount, potentially attributing the effect seen at lower w/c to be a lack of water in the concrete as mediators.

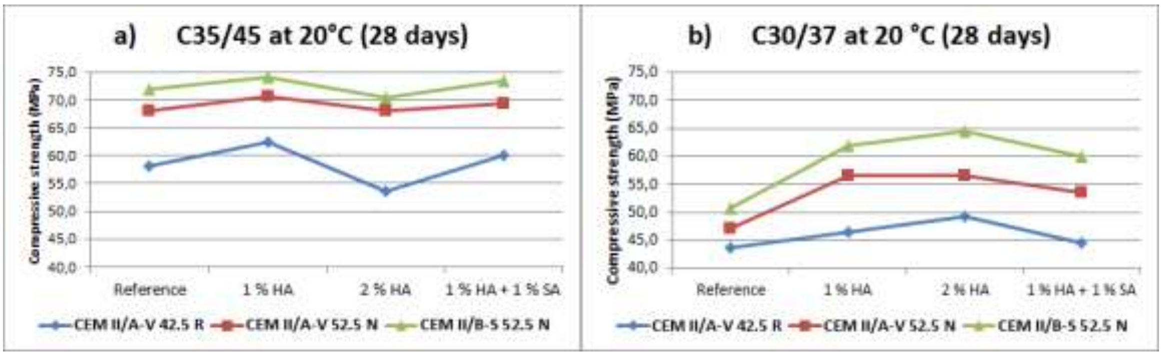

Figure 7 The compressive strength of C35/45 and C30/37 concrete with the indicated cements with different amount and or types of accelerators after 28 days at 20 °C.

5.3 Effect of chemicals accelerators on the slump of the concrete with blended cement:

Figure 8 illustrate the slump values measured after 5 min for all concrete mixes. Figure 8 a,b divulges that there are only minor changes of the slump values for the different cements types and amount of the accelerators. It is well known that the slump values conducted by using a cone test method have an error of 10 mm, taking these values in our calculation; the values of slumps were not affected by adding accelerators.

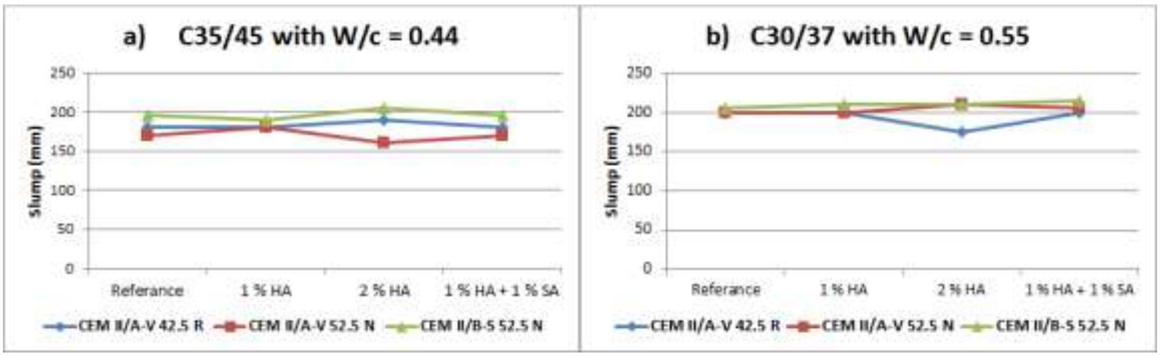

Figure 8 Effect of different accelerators with the concentration indicated on the slump for the cements indicated for both C35/45 and C30/37 concrete classes.

6. Conclusions

- The accelerators give a significant increasing of the early compressive strength at both low and normal temperatures.
- The optimum dosage of the accelerator HA is very much depending on the cement type, temperature, and concrete class.
- The accelerators will not affect the strength after 28 days significantly. An increasing of the strength after 28 days is obtained for all kind of cement and concrete class with 1 % HA.
- It has been found that the use of accelerators can enhance the early strength of concrete without any influence on the flowability of the fresh concrete.

Acknowledgments

The authors want to acknowledge COIN (Concrete Innovation center, www.coinweb.no) for development of HA product and facilitating the research behind this paper.

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