THE USE OF ANTI-FREEZE AGENTS

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Introduction

The principle idea behind the use of anti-freezing agents is to prevent water from turning into ice. As long as water is in liquid form, the hydration process will continue. Cement and water react to form fibres and thus contribute to the strength development of the cement based product. This process is extremely dependent on temperature, so the process is significantly slowed down as temperatures drop.

When an anti-freeze agent is added to the water, it disturbs the formation of structures enabling the water turn into a solid (i.e. ice). Different chemicals can be used, and their efficiency as anti-freezing agents is varying.

- Calcium chloride ($CaCl_2$),
- sodium chloride (NaCl),
- sodium nitrate ($NaNO_3$),
- calcium nitrate ($Ca(NO_3)_2$),
- potassic carbonate (K_2CO_3),
- ethylene glycol ($C_2H_6O_2$),
- sodium formate (HCOONa).

As for potassic carbonate (potash), its influence on the setting (unreliable, but normally very fast setting) and for ethylene glycol in sufficient amount, a strong retardation – these products are normally not used. And though both sodium and calcium chlorides will be efficient to lower the water's freezing point, water soluble chlorides are not to be used in concrete structures containing reinforcement (corrosion).

Experimental setup

We have tested anti-freeze agents in concretes based on aggregates up to 8 mm, with different cement types, and at water to cement ratios of 0.51 to 0.57. Mixing of approximately 6 litres batches by drill and whisk in a bucket. The "mini"concrete ("finsats") is cast in forms 70.7 x 70.7 x 70.7 mm and immediately placed covered by plastic sheets in rooms with ambient temperatures of +20 °C, +5 °C, -5 °C and -10 °C. 5 hours prior to the testing of compressive strengths, all specimens are placed in test room at +20 °C.

Initially we tested setting time (Vicat measurements) for sodium nitrate based anti-freeze agent in standard mortar with water to cement ratio of 0.50. In two different cements (CEM I 42.5 and CEM II A/V 42.5) there were no significant difference in setting time between reference mortars with no admixture and one with 15 % of a 42 % solution of sodium nitrate. What was also revealed was that compressive strengths are significantly reduced when adding sodium nitrate. We registered a reduction of compressive strengths of approximately 1/3 after 24 hours and between 23 and 28 % after 28 days for test specimens cured at 20 °C.

The use of sodium nitrate

Two dosages of pure sodium nitrate in “mini”concrete with water to cement ratio of 0.57 were tested (3 % and 6 % of active matter by cement weight). The specimens were stored at +20 °C and - 10°C. Again, we found a loss in compressive strengths for cubes stored at 20 °C, more in CEM II than in CEM I cements. Obviously the sodium nitrate affects the formation of C-S-H gel in a negative way, so the established structures are weaker than for the reference without admixtures.

The point with an anti-freeze agent is to establish a compressive strength even when temperatures in the mass drop below zero.
For Norcem Standard (CEM I-cement) we got practically no strength at all in the reference after 28 days at - 10°C, the lower dosage (3 %) gave 6.6 and 10.8 N/mm² after 7 and 28 days, while with double dosage, the compressive strength had increased to 8.0 and 13.6 N/mm² respectively. None of the tests yielded strengths at 24 hours.
For Norcem Standard FA (CEM II with fly ash), we again got no strength in the reference, while both low and high dosages with sodium nitrate showed acceptable compressive strength after 7 and 28 days. 3 % SN with 5.8 and 8.6 N/mm² and 6 % SN 7.6 and 12.8 N/mm².

Conclusion:
Sodium nitrate is an efficient anti-freeze agent that in dosages as low as 3 % of active matter decreases the freezing point to a level that permits a concrete’s temperature to drop to -10 °C. But, the final strength of such concrete is affected by the addition of sodium nitrate.

The use of sodium formate

Sodium formate is at product available in powder and I solution (30 %), Precipitation can occur (for liquid) if stored below 15 °C. The product is hygroscopic (solids) so it must be stored dry to avoid caking. Its normal use is as an intermediate product for sodium hydrosulphite and formic acid, and for leather tanning and enzymic stabilizer in detergents. We have made a 40 % liquid solution and tested it in “mini”concrete with two cement types (CEM I – 52.5 R and CEM II A/V 42.5) with water to cement ratio of 0.57 - dosages of 2 % and 4 % of active matter.

At 20 °C we the same tendency as with sodium nitrate, that the compressive strengths are reduced with increased dosage of sodium formate. After 28 days, the highest dosage reduced the compressive strength (same w/c-ratio) with 14 and 23 % for CEM II and CEM I respectively. On the other hand, the workability, which was unchanged with sodium nitrate, was slightly improved with sodium formate. This indicates that it might be possible to reduce the water to cement ratio, compensating some of the loss of strength (only marginally).

The reference with CEM II –cement gave no strength until 28 days, while the use of CEM I yilded strength with the addition of sodium formate already after 24 hours. The achieved strengths are though very modest - 1.4 and 1.2 N/mm².

The CEM II-mixes gave 7 and 28 days compressive strengths of 4.4 and 9.2 N/mm² for “low” dosage, and 6.0 and 11.2 N/mm² with “high” dosage. The CEM I – a rapid cement – gave 7.6 and 10.6 N/mm² at 2 % dosage and 8.6 and 15.4 N/mm² with 4 % addition.

Conclusion:
Sodium formate works as a anti-freeze agent. The dosage of 2 % of active matter yields results comparable to 3 % of sodium nitrate. But while an increase in dosage of sodium nitrate gives you higher strengths, the double of sodium formate only marginally increases the compressive strengths. And as for sodium nitrate, the "final" strengths are reduced when you use sodium formate.

The use of calcium nitrate

Calcium nitrate is an admixture used mainly to reduce the setting time of concrete. In flooring, the normal dosage of calcium nitrate is 0,5 to 1.0 % by weight of cement (active matter). The product is available in liquid solution of 50 % solids. Investigations done at SINTEF in Trondheim suggest that it can also be used as an anti-freeze agent. Their experimental setup differs though a lot from other tests, so comparable results are not available. The aim in their tests were to "prove" that by adding a sufficient amount of calcium nitrate, the concrete would reach a compressive strength of 5 N/mm² before it was allowed to freeze. The conclusion of their test: "A set up with 27 litre plywood box (either insulated or not) placed in a freeze of set temperature and with concrete cores drilled out after 17 h seems to be working fine and are closer to practice than any other test. In this set-up calcium nitrate seems to be working as an "anti-freeze" by starting heat of hydration earlier and thus preventing too much cooling of the concrete so it will not set before freezing. Concrete can withstand freezing when compressive strength is > 5 Mpa. CN is however working by indirect set accelerator effect, but is still sold as "anti-freeze"."

The dosages used in the SINTEF tests showed that there is a need of higher dosages. We performed tests similar to the ones for sodium nitrate and sodium formate with a dosage of 3,75 % (solids) by weight of cement (CEM I – 42.5). The workability was slightly reduced, but these were the results (in parentheses the results with 3 % Antifreeze N):
At 20 °C:

24 hrs	9.2 (14.0)
7 days	38.2 (29.8)
28 days	43.0 (36.0)

What is interesting here is of course the fact that CN does not reduce the compressive strengths – even with such high dosages.

At - 10°C

24 hrs	0.9 (0)
7 days	2.4 (6.8)
28 days	4.4 (11.4)

Conclusion:
The test results clearly indicate that calcium nitrate is not very efficient as an anti-freeze agent. If used as such, additional measurements must get priority – warm concrete, insulation et cetera. These are activities that will normally make an anti-freeze agent superfluous in all cases.

Combination products.

To counteract the loss of strength, we have tested a combination of sodium nitrate, which acts as an efficient anti-freeze agent, and a superplasticizer to reduce the water to cement ratio. There are quite a number of possible combination, both in the choice of superplasticizer and in the ratio between the anti-freezing agent and the superplasticizer. From testing of different possibilities, we have developed a new product, called Antifreeze N/10.

Tests are performed in the same way as previously. The point is to reduce the water to cement ratio and maintain the same workability. An increase in dosage of Antifreeze N/10 is to be followed by a reduction of added water. We have tested this in three different types of cement (CEM I – 42.5, CEM I – 52.5R and CEM II A/V 42.5) and stored at three different ambient temperatures -10°C, + 5 °C and +20°C, and with dosages varying from 5 to 15 % (40 % solution).

The results are not fully consistent, but the tendency is clear – Antifreeze N/10 reduces the negative effect of sodium nitrate on the compressive strength significantly:

These are the relative strengths at 20 °C when CEM I 42.5 is used.

	No admixture	Antifreeze N		Antifreeze N/10	
	Dosages	7.5%	15.0%	7.5 %	15.0 %
24 hours strength	100	113	81	126	129
7 days	100	88	70	93	91
28 days	100	88	76	94	91

The results at -10 °C are of course as important:

	No admixture	Antifreeze N		Antifreeze N/10	
	Dosages	7.5%	15.0%	7.5 %	15.0 %
24 h strength	0	0	0	0.9	0.9
7 days	0	6.8	8.4	5.2	10.2
28 days	1.6	11.4	15.0	9.2	15.6

This shows that both Antifreeze N and Antifreeze N/10 are efficient anti-freezing agents and that increasing dosages have an effect.

The water reduction by the use of Antifreeze N/10 is approximately this:

Dosage Antifreeze N/10 (%)	Water reduction (%)
5	5
10	11
15	18

Test results from CEM I 52.5 R and CEM II A/V 42.5, stored at – 10°C

	CEM I – 52.5 R		CEM II A/V 42.5	
	5 %	10 %	5 %	10 %
24 h strength	1.2	1.2	0	1.0
7 days	4.2	9.2	3.2	7.0
28 days	8.0	13.0	7.6	10.6

Even at dosages as low as 5 % (i.e. 2% of active matter) it is possible to achieve some compressive strengths after one or two days, but it is recommended to increase the dosage so as to reach the "safe" lower limit of 5 N/mm² to allow the concrete to freeze without seriously damaging the final compressive strength.

Conclusion:

Of the different anti-freezing agents we have tested, the sodium nitrate performs best relative to its expenses. The newly developed product Antifreeze N/10 is a way of securing a final strength that is not reduced significantly, as can be the case with any anti-freezing agent.

Recommended dosages of Antifreeze N and Antifreeze N/10 (approximately 40 % solution):

Ambient temperature	**Dosages (in % of cement weight)**	
	w/c-ratio < 0.45	**w/c-ratio > 0.45**
Down to - 5 °C	**4**	**5**
Down to – 10 ° C	**7**	**8**
Down to – 15 ° C	**10**	**12**

The necessary dosage can be reduced by 1 % when using a CEM I – 52.5 R (rapid cement)