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# Calcium Nitrate as admixture for concrete brick production

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## ABSTRACT.

*This paper wants to stimulate knowledge transfer from ready mix concrete to concrete brick and element production. The production of concrete elements and bricks needs to be sustainable and cost efficient, and admixtures can help to reach this objectives. Especially partial replacement of steam curing by use of admixtures can be interesting, too. A potential candidate for such an admixture is Calcium Nitrate that is today mostly used as stand-alone admixture or part of formulations in ready mix concrete.*

*KEYWORDS: Calcium Nitrate, accelerator, setting*

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## 1. Introduction

The production of concrete elements and bricks needs to be sustainable and cost efficient. Admixtures can help to reach these objectives.

A major improvement regarding sustainability comes from today's cement types. Those incorporate increasingly amounts of cement replacement materials (CRMs). CRMs like fly ash, lime stone or ground granulated blast furnace slag are helpful to reduce the CO<sub>2</sub> footprint, improve durability and reduce material cost. Consequently a variety of blended cements from CEM II/A to CEM III/B are available and in use. The downside of CRMs is the overall reduced reactivity, based on the fact that those materials in itself are usually not reactive. The CRMs need to be activated in a secondary reaction, generally by the rise of pH value due to the cement hydration process. Thus the wanted effect of reduction of CO<sub>2</sub> footprint comes usually at the price of reduced performance. In case of industrial production of concrete elements, like in pre-cast industry and masonry brick production, this leads to increased production cost.

Consequently and in order to maintain production rates, measures of acceleration are needed. Of course measures that don't increase cost would be preferred. Both steam curing and use of chemicals are measures to increase production rate and by that reduce overall cost.

Steam usually needs to be produced by energy conversion and comes as a cost. Additionally, steam can support the hydration process of cement, but does not improve the concrete properties. Thus steam is basically working as a hardening accelerator.

Different chemical accelerators can be used in dependency of reinforcement and concreting best practice. The classic accelerator is calcium chloride that is corrosive for all types of reinforcement – what limits its use. A second common accelerator is calcium formate that is not corrosive but comparatively expensive. The third group of accelerators is nitrate based. Those can be complex, like BASF's X-Seed, or rather simple, like plain Calcium Nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>; "CN").

## 2. Calcium Nitrate application in ready mix concrete

Today CN is used as ingredient in concrete admixtures for ready mix concrete in accordance with EN 934-2.

CN is in the first place established as setting accelerators for ready mix concrete. It is used especially when a non-corrosive, non-hazardous accelerator is needed, that also can (unlike sodium nitrate) maintain long term compressive strength. Various studies from JUSTNES and NYGAARD (1994) to CULLU and ARSLAN (2013) described the use of CN as setting accelerator at different temperatures and in different regions. And there seems to be a synergy with some super plasticizers as

well, as JUSTNES and FRANKE (2014), giving much shorter setting times than for CN application alone.

Furthermore JUSTNES and DAHL (1999) found that CN reduces the drying shrinkage of concrete by early surface hydration and by that in addition reduces surface cracking. This was also observed in a study regarding wall elements, presented by JUSTNES (2010). When it comes to durability, studies by AL-AMOUDI et al (2003), BALONIS et al. (2011) or JUSTNES (2004) documented the corrosion inhibitor effect. Additionally JUSTNES et al. (2001) investigated the increase of long term compressive strength. FRANKE et al. (2014) indicated that there is also a positive effect on the freeze-thaw-resistance, when CN and an air entrainer are used in combination.

### **3. Potential benefits of Calcium Nitrate in element production**

CN can alter some properties of concrete besides reducing setting time. For the element production relevant are reduced surface shrinkage (leading to improved surface quality) and increased long term compressive strength. Those effects are expected to happen for dosage levels of 0.5%-2% by weight of cement (bwoc.). Setting time reduction is in the range from 1 hour to 4 hours depending on the cement type and ambient temperature. Also the combined use of a super plasticizer and CN might show a synergy in an even further reduction of setting time, what might be especially for self-compacting concrete interesting.

The setting time acceleration can be beneficial in two ways.

1. The overall time of a production cycle can be reduced. Commonly steam curing is applied after the concrete started to set. Thus the longer setting takes, the longer takes the cycle. But today's blended cements are increasing setting time. Thus a set accelerator can counteract such delay.
2. The demand to intensify the hardening by steaming can be reduced. By shortening the setting time, the hardening time can be longer and less intense for a given cycle time. Therefore less steam is needed as hardening can happen at a lower temperature.

### **4. Case study: Calcium Nitrate effect on hydration reactions**

A lab experiment is conducted regarding the hydration temperature of cement paste. Temperature is considered a good indication for the progress of the hydration reactions.

Cement of the type CEM II/A-V 42.5 (Norcem Standard FA) is used. The paste is prepared with w/c-ratio of 0.5, including the water coming from the admixtures.

Technical quality CN is added as 50% solution (Yara NitCal 50), and dosages are 1% and 2% of active ingredients and bwoc. (meaning 2% and 4% of product are added). Each cement paste sample has a volume of 500 ml. Temperature is measured with PT-100 sensors (Danfoss MBT 153 – 4 wire) and monitored with a data logger (E&H Memograph). Experiments are conducted at 20°C (ambient temperature in the lab) and 30°C/40°C/50°C in a water bath with temperature control. Temperature is observed over 24 hours.

The results are plotted in the figures 1 and 2.

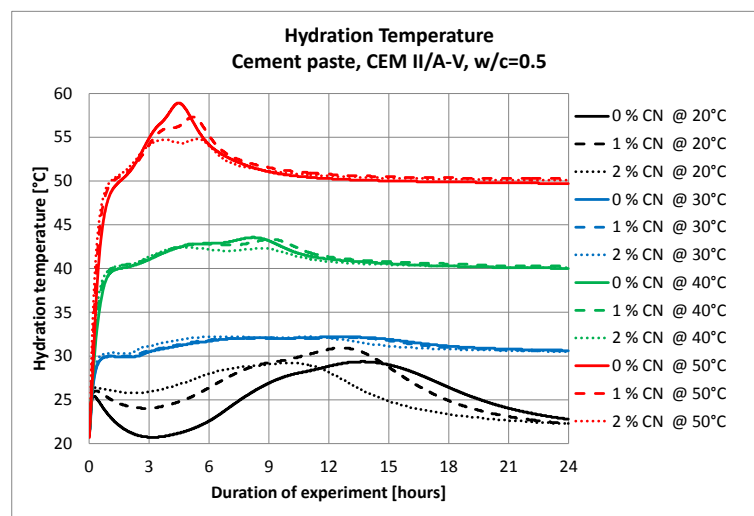


Figure 1. Hydration temperature, presented in linear time scale

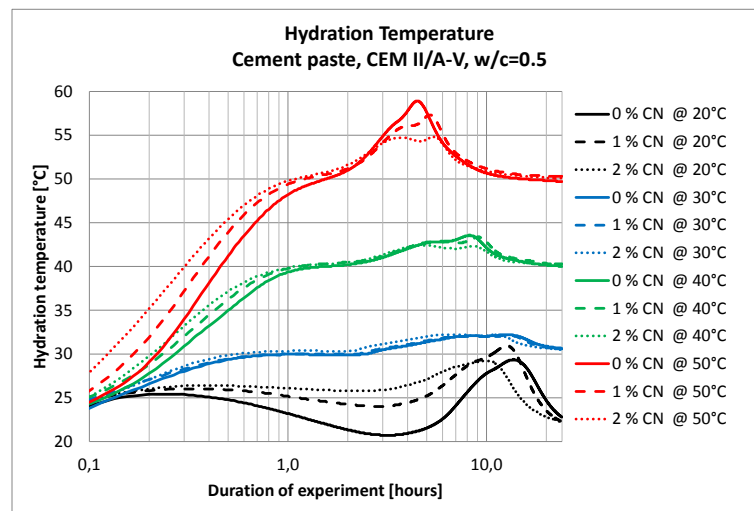


Figure 2. Hydration temperature, presented in logarithmic time scale

Setting acceleration of several hours can be observed at 20°C, as the incline of temperature starts earlier and also the peak temperature is reached earlier, too.

Hardly any effect can be observed for 30°C.

For higher temperatures this changes, and the setting acceleration effect is reduced to approximately 1 hour. But more important, reactions are shifted from the hydration peak stage to the hydration incline stage. With increasing ambient temperature the peak temperature is cut off; at 40°C the maximum is reduced by 2°C and at 50°C the maximum is reduced by 5°C.

In this experiment the combination of 2% of CN and 50°C as heating temperature leads to earlier setting, compared to 30°C or 40°C environments, and avoids overheating above 55°C and thus delayed ettringite formation. The reactions in the 50°C environment stopped mostly at 12 hours and for 40°C at 18 hours respectively. Energy demand (heating up by 30 K instead of 20 K) is balanced, as the duration is shorter (12 versus 18 hours). Thus CN does not affect the energy balance significantly, it just controls certain cement timing.

An additional benefit can arise from reducing the heating after the peak heat is reached. In this experiment heating might have reduced for 50°C environment after 3 hours already, whereas for 40°C it would have been 5 hours respectively.

Concluding, the CN addition of 2% provides earlier setting. Additionally the system can be heated up comparatively high, and the CN leads to a reduction of the peak heat.

## 5. Case study: Calcium Nitrate effect on curing costs

For pre-cast steam curing purposes the temperature is typically increased up to a level of 50°C. Assuming an ambient temperature of 20°C, this means the steam needs to provide the energy to rise the temperature by 30°C or 30 K. Common concrete has a heat capacity of about 900 J/(kg\*K). This translates into an energy demand of  $30 \cdot 900 \text{ J/kg} = 27 \text{ kJ/kg}$  concrete for steam curing. Bearing in mind the conversion  $1 \text{ kJ} = 0.00027 \text{ kWh}$ , the heat demand is about 7.3 kWh/kg concrete. With an average price for electricity of 0.07 €/kWh the resulting costs are approximately 0.5 €/t for steam curing. This does not include any losses due to conversion electricity/steam as well as heat transfer and the actual heating up process of the concrete. Estimating the overall efficiency with 80% the costs are probably 0.6 €/(t\*h).

CN as an admixture has a market price of 500 – 1,000 €/t as certified products. This translates to a price for the active ingredient of 250 – 500 €/t for a 45% or 50% solution, and an average of 375 €/t CN. Concrete is commonly produced by using about 350 kg of cement per m<sup>3</sup> that will have an average density of about 2.3 t/m<sup>3</sup>.

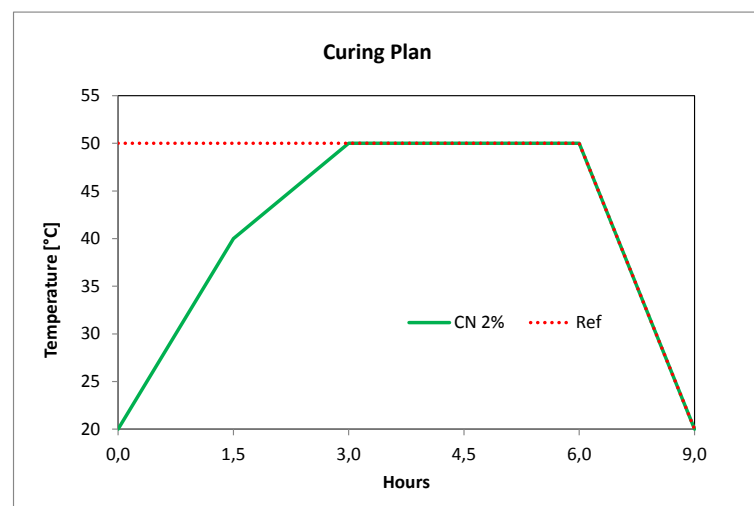
The dosage of CN is commonly 1% bwoc.. Therefore a dosage of 3.5 kg CN for the production of 2,300 kg concrete is usually recommended. The resulting costs are in average perhaps 0.6 €/t.

In this hypothetical example, it becomes obvious that steam curing costs at least 0.6 €/(t\*h), and the addition of CN costs probably 0.6 €/t. For a time saving of at least 1 hour both techniques lead to similar costs. In cases of higher time saving – what is especially for blended cements to be expected - the cost benefit of partly replacing or combining steam curing with CN addition becomes obvious.

This example does not reflect the investment cost for the casting system though. But it is obvious that increasing the number of shifts per day can reduce the cost per element. Thus the combined use of CN (setting acceleration) and steam (hardening acceleration) can increase the factory productivity. And besides of that, product properties can be improved as well (surface quality, compressive strength).

The observed setting acceleration allows modifying the curing plan, too. In a second hypothetical case the total curing plan foresees 9 hours per shift, what includes 3 hours cooling time. According to hydration curves, it should be possible to have a two-step curing process, to reach 50°C target temperature and use CN as an admixture. The curing plan is given in Figure 3.

Based on cost estimations above, overall cost of 2 step curing would be 1,6 €/t comparing to 3,8 €/t for normal curing (constant temperature). Adding 1,2 €/t cost of CN (for 2% bwoc.) to the total cost, but reducing the energy consumption following the reduced temperatures, gives a saving of 1 €/t. In addition this method reduces the risk of elevated temperature at the hydration peak and gives an overall smoother hydration process.



**Figure 3.** Hydration temperature, presented in logarithmic time scale

## 5. Conclusions

CN is an established admixture for ready mix concrete, and element production might benefit from some effects, too. From theoretical and experimental point of view, the use of CN can improve the product surface quality and compressive strength. Also the heat peak can be reduced.

Taking the overall process in account, a case specific combination of steam curing and CN admixture addition can enable to minimize cost, reduce peak hydration heat, reduce energy consumption and optimize production cycle time. This can be used for instance to increase productivity of a factory. Of course it might be also used to optimize the production rate when blended cement types are used.

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