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Experimental Study on Properties of Hydraulic Mortars with Mixed in Crystallisation Inhibitors

Ameya Kamat(✉), Barbara Lubelli, and Erik Schlangen

Delft University of Technology, Delft, The Netherlands
a.a.kamat@tudelft.nl

Abstract. Sodium chloride (NaCl) is one of the most commonly occurring weathering agents, responsible for a progressive damage in mortar. Current solutions to mitigate salt damage in mortar, such as the use of mixed-in water repellent additives, have often exhibited low compatibility with the existing building fabric. In the last years, research has shown promising results in mitigating salt decay by making use of crystallisation inhibitors. Sodium ferrocyanide is one of the inhibitors that has proven to be particularly effective to reduce damage due to sodium chloride crystallisation.

In this research the possibility of developing hydraulic mortars with mixed-in inhibitor (sodium ferrocyanide) for an improved resistance to sodium chloride crystallisation damage is investigated. As a first step, the interaction between the inhibitor and the hydraulic binder: natural hydraulic lime (NHL), was studied; the results are presented in this paper. Various concentrations of sodium ferrocyanide were tested (0%, 0.1% and 1% by binder weight). The effect of the inhibitor on several physical (hydration, water absorption, pore size distribution) and mechanical (compressive and flexural strength) properties was experimentally assessed, using several complementary methods and techniques. The results show that the addition of the sodium ferrocyanide does not affect the fresh and hardened properties of mortar. These results are promising and open new possibilities for the application of inhibitors to improve the durability of hydraulic mortars.

Keywords: Repair mortars · Natural hydraulic lime · crystallisation inhibitor · salt damage · sodium chloride · sodium ferrocyanide · conservation

1 Introduction

Salt crystallisation is a common cause of decay in historic buildings. Among damaging salts found in historic buildings, sodium chloride is one of the frequently occuring, due to its multiple sources [1]. Plasters and renders, as well as pointing mortars, particularly suffer from salt decay. Their high susceptibility is due to several reasons. First of all, they lie at the surface of construction, where most of the salts accumulate, and they are exposed to the environment (wind, sea salt spray, RH and T changes). Moreover, these materials have a bimodal pore size distribution with coarse and fine pores, which can lead to a development of high crystallisation pressure. Traditional air lime-based mortars have a limited mechanical strength, which can be easily overcome by the pressure developed

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due to salt crystallisation. Salt damage in mortars manifests in the form of loss of surface cohesion (powdering, scaling, spalling etc.) or loss of adhesion between the mortar and the substrate or between the mortar and the paint layer on top.

Current solutions to improve the durability of mortars to salt crystallisation damage involve the use of cement as binder, to increase the mechanical strength, or the addition of water repellent additives in the mass, to reduce the ingress of salt solution in the mortar. However, these solutions have often a low compatibility with the existing, historic fabric, worsening the problem they were supposed to solve [2].

In order to further improve the durability of mortars to salt decay the use of crystallisation inhibitors has been considered in the past years, as a novel approach to mitigate salt crystallisation damage. Crystallisation inhibitors are chemicals that tweak the process of crystallisation by delaying the nucleation and/or by altering the crystal habit [3]. Such crystallisation inhibitors are often salt specific, i.e. they are effective only for a specific salts.

Alkali ferrocyanides (FeCN), which are common anti-caking agents of NaCl, have shown to be particularly effective in inhibiting the growth of sodium chloride (NaCl) crystals [4]. Application of FeCN solution in porous building materials has also shown to modify NaCl crystallisation in a way which can limit salt decay. A study with FeCN solution in NaCl contaminated bricks reported a delay in nucleation of the salt, enabling higher advection of salt ions to the evaporating surface [5]. Other researchers reported an increase in the amount of harmless efflorescence, confirming the above mentioned enhancing of salt transport to the surface [6–8]. FeCN modifies the crystal habit of the NaCl crystal, from cubic to dendritic; this habit change also contributes to enhanced salt transport via creeping (i.e. the self-amplifying transport mechanism by which salt solution is transported along growing crystallite tips) [9]. The application of FeCN in lime mortar was observed to lead to a higher nucleation density and smaller crystals, possibly leading to a lower pore clogging. Thus, leading to a positive effect on salt transport and lowering of crystallisation pressures [10]. In early studies, FeCN was introduced along with NaCl to building materials via capillary suction. However, it was shown that FeCN was effective only during the nucleation stage and had negligible effect on dissolution of already present salt crystals [6]. Thus, addition of FeCN before NaCl ingress can be a solution to prevent salt damage. This has been first tested in hydrated lime-based mortars by adding FeCN directly during the mixing of the mortar [11, 12]. This application of inhibitor offers an advantage that the FeCN ions are already distributed in the mortar and can react to salt ingress at an early stage, preventing or effectively reducing salt crystallisation damage. Granneman et al. report that the mortar with the FeCN inhibitor showed an increased resistance with respect to the reference mortar, after an accelerated crystallisation test, while not showing any change in other relevant physical and mechanical properties [12, 13]. On the other hand, Natural hydraulic lime-based mortars can offer a good compromise, having both sufficient durability and compatibility with the historic, valuable materials [14].

Mortars based on hydrated lime, although ideal from the point of compatibility with historic building fabric, have still a quite limited durability and require thus frequent maintenance, resulting in high costs. Owing to these issues, in the field of conservation of historic buildings, hydraulic binders such as natural hydraulic lime (NHL) are more often used, as they generally provide a better durability while keeping a good compatibility with the existing historic materials. This research investigates the possibility of mixing in FeCN inhibitor in NHL based mortars, and assess whether any interaction between the inhibitor and the hydraulic components of the binder occurs, possibly altering the propertied of the fresh and hardened mortar.

Unlike air lime which gains its strength via carbonation, hydraulic mortars also involve the process of hydration i.e. the exothermic reaction between binder and water. Thus, microstructure development and material behaviour of NHL and air lime are different and the possible effects of the inhibitor is still unknown. This needs to be carefully investigated as first step towards the development of mortars with mixed-in crystallisation inhibitors.

In this paper, the interaction between alkali ferrocyanides and natural hydraulic lime mortars is investigated, by the use of a several complementary techniques and methods.

2 Materials

2.1 Binder, Sand, Inhibitor

Natural hydraulic lime (NHL) with a strength class of 3.5 from Saint Astier was used as the binder. CEN standard sand, with a grain size distribution between 0.08–2 mm, was used as per EN 196–1 [15]. Analytical grade sodium ferrocyanide decahydrate ($Na_4Fe(CN)_6.10H_2O$) was used as the crystallisation inhibitor. The inhibitor was purchased from Sigma Aldrich.

2.2 Specimen Type, Preparation and Storage

Two different types of specimens were prepared: binder paste specimens and mortar specimens.

Binder Paste Specimens Paste specimens were prepared by mixing NHL with distilled water. The water-binder (w/b) ratio was maintained at 1 by weight. Specimens with mixed-in inhibitor were prepared by first dissolving sodium ferrocyanide in distilled water. Specimens with different inhibitor concentrations were prepared: 0.01%, 0.1% and 1% (weight of inhibitor with respect to the weight of the binder). Additionally, specimens without inhibitor were prepared as reference.

Mortar Specimens

Mortar specimens were prepared according to EN 459–2 [16]. A binder to aggregate ratio (b/a) 1:3 by weight was used. FeCN was added in the amount of 0.1% and 1% with respect to the binder weight. FeCN was first dissolved in water and added to the specimens during the mixing process to obtain a homogenous distribution of the inhibitor in the mortar. The w/b ratio was adjusted to 0.6 as per EN 459–2. Reference specimens were prepared without inhibitor.

Mortar specimens were cast as prisms or as slabs. The prismatic beams were cast in polystyrene mould of 160x40x40 mm and compacted using mechanical vibrating table as per EN 196–1 [15]. Each mortar slab was cast on a red clay brick to obtain properties comparable to that of the mortar when applied in the field [17, 18]. A paper towel was placed on top of the brick before casting the slab, in order to facilitate demoulding. The slabs had a dimension of 200 × 100 × 20 mm and were hand compacted.

All specimens were covered in plastic for the first 24 h. They were demoulded or detached from the brick substrate after 5 days. The specimens were then stored in a curing chamber with a relative humidity greater than 95% and a temperature of 20 °C until tested, in order to minimise carbonation.

3 Test Methods

3.1 Characterisation of the Early Age Properties

Several measurements were carried out to assess the effect of the inhibitor on the properties of the fresh and hardened mortar. An overview of test methods and type of specimens is provided in Table 1.

Table 1. An overview of test methods and specimens

Test method	Measured property	Specimen type	Size/weight	Inhibitor concentration[a]	Replicates
Isothermal calorimetry	Heat of hydration	Binder paste	5.5 g	Ref, 0.01%, 0.1%, 1%	2
Vicat penetration test	Setting time	Binder paste	–	Ref, 1%	2
Mechanical testing	Compressive and flexural strength	Mortar prisms	160 × 40 × 40 mm	Ref, 0.1%, 1%	3
MIP/ N2	Pore size distribution	Mortar slabs	~ 1 cm^3	Ref, 0.1%, 1%	1
Capillary absorption and drying	Water absorption coefficient	Mortar slabs	50 × 20 × 20 mm	Ref, 0.1%, 1%	4

[a] percentage of binder weight

Measurement of Heat of Hydration. The development of microstructure and, in turn, the properties of hardened mortar depend on the hydration reaction (i.e. the exothermic reaction between water and the binder). Therefore, measuring the heat released during the hydration indirectly provides information on the early age hydration products and microstructure development.

Heat evolution and rate of hydration was measured on binder paste specimen by the use of an 8 channel thermometric isothermal calorimeter (TAM-Air). The test procedure is based on EN 196–11 [19]. Each sample consisted 5.5 g of binder mixed with equal amount of water (w/b = 1). The heat evolution was monitored continuously for 168 h and the chamber was maintained at a constant temperature of 20 ± 2 °C. Quartz specimens with a known specific heat capacity were used as a reference to eliminate the background noise.

Setting Time. The setting time, i.e. the time required for the binder to completely lose its plasticity and attain a certain resistance to pressure, was measured using an automated Vicat penetration test. The test was performed in accordance to EN 459–2 on paste specimens [16]. A comparison was made between specimens without inhibitor and specimens with 1% sodium ferrocyanide (as percentage of dry weight).

Workability. Workability is the ease at which mortar can be placed/ compacted during construction; this property is important for an easy application of the mortar in practice. A flow table test, according to EN-1015–3 [20], was performed on the fresh mortar to measure its workability. The freshly mixed mortar was placed on a standard flow table and jolted 15 times at a rate of 1 jolt/ second. The diameter of the resulting mortar was measured at right angles using a calliper.

3.2 Characterisation of the Properties of the Hardened Mortar

Measurement of Mechanical Properties. Mechanical properties provide insights into the load bearing capacities of mortars and thus give a (partial) indication of their expected durability. Compression and flexural strength was measured as per EN 1015–11 on mortar prisms of 160×40×40 mm [21]. The test was performed at 28 days after casting. The loading rate was 0.1 kN/s and 5 N/s for compressive and flexural strength respectively.

Determination of Porosity and Pore Size Distribution. Open porosity and pore size distribution were measured using Mercury intrusion porosimetry (MIP). The test was performed on samples of about 1 cm^3 collected from the mortar slabs after 28 days of curing. The specimens were dried to a constant weight in a freeze drier, before performing the test. The specimens were subjected to a maximum intrusion pressure of 210 MPa; pore throats between 100 μm and 0.01 μm could be measured my MIP. The contact angle between the Mercury and the mortar samples was assumed to be 141°.

Additionally, N_2 adsorption measurements were performed to obtain information pertaining to pores smaller than 0.01 μm, that could not be assessed using MIP. The sample were prepared as for the MIP test but in this case smaller binder samples (2–4 mm particle size, separated by the use of a sieve) were used. The air in the testing chamber was first evacuated at a rate of 500 mm Hg/min before performing N_2 adsorption. No separate degassing procedure was performed.

Capillary Absorption and Drying Test. The effect of FeCN on moisture transport properties of the mortar was assessed by performing capillary water absorption followed by a drying test.

The water absorption by capillarity of mortar was measured using EN 1925 [22] as a guideline. The test was performed on 50 × 50 × 20 mm mortar specimens, obtained from larger mortar slabs. After the 28 day curing period, the specimens were dried to a constant weight in an oven at 40 °C. The sides of the samples were sealed using a paraffin film to have uni-directional absorption and drying. The water absorption was measured using a weighing scale with a precision 0.01 g at prescribed time intervals as per EN 1925. The water absorption coefficient (WAC) was obtained and used for comparison across different inhibitor concentrations. Following capillary saturation, specimens were dried at 40 °C and a relative humidity of 15 ± 5%. The weight of the specimens was measured at different time intervals to obtain the drying curves.

4 Results and Discussions

4.1 Effect of the Inhibitor on Early Stage Properties

The results obtained from the Vicat penetration test, presented in Fig. 1, show that the penetration curve is unaffected by the addition of the inhibitor. The initial (~420 min) and final set (~1200 min) for both specimens with and without inhibitor are in a similar range.

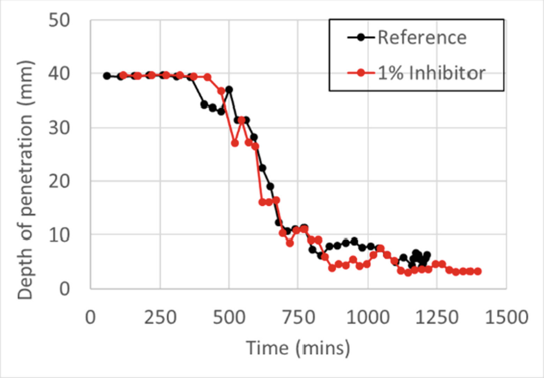
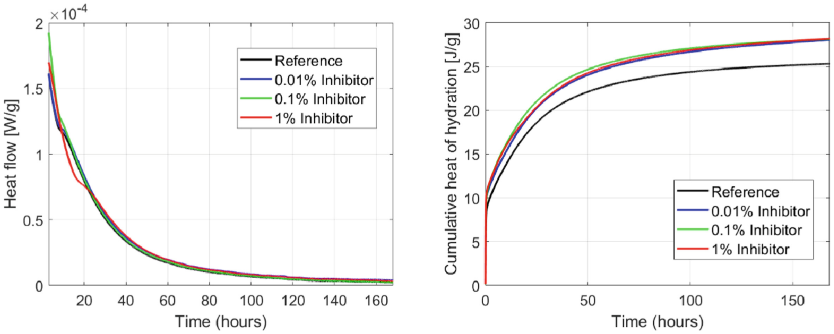


Fig. 1. Comparison of Vicat penetration test results on specimens with and without inhibitor.

The heat of evolution obtained from the isothermal calorimeter is presented in Fig. 2. The results are normalised to the weight of the specimens. It can be seen that there is a negligible difference between reference specimens and specimens with the inhibitor. The cumulative heat of hydration obtained after 168 h is 26 ± 2 J/g, irrespective of the inhibitor concentration. From these results, it seems that the hydration kinetics are not significantly affected by the addition of the inhibitor.

The workability of the fresh specimens was measured using the flow table test. The results, presented in Table 2, show that the flow decreases slightly with the addition of the inhibitor, but not necessarily in proportion to the amount of inhibitor. It should be noticed that there is a large scatter in the data. This is probably due to factors like mixing speed and mixing time, which are not easily controlled and may affect the flow. Considering the variation observed between replicates, the impact of the inhibitor on the flow is minor.



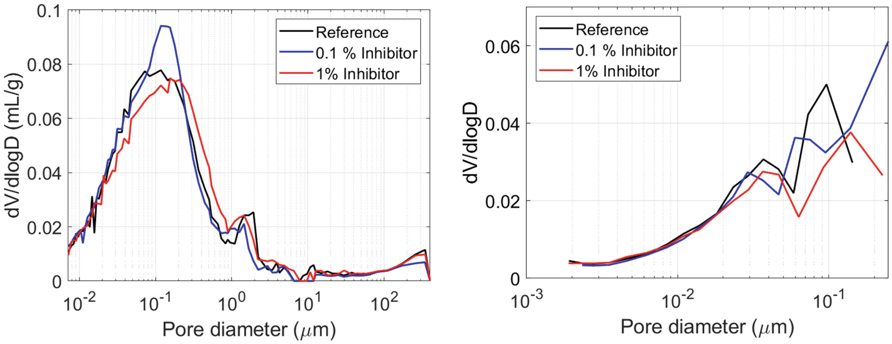
(a) (b)

Fig. 2. **(a)** Heat flow rate **(b)** cumulative heat of hydration for different concentrations of inhibitor.

4.2 Effect of the Inhibitor on Properties of the Hardened Mortar

The mechanical properties of the mortar containing different amounts of inhibitor are reported in Table 2. The strength of specimens with inhibitor show only minor deviation from reference samples.

The pore size distribution and open porosity of the mortar was measured using MIP, for pores throats between 100 μm and 0.01 μm and N_2 for pore throats smaller than 0.01 μm. The results are presented in Fig. 3. It is possible to conclude that the addition of the sodium ferrocyanide did not significantly affect the pore size distribution, in the range of both larger and smaller pores by the addition of FeCN. The mean diameter as obtained from MIP varies between 0.1 and 0.2 μm. The open porosity of mortar with and without inhibitor as obtained from MIP is also very similar (Table 2).

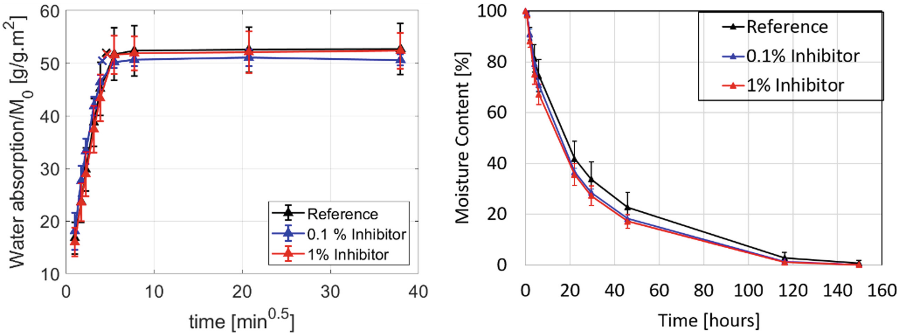


(a) (b)

Fig. 3. **(a)** Pore size distribution as measured by MIP **(b)** Pore size distribution as measured by N_2 adsorption for pores smaller than 0.01 μm

The water absorption curves of mortar specimens with different concentrations of inhibitor were measured and the results normalized to the dry weight of the specimens.

This was done to take into account for the slight variation in the sample thickness of the specimen, due to hand compaction of the slabs. The intersection point of the two absorption stages, necessary for the determination of the water absorption coefficient (WAC), was obtained by performing a linear regression on the two stages. Figure 4a shows that the water absorption curves and the WAC (Table 2) of mortar specimen with and without inhibitor are similar. The drying curves of specimens with and without the inhibitor, (Fig. 4b) are similar. These results confirm that the moisture transport of the mortar is not significantly affected by the addition of the inhibitor in the studied concentrations.



(a) (b)

Fig. 4. **(a)** Capillary absorption **(b)** Drying behaviour of specimens with different inhibitor concentration.

Table 2. Summary of mortar properties for different inhibitor concentrations

Property	Reference	0.1% Inhibitor[a]	1% Inhibitor[a]
Flow table [mm]	143.2 ± 1.8	139 ± 3.7	136.5 ± 2.1
Compressive strength [MPa]	3.22 ± 0.24	3.52 ± 0.06	3.75 ± 0.09
Flexural strength [MPa]	1.30 ± 0.02	1.44 ± 0.13	1.44 ± 0.04
WAC [g/m^{2}s$^{0.5}$]	137.11	123.46	131.97
Open Porosity [%]	23.44	23.51	23.54

[a] Percentage of binder weight

5 Conclusions and Outlook

In this study, the effect of sodium ferrocyanide (an inhibitor for sodium chloride crystallisation) on various relevant properties of NHL-based mortar was studied. The results clearly show that the addition of sodium ferrocyanide, in concentrations up to 1% of binder weight, do not significantly alter the properties of the mortar, both in its fresh and hardened state. Based on these results, it can be concluded that sodium ferrocyanide remains inert and does not participate in the microstructure development of these mortars. This is a positive result and a significant first step in development of NHL-mortars additivated with crystallisation inhibitors, for application in conservation interventions as well as in new buildings located in areas at risk of high salt loads, such as e.g. coastal areas. In the future, further research is planned to rule out possible chemical binding between the sodium ferrocyanide which could limit its effectiveness. Finally, the durability of the mortar with respect to salt damage will be investigated by means of accelerated salt crystallisation tests in laboratory and application in the field on case studies.

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