

STUDY OF THE POSSIBLE APPLICATION OF SODIUM FERROCYANIDE FOR THE PREVENTION OF SODIUM CHLORIDE DAMAGE IN BUILDING MATERIALS

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SUMMARY

This paper reports the results of an experimental study on the effects of a crystallization inhibitor (sodium ferrocyanide) on sodium chloride crystallization damage in porous building materials. The research consisted of laboratory experiments and field tests.

The laboratory results show that sodium ferrocyanide, when mixed in salt solution, enhances the solution transport favouring the appearance of efflorescences, instead of much more harmful crypto-florescences. This suggests the possible use of this inhibitor for minimizing sodium chloride damage and improving desalination treatments. Nevertheless, our crystallization tests and field experiments, show that the effect of ferrocyanide, when applied on substrates already contaminated with sodium chloride, is very limited: neither damage is significantly reduced nor desalination enhanced.

INTRODUCTION

Salt crystallization in porous materials constitutes one of the most frequent causes of decay of building materials. Pressures created by crystallization of the salt in the pores weaken the material until its mechanical strength is overcome and damage occurs. Inhibiting or limiting the crystallization of the salt would therefore prevent or slow down the material decay.

It is known that products exist, that are able to delay salt crystallization [Veintemillas-Verdaguer 1996; Füredi-Milhofer and Sarig 1996]. These products (i.e. their composing ions or molecules) are called crystallization inhibitors. Crystallization inhibitors work by preventing or delaying nucleation (nucleation inhibitors) and/or by reducing the growth rate of specific crystal faces, thus modifying the habit of the crystals (habit modifiers).

Among the inhibitors of sodium chloride crystallization, sodium ferrocyanide is the most promising [Rodriguez-Navarro et al. 2002]. Nevertheless, in spite of its proven effectiveness in delaying crystallization in bulk solution, its actual capability of preventing salt decay in building materials is still object of discussion. The experimental results published until now indicate that this inhibitor may have a positive effect on the salt damage by delaying salt crystallization and by enhancing salt transport towards the surface and thereby promoting the formation of efflorescences instead of much more harmful crypto-florescences [Rodriguez Navarro et al. 2002; Selwitz and Doehne 2002]. Besides, it has been suggested that sodium ferrocyanide may have positive consequences for the

damage by modifying the crystallization morphology of NaCl [Lubelli et al. 2006]. On the other hand, the theory on salt crystallization [Scherer 2004] states that the higher supersaturation is achieved, the higher the risk may be, at the moment crystallization finally occurs. The risk is due to the fact that crystallization will take place at higher supersaturation and therefore greater pressures will be developed and more severe damage may occur.

The experiments performed until now do not give a definitive answer. In fact all of them consist in introducing the salt and the inhibitor, dissolved in the same solution, simultaneously in the substrate. This procedure does not reproduce the actual situation in practice, where the salt has already crystallized in the pores of the substrate at the moment the inhibitor is applied.

From the above discussion, it emerges that experimental studies, reproducing as much as possible the application of the inhibitor in practice, are necessary to assess benefits and risks of the application of inhibitors on salt contaminated materials.

The present paper reports a series of systematic investigations aiming at assessing the actual efficiency of sodium ferrocyanide in minimizing sodium chloride crystallization damage. Both laboratory experiments and field tests on a building affected by NaCl damage have been performed.

EXPERIMENTAL SECTION

The research consisted of laboratory experiments and field test. In the laboratory experiments the effect of sodium ferrocyanide on damage occurring in different substrates contaminated with NaCl has been investigated. In the field tests the effect of the crystallization inhibitor in minimizing salt damage and improving the efficiency of desalination treatments has been studied.

Laboratory experiments

The experimental research has been carried out on different materials, which were selected because of their very different chemical, physical and mechanical properties.

- Spanish limestone: it is constituted at 90 wt% by calcite [Rodriguez-Navarro 1994]. It has a porosity of about 30 vol%, with a high percentage of pores of a diameter between 10 and 50 μm
- Czech sandstone: it is constituted up to 90% by quartz with a little percentage of clay minerals (up to 10%) [Rodriguez-Navarro and Ruiz-Agudo unpublished]. It has a porosity of about 30 vol% with a unimodal pore size distribution (pore diameters between 10 and 30 μm)
- Dutch fired-clay brick: it is a brick from industrial production. It has a total porosity of 33 vol% with most of the pore diameter sizes in the range between 0.5 and 8 μm .
- Calcium silicate brick: it has a porosity of about 27 vol% and pore sizes spread within the range 0.01-20 μm , with a large percentage of small pores.
- restoration plaster: it is a cement based plaster produced for salt contaminated substrates, thus expected to have a high resistance to salt crystallization damage. It has a high porosity (about 57 vol%), a bimodal pore size distribution with a large amount of very small pores (diameter smaller than 0.2 μm).
- lime-cement mortar: it has a lime : cement : quartz : sand ratio of 3 : 1 : 20. It is therefore a very weak mortar, with an open porosity of 27 vol% and a bimodal pore size distribution with pores between 0.2 and 0.5 μm and between 50 and 80 μm .

The pore size distribution of the substrates is reported in Figure 1.

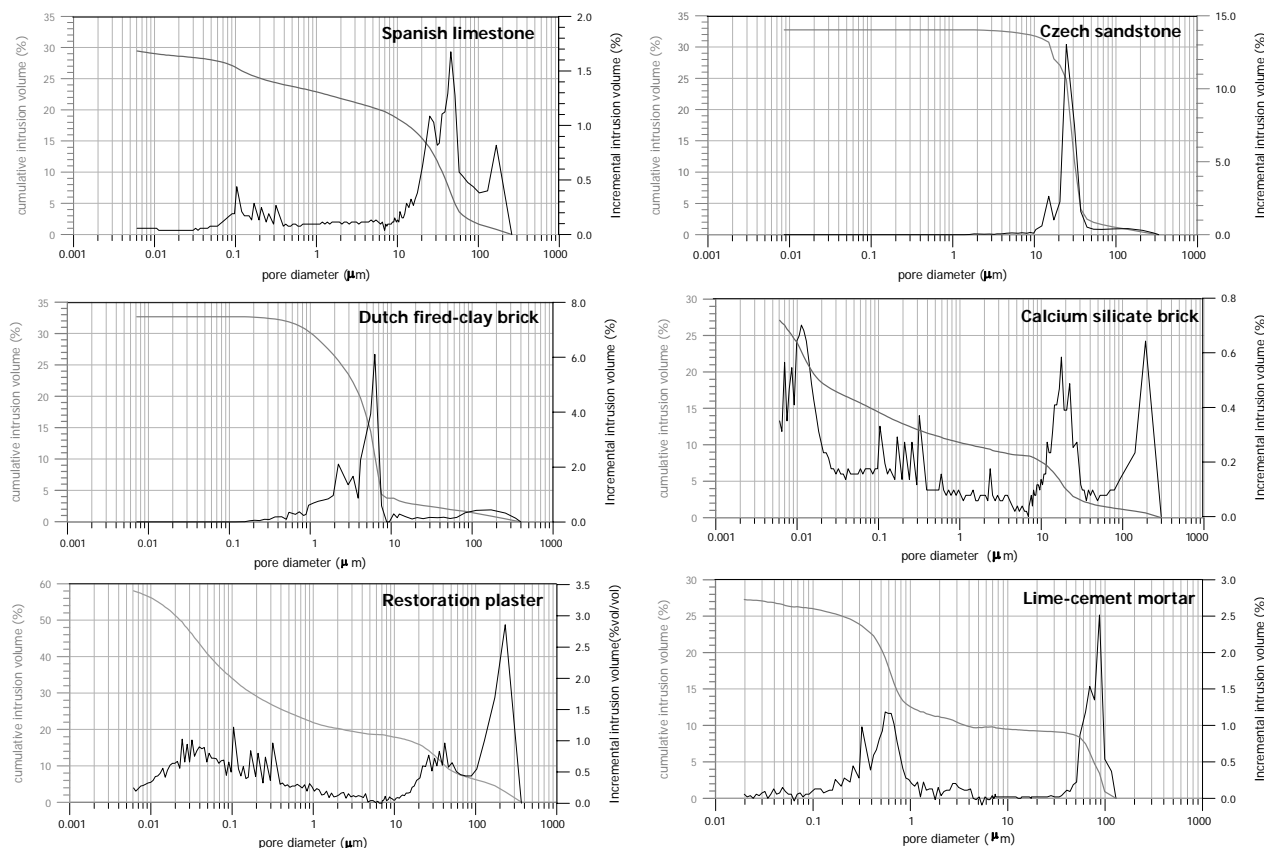


Figure 1. Pore size distribution of the substrates as measured by Mercury Intrusion Porosimetry

Sodium-ferrocyanide (in the text abbreviated as NaFeC) ($\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$) at 0.001M concentration has been used as salt crystallization inhibitor. The type and the concentration of the inhibitor have been selected on the basis of experiments performed within the framework of the research project SALTCONTROL Prevention of salt damage to the built cultural heritage by the use of crystallisation inhibitors (EC Project no. 5015710).

Two different tests have been performed: a drying test and a salt crystallization test. In the drying test the inhibitor and the salt, mixed in solution, have been introduced together in the substrate, whereas in the crystallization test the inhibitor in aqueous solution has been introduced afterwards in substrates already contaminated with salt. The drying test has been carried out on the Spanish limestone, the Czech sandstone and the fired-clay brick. The crystallization test has been performed on all materials.

Drying test

The test aimed at studying the effect of the inhibitor on salt solution transport.

The specimens, of the size of 5x5x5cm, were sealed on the 4 lateral sides and saturated with 10 wt% NaCl solution with and without NaFeC (0.001M). Specimens saturated with demineralised water were used as reference. Once saturated, the specimens were sealed on the bottom side as well and allowed to dry at 20 °C 50% RH. Their weight was recorded regularly. All experiments were carried out in threefold.

For each material/solution combination the salt distribution at the end of the drying test was determined on one specimen. First the surface of the specimen was brushed and the efflorescences

collected and weighed. Then the outer part (5 mm) of each specimen was ground in 1mm slices, and the rest of the specimen was cut in slices (without the use of water to avoid salt dissolution).

The obtained samples were then stored at 20 °C 96% RH for six weeks. The weight gain, i.e. the Hygroscopic Moisture Content (HMC), was measured. The HMC provides a reliable indication of the salt content in cases like this in which only one salt type is present [Lubelli et al. 2004].

The effect of the inhibitor on the morphology of the salt crystallizing in the stone has been studied. Inhibitors are expected to modify the crystallization habit of the salt, both by allowing crystallization at high supersaturation and by favouring the preferential growth of specific crystal faces. At the end of the drying experiments broken cross sections of the specimens have been investigated by means of a FEI Tungsten XL 30 Environmental Scanning Electron Microscope (ESEM) equipped with an Energy Dispersive X-ray system. Low magnifications were used to study salt distribution and location, while higher magnifications were used to investigate crystal shapes. The pressure in the ESEM chamber varied between 0.3 and 0.4 Torr, corresponding to a RH of 1.7 – 2.3 % at 20 °C. This means that with the specimens being dry when they were introduced in the ESEM, no change in the structure of the salt would occur during the ESEM investigation.

Crystallization test

The test aimed at verifying the capability of NaFeC to minimize sodium chloride crystallization damage. The procedure set up for the crystallization test aimed at reproducing as much as possible the situation occurring in case the inhibitor would be applied on a salt contaminated building. For this reason, the inhibitor was not dissolved in the salt solution (as in the drying test), but applied in aqueous solution on the salt loaded substrates.

The specimens, sealed on the lateral sides, were contaminated with NaCl solution. The amount of solution was equal to the capillary moisture content (CMC), i.e. the amount of solution sufficient to wet the upper surface of the specimen when absorption takes place by capillary rise from the bottom. The concentration of the solution was calculated in order to have 2% of salt in the specimen (weight of the salt/weight of the dry specimen). The specimens contaminated with salt solution were sealed with removable tape on the bottom surface and allowed to dry at 20 °C 50% RH for 5 days. They were then dried in an oven at 70°C until they reached a constant weight and cooled down at room temperature. In this way salt accumulation near the evaporation surface of the specimens was obtained, a salt distribution similar to the one usually found in buildings.

The surface of the specimens was then sprayed with the inhibitor (0.001M) dissolved in demineralised water. An amount equal to 50% of the CMC was used. This amount of water allowed to wet the outer centimetres of the specimen where, due to evaporation, salt had accumulated. When the specimens reached a constant weight the crystallization test started. The specimens were subjected to wet dry cycles: each time that 90% of the water had evaporated, they were re-wetted from the bottom surface with an amount of demineralised water equal to the CMC. Depending on the material type and on the presence or not of salt, 2 to 5 wet-dry cycles were performed in a period of about 8 months.

Field test

The field test aimed at verifying the capability of ferrocyanide to limit salt crystallization damage and enhance desalination. A masonry building with a high NaCl content was selected as case-study. Areas of about 50x50cm were selected for the application of the inhibitor. Next to them,

reference areas to be treated with only water were selected. Brick powder samples were collected in the areas to be treated as well as from nearby reference areas. The moisture (MC) and hygroscopic moisture content (HMC) of these samples were determined. These data constitute the initial situation, with which the situation after the inhibitor application has to be compared.

The inhibitor was applied by poulticing. Two types of poultice material were used:

A: cellulose poultice (Arbocell 200 + Arbocell 1000)

B: poultice of industrial production (Remmers “Funcosil Entsalzungskompressen”) consisting of a mixture of clay, quartz sand and cellulose.

The inhibitor (NaFeC) in the concentration of 0.001M was added to the water used to prepare the poultice and the compresses. A ratio dry cellulose / water (or inhibitor solution) of 1: 7 was used. A ratio dry poultice / water (or inhibitor solution) of 1:3 was used for the clay-sand-cellulose poultice, according to the prescription of the producer.

The cellulose poultice has been applied in a 2 cm thick layer. In order to guarantee its good adherence to the wall, a plastic net was used. The clay-sand-cellulose poultice was applied in a 2 cm thick layer. Prior to the application the wall was pre-wetted either with water or with inhibitor solution (1 liter/m²). After three weeks from the application, both the poultices and the compresses were removed and replaced with new ones. After 3 more weeks these were removed too.

Conductivity measurements were performed on the poultices removed from the wall in order to have an indication of the amount of salt extracted. The following procedure was used to measure the conductivity of the poultices. Each of the four poultices was dried at 70°C until constant weight and then ground. One sample was collected from each of the poultices for the conductivity measurements. A defined amount of demineralised water was added to the poultice. After stirring for 24 hours, the solution was filtrated and the conductivity measured.

Immediately after the removal of the second application of poultices new sampling of brick powder in the treated (with water and with inhibitor) and untreated areas (reference) was performed. The HMC of these samples was measured and compared with the HMC before the treatment. An additional survey of the damage was performed after 4 months from the treatment, to check eventual changes in the distribution of the efflorescences and of the damage.

RESULTS

Laboratory experiments

Drying test

The drying curves for each material are reported in Figure 2. As expected, the specimens contaminated with NaCl solution dry slower than the ones saturated with water. In fact, the presence of soluble salts depresses the RH of equilibrium of the solution, thus the driving RH gradient for vapour transport between the surface and the environment becomes also lower and drying slows down.

The NaFeC enhances the drying but the relevance of this effect strongly depends on the material type. In the Spanish limestone and in the brick drying is clearly enhanced when NaFeC is added to the NaCl solution. In contrast, no effect is observed in the Czech sandstone.

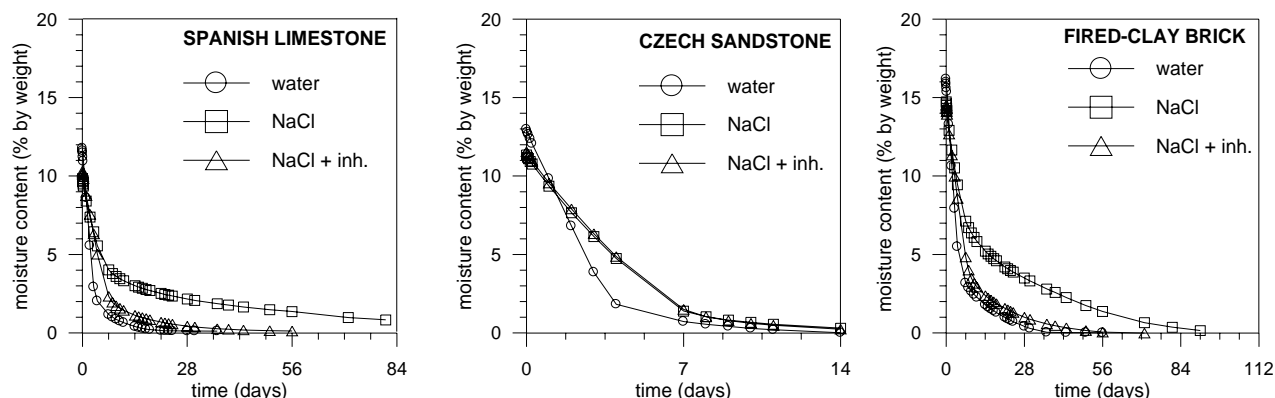


Figure 2. Drying curves at 20 °C 50% RH of the Spanish limestone, the Czech sandstone and the fired-clay brick saturated with water, 10 wt% NaCl solution and 10 wt% NaCl solution with 0.001M NaFeC

The explanation of these differences may be that the precipitation of salt, in the stone or at the surface of it, interferes with the drying process, delaying it (in case of occlusion of the pores or appearance of salt crust) or enhancing it (in case of fluffy efflorescences increasing the evaporation surface).

The location (inside the stone or at the surface) and the morphology (dense crust or fluffy crystals) of salt may in fact influence the drying. NaFeC has shown to be very effective in changing the morphology of the halite: in presence of NaCl only, a dense agglomeration of halite crystals appears on the surface of all the materials, while in case NaFeC is added, efflorescences assume a branched shape having a much larger evaporation surface.

The drying curves clearly show the effect of the precipitation of salt on the drying: in the first hours, when the surface of the specimen is still wet and liquid transport is the governing mechanism, no significant differences are observed between specimens with and without NaFeC; after a few days, once salts start efflorescing at the surface, drying of specimens containing NaFeC is faster than the drying of specimens contaminated with NaCl only. This may be due to the larger evaporation surface of the branched efflorescences as well as to the fact that, thanks to the inhibitor delaying crystallization, less salt precipitates in the stone occluding the pores.

The limited effect of the NaFeC on the drying of Czech sandstone might be related to the unimodal pore size distribution of this stone. Because of this drying by water vapour transport might have started earlier in this stone, inhibiting further solution transport to the surface. The effect of the inhibitor will then be less important.

Summarizing, the rate of drying is the following:

- for the Spanish limestone and the fired-clay brick: $\text{Water} > \text{NaCl} + \text{NaFeC} \gg \text{NaCl}$
- for the Czech sandstone: $\text{Water} \gg \text{NaCl} + \text{NaFeC} = \text{NaCl}$

In order to have a definitive confirmation of the effectiveness of the inhibitor in enhancing the salt solution transport to the surface, the salt distribution at the end of the drying test was measured, including the efflorescences on the surface. The HMC results are reported in Figure 3; the numbers at the top of the first columns in the graph indicate the amount of efflorescences (in grams) brushed from the surface at the end of the drying test.

The distributions confirm the indications given by the drying curves: the enhanced drying corresponds to a larger amount of salt at or near the surface. In the Spanish limestone and in the

brick the presence of NaFeC enhances the transport of salt (NaCl) to the surface and therefore crystallization in the form of efflorescences instead of crypto-florescences. In the Czech sandstone the NaFeC does not have any effect.

The effect of the inhibitor on the crystal morphology is clearly visible on the efflorescences precipitated on the evaporation surface of the specimens: the salt forms dendritic crystals, clearly different from the crystals precipitating in absence of NaFeC. Also the morphology of NaCl precipitating inside the stone is influenced by the presence of the inhibitor. Figures 4a and b show the cross sections of NaCl contaminated Czech sandstone with and without inhibitor respectively. It is observed that in the absence of inhibitor halite precipitates mainly as a layer on the pore wall, whereas in the presence of the inhibitor an agglomeration of small crystals is visible, filling the pore spaces (this confirms previous observations [Lubelli et al. 2006]).

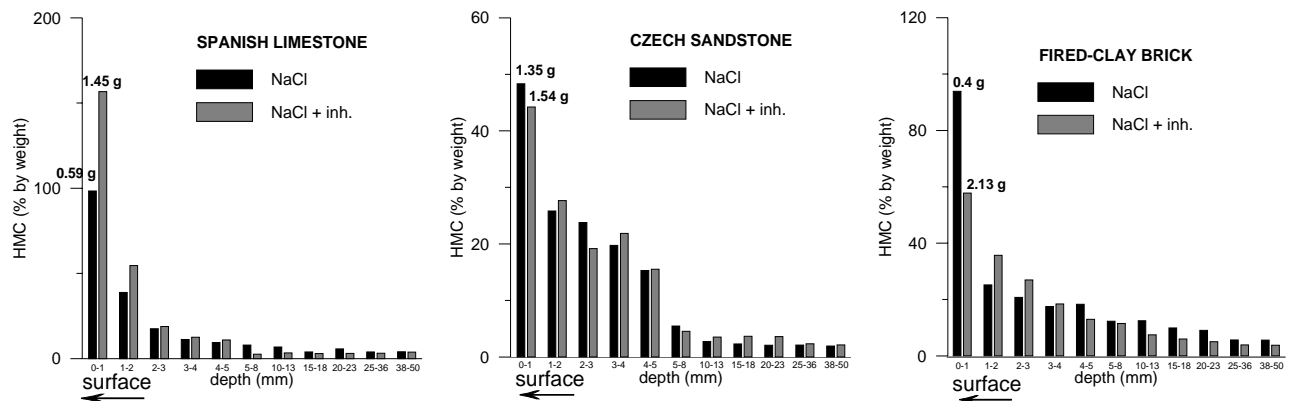


Figure 3. HMC distribution measured at 96% RH in the Spanish limestone, the Czech sandstone and the fired-clay brick specimens at the end of the drying test

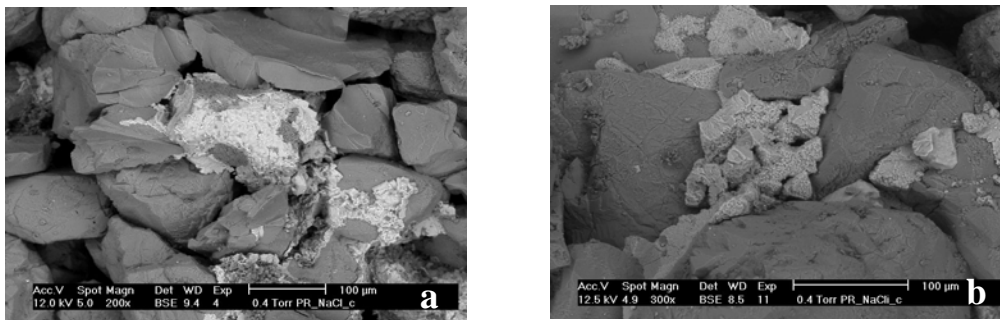


Figure 4. NaCl crystallized in absence (a) and presence of inhibitor (b)

Salt crystallization test

The results of the salt crystallization test are evaluated on the basis of the photographic monitoring and of the quantification of the material and salt loss.

The application of the inhibitor (dissolved in water and sprayed on the surface) has lead to the appearance of efflorescences. The water has dissolved the salts and transported them to the surface where they have crystallized. The efflorescences clearly show in their branched shape the presence of the inhibitor.

Significant damage after 5 wet-dry cycles occurred only in the case of the lime-cement mortar. In this case the NaFeC had no effect on the amount of damage (the material loss between specimens with and without the inhibitor was the same) but influenced the type of decay: in the absence of the inhibitor bulging and scaling occurred, while sanding was observed in the presence of NaFeC (Figure 5). The other materials, untreated and treated with the inhibitor, did not suffer any significant damage in the time period of the experiment.

The total amount of efflorescences that could be brushed from the surface during the crystallization test was, in the case of the fired-clay brick and of the calcium silicate brick, higher in specimens with NaFeC than in specimens with only NaCl. The application of the inhibitor on the other materials did not lead to any significant increase in the total amount of efflorescences.

The control specimens with no salt, subjected to wet-dry cycle with pure water, did not suffer any damage.

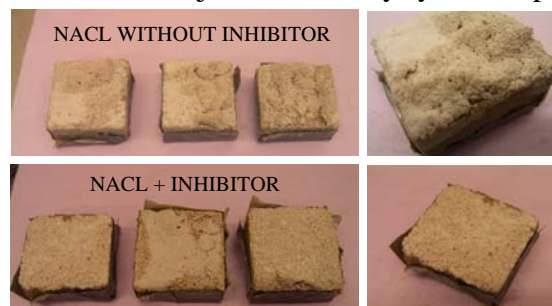


Figure 5. NaCl contaminated lime-cement specimens after 5 crystallization cycles: in specimens treated with the inhibitor sanding occurs, whereas bulging and scaling are present in untreated specimens

Field test

The results of the conductivity measurements performed on the desalination materials applied on site are reported in Figure 6. The conductivity has been expressed as mS/cm^2 of desalinated area instead of mS/g of poultice [Vergès-Belmin V. and Siedel H.]. Expressing the conductivity in mS/g of poultice would in fact lead to a misleading interpretation due to the different density of the two poultices. The graph shows that the conductivity of the poultices with and without inhibitor is about the same: it can therefore be concluded that in this case the inhibitor does not improve the effectiveness of desalination.

The HMC of the bricks (at the depths of 0-1cm and 1-5cm) before and after the treatment has been measured in order to further evaluate the effect of the inhibitor on desalination. The obtained results are reported in Figure 7. No clear positive effect of the inhibitor on desalination is observed. This confirms the results of the conductivity measurements.

Regarding the desalination efficiency of the two poultices used some observations can be made, even if this research did not aim at evaluating the different desalination materials but at assessing the effect of the mixed in inhibitor on the desalination. In Figure 8 the HMC remaining after desalination as percentage of the initial HMC is reported. From these results it can be concluded that:

- a general reduction of the salt content is measured;
- as expected, the reduction of the salt content is higher in the outer one centimetre of the wall than at 1-5cm depth;
- in general the efficiency of the clay-sand-cellulose poultice is better than the one of the cellulose, i.e. the reduction of the salt content is higher at both depths

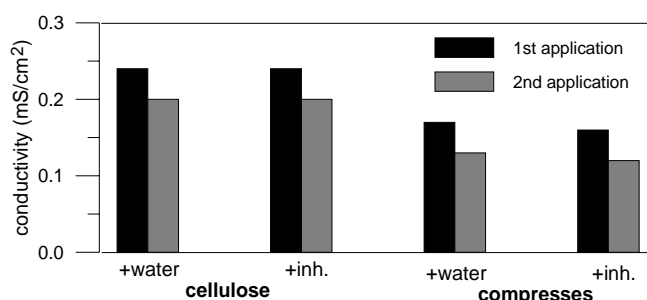


Figure 6. Conductivity of the poultices (1st and 2nd application)

It should be reported that the cellulose with mixed-in inhibitor showed a change in colour (towards blue and green) during drying. This discoloration may become a problem if this inhibitor is applied on white or light coloured substrates.

After four months from the application of the treatment an increased amount of efflorescences was visible on the areas treated with inhibitor with respect to the ones treated with water only. The branched shape of the efflorescences indicates the effect of the inhibitor. No significant differences in damage between areas with and without inhibitor were observed.

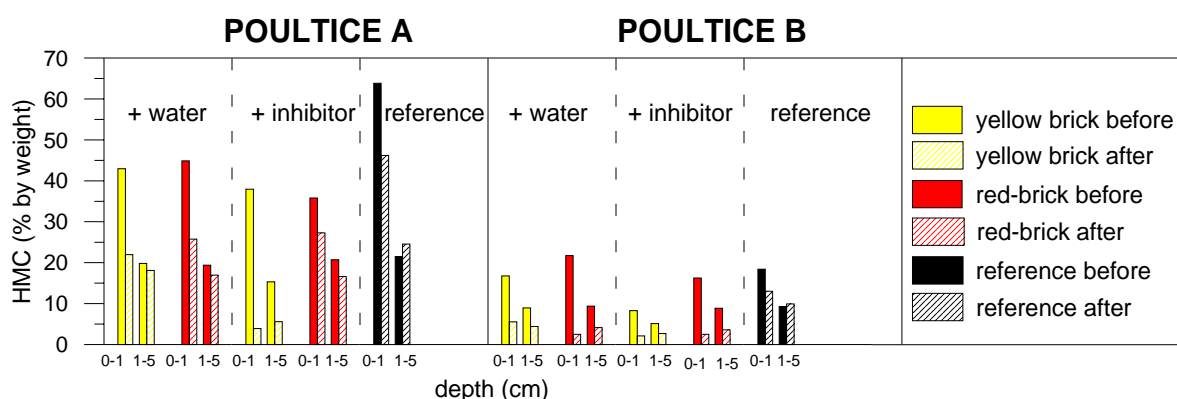


Figure 7. HMC at 96% RH measured in treated bricks before and after the treatment with demineralised water and inhibitor in aqueous solution and in not treated (reference) bricks

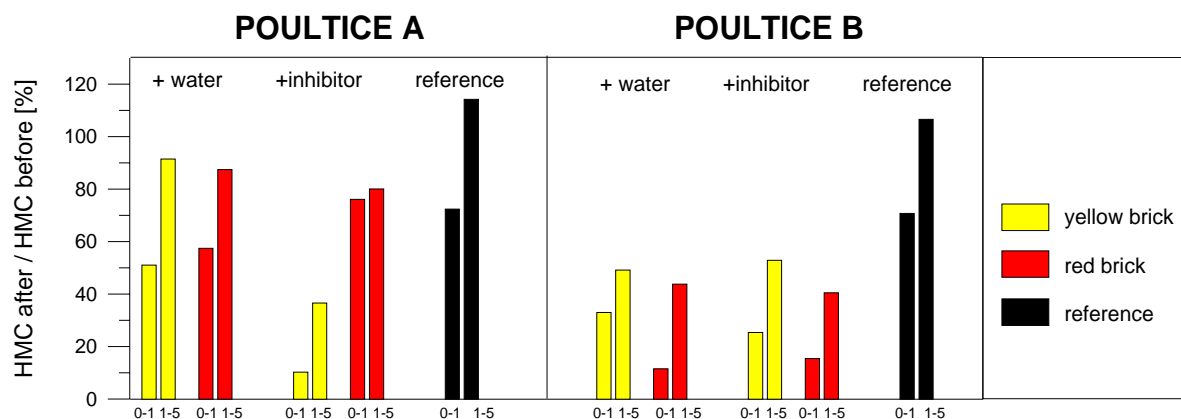


Figure 8. HMC at 96%RH after desalination expressed as percentage of the initial HMC

DISCUSSION AND CONCLUSIONS

In this research the use of crystallization inhibitors has been studied for the first time systematically in a practice oriented context. In spite of the encouraging results obtained with the use of inhibitors in bulk solutions, the performance of these products when applied on salt laden substrates has shown much more complicated.

This research has pointed out that sodium ferrocyanide, if introduced directly in the salt solution, enhances the solution transport and the appearance of efflorescences. This suggests that this inhibitor may minimize NaCl damage and improve the efficiency of desalination treatments. However, our laboratory crystallization experiments indicated that if this inhibitor is applied afterwards on the material already contaminated with salt, its positive effect on salt damage is very limited.

The application of NaFeC on salt contaminated brick masonry did not improve the efficiency of desalination: the amount of salt extracted in areas treated with inhibitor and areas treated with only water was similar. Nevertheless, after 4 months from the removal of the poultices an increased amount of efflorescences was observed in areas treated with the inhibitor. At the moment it is not possible to draw conclusions on the effects of the inhibitor on the damage. Additional inspections in the coming months/years are necessary to see whether the enhanced efflorescences resulted also in a reduction of the damage to the substrate.

On the basis of this research it is only possible to conclude that sodium ferrocyanide has a very limited effect on salt damage if introduced in materials already contaminated with NaCl. If the inhibitor is introduced in the material together with the salts, it can have a positive effect enhancing salt solution transport and efflorescences. This suggests that the application of the inhibitor in processes in which a large amount of water is involved (for example desalination by bath method) might give positive results. Future research on this inhibitor should therefore look in this direction.

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