



EVALUATION OF THE EFFICIENCY OF SODIUM FERROCYANIDE AS A CRYSTALLIZATION INHIBITOR IN MONUMENTAL SANDSTONES IN PETRA – JORDAN

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Abstract

This study examines the capability of sodium ferrocyanide to retard salt crystallization damage to sandstone monuments of the Outstanding Universal Value site of Petra. For the purpose of this study samples from Disi Sandstone Formation (Ordovician) and Upper Umm Ishrin Sandstone Formation (Cambrian) exposing in Petra were preliminary taken into consideration. Only 23 samples, with similar physical properties, were taken for further experimentation. The 23 selected samples were salinated by NaCl solution or a salt mixture solution of NaCl and KCl. Some of the samples were then desalinated by distilled water and other samples were desalinated by applying sodium ferrocyanide solution, the percentage of the removed salts was calculated in each case. Evaluation of the efficiency of the sodium ferrocyanide to prevent salt crystallization damage based on three parameters: drying behavior of the samples, the percentage of salts extracted by desalination process with and without salt inhibitor and the form of salt formed on the surface of the samples after desalination. The results showed that the presence of inhibitor modifies the drving behavior of salt solutions inside the samples and makes the drying process for the samples desalinated by sodium ferrocyanide was faster than for those desalinated by distilled water. This allows the movement of a salt solution from the samples up to their surface, which results in the formation of non-destructive efflorescences instead of destructive subflorescences. However, formation of salt efflorescence in samples containing a mixture of salts was more obvious than in samples salinated with pure single salt only.

Keywords: Salt deterioration; Salt mixture; Sodium ferrocyanide; Crystallization inhibitor; Monumental stones.

Introduction

Salt deterioration is one of the severest contributors to the weathering of monumental stones worldwide, consequently, it is crucial to understand the mechanisms of this type of weathering to apply an effective treatment plan to prevent, or at least to retard, such deterioration. Inhibiting or limiting the crystallization of these salts is an important process towards the preservation of our cultural heritage [1]. Desalination, as a contribution to monument preservation, is considered one of the most important processes for extracting salts from monumental stone [2]. However, the great variety of salts and salt mixtures, the considerable differences in composition, concentration and distribution of salt load over depth, and especially the partly very high depth-effect of salt loading appear to impede the target success of the standardized desalination process [1].

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Historically, desalination of building stone by using distilled water has been applied in order to reduce the impact of salt weathering with considerable different success. A fairly new field of research is the use of salt crystallization inhibitors; it has attracted interest for improving desalination as well as for reducing aggressiveness and damage potential of salt weathering regimes. To date, however, fundamental knowledge with respect to the interaction of such additives with salts in stone monuments and its implications on stone deterioration processes is still lacking [1, 2].

This study takes into consideration the rock-cut monuments in Petra – Jordan. The ancient city of Petra is of outstanding universal value; in 1985 it was inscribed on the UNESCO list of World Heritage. In 2007 it was elected one of the "New Seven Wonders of the World". In Petra several hundred monuments were carved by the Nabataeans from clastic sedimentary bedrocks some 2.000 years ago. The World Monuments Fund (WMF) repeatedly included the archaeological site of Petra on the list of the one hundred most endangered monument assemblies of the world. All rock-cut monuments show weathering damage, partly to a very high extent [1].

The progression of deterioration appears to be accelerating. In this respect, salt weathering is considered a major cause of damage to Petra's monuments. Results of previous research works in Petra revealed a wide range of salts and salt mixtures, occurring as efflorescences, subflorescences or salt crusts. The highest damage potential is attributed to the subflorescences, due to the generation of internal stress which they exceeds the strength of the stone and causes surface scaling, spalling, peeling and detachment and the internal stress generated due to volumetric expansion of the salt crystals inside pores [3-6].

In general, it is not possible to prevent the formation of salt crystals inside the stone or the penetration of the crystallizing solution [7], especially in areas like Petra with underground salts. In this case, it is essential to understand the mechanisms of salt action in order of to prevent salt damage or to reduce its rate. There is still a lot of misunderstanding and knowledge deficiency about salt weathering mechanisms, nevertheless, it is agreed that the main mechanisms responsible for salt weathering are linked to crystallization pressure, hydration pressure and thermal expansion [1, 8, 9].

The present paper addresses the application of salt crystallization inhibitor on the rockcut monuments in Petra – Jordan and compares its efficacy with desalination using distilled water alone to reduce the aggressiveness and potential damage of monumental stones by the action of salts.

An example of a well-known anti-caking agent used for sodium chloride (NaCl) is sodium ferrocyanide $[Na_4Fe(CN)_6]\cdot 10H_2O$. Ferrocyanide has a very strong anti-caking influence; it modifies the crystal habit of sodium chloride. In addition, it inhibits crystal growth and nucleation of salts. In the presence of a significantly small amount of ferrocyanide, sodium chloride crystals grow dendritically instead of in cubic form [1, 10]. The mechanisms of the inhibiting action of sodium ferrocyanide ions on NaCl and KCl crystallization is that ferrocyanide ions ([Fe(CN)₆)]⁴⁻) replace the chloride ion (Cl⁻) on the surface of NaCl and KCl. In this case, one cyanide group replaces the chloride ion (Cl⁻) [10]. Resulting in replacing the sodium and potassium chloride lumps on the surface and block any further growth because of the different in ion charge [1, 10, 11].

In the case of porous materials, this effect allows the ferrocyanide to work on reducing the evaporation rate of the salt solution inside the pore structure of the stone, and on permitting the NaCl and KCl to crystallize on the surface of the stone in the form of efflorescence instead of subflorescence [1, 12].

Materials and methods

Cubic samples $(6 \times 6 \times 6 \text{cm}^3)$ from the Disi sandstone formation (Ordovician) and samples with similar shape and dimensions from Umm Ishrin sandstone formation (Cambrian) were preliminary taken from the archaeological city of Petra. All the monuments of Petra were

carved into these two formations. The physical properties: porosity, water absorption at atmospheric pressure, water absorption at vacuum, saturation coefficient and water absorption coefficient for all the samples were measured.

Ordovician sandstone samples were collected from the archaeological city of Petra. Because it was not possible to take stone samples directly from the stone monuments, the samples were gathered from the area around the archaeological city, specifically from Al-Beidha (little Petra). Cubes of $6x6x6cm^3$ were cut from the blocks. Additionally, samples (blocks) of Cambrian sandstones (Umm Ishrin sandstone formation) were kindly provided by Dr.-Ing. Bernd Fitzner, former Director of the Working Group "Natural stones and weathering" at the Geological Institute of the RWTH Aachen University. These samples had been collected for a previous research project in Petra – Jordan (1996 – 1999). Drill core samples of different length (but as long as possible) were taken from these blocks [1]. Table 1 summarizes the samples stratigraphy, lithotypes and their physical properties.

After the hygric properties were measured, the samples were classified into two main groups according to their physical properties. Each group was subdivided into three subgroups in order to use the similar samples in the same test phase to make the results comparable (Table 2).

The samples were sealed with Tesa tape on all sides except on the top and the bottom of the sample in order to allow unidirectional salt solution movement from the bottom of the sample and drying from the top surface during the crystallization test in order to estimate the same behavior in practice.

Two types of salts, NaCl and KCl, were introduced into the samples by capillary rise. These salts were chosen because they were detected in the sandstone monuments at the archaeological city of Petra, and are considered significant salts causing damage to Petra's rock-cut monuments [1, 17-19]. Some samples were salinated with NaCl and others with a mixture of NaCl and KCl in the proportion of 5:1 (m). This proportion was estimation from real data of Dr. Kurt Heinrichs from his previous project results in Petra – Jordan (2005 and 2008).

The samples were dried under controlled temperature and relative humidity $(60^{\circ}C \text{ and} \text{ almost 5\% RH})$. During the drying process, the bases of the samples were sealed to compel evaporation to occur only through the surface of the stone during the drying process. This was to simulate reality as closely as possible. The evaporation of the salt solution was measured periodically by weighing the samples two times a day until they reached a constant weight. The salt content in each sample was calculated by measuring the weight difference of the samples before and after salination.

The inhibitor solution, $[Na_4Fe(CN)_6] \cdot 10H_2O$ with a concentration of 0.1, 1.0 and 2.0% was introduced into the samples, previously salinated, by capillary rise. The type and the concentrations of inhibitor used in this study have been selected because it was proved by several scholars who claimed that using this crystallization inhibitor could reduce the potential damage caused by salts significantly.

Each sample was treated individually in a separate box, to prevent the introduced salts from being mixed up in the course of the test setup [1].

During the absorption procedure, the weight and the height of the inhibitor solutions were registered periodically until the solution reached the surface of the sample. After saturation, the samples were covered on the reverse side, turned upside down to allow water to evaporate from the same surface which absorbed the treatment solution, the drying surface is the wetting surface, as suggested by *G. Borsoi et al* [20] and the samples were then placed in a chamber for drying.

The samples were dried at 35° C, in order to be as close as possible to realistic conditions in the field [1]. During the drying process, the weights of the samples were measured periodically. The efflorescences which developed on the samples during the drying process

were periodically documented on photos. At the end of the drying process, those efflorescences were collected and weighed. To estimate the effect of the inhibitor without having the dissolution effect of the distilled water, some samples were desalinated by distilled water alone (0% inhibitor) the same procedures that applied to the previous samples were also applied in this case.

| Stratigraphy (according to Jaser | Lithotype | (14, 15 and 16) | Samples | | |
|--|---|--|---|--|--|
| and Barjous [13]) | (according to Heinrichs [| [14, 13 and 10]) | No. | Description | |
| Umm Ishrin Sandstone Formation — middle part (mIN) | Multicoloured, mainly fine-grained, massive sandstone | | 1-1 1-2 | Drill cores Length: 12.5cm Diameter: 4.5cm | |
| | partly with gravel layers and scattered quartz pebbles planar, trough or overturned cross- bedding colour banding most frequent lithotype in the middle part of the Umm Ishrin Sandstone Formation most of the Petra monuments carved from this lithotype | Red variety | 1-3 1-4 | Drill cores Length: 10cm Diameter: 4.5cm | |
| | | | 2-1 2-2 2-4 | Drill cores Length: 8.5cm Diameter: 4.5cm | |
| | | Grey variety | 3-3 3-4 3-5 3-6 | Drill cores Length: 10cm Diameter: 4.5cm | |
| | | White variety | 4-2 | Drill cores Length: 11cm Diameter: 4.5cm | |
| - | White-grey to pale vi very fine-grained s - horizontal bedding - colour banding - medium to thick beds thinn | olet, clayish, sandstone ing-out of beds | 5-3 5-4 | Drill cores Length: 9.5cm Diameter: 4.5cm | |
| | Multicoloured, mainly m | edium-grained, | | | |
| 11mm Ishrin - | massive sands - partly with gravel layers an pebbles - planar, trough or overturna - colour banding - most frequent lithotype in the Umm Ishrin Sandstone For | stone nd scattered quartz ed cross-bedding he upper part of the mation | 7-5 | Drill cores Length: 10.5cm Diameter: 4.5cm | |
| Sandstone Formation | Multicoloured, mainly m | edium-grained, | | | |
| middle part (mIN) - partly with gravel layers and scattered quartz pebbles planar, trough or overturned cross-bedding colour banding most frequent lithotype in the upper part of the Umm Ishrin Sandstone Formation | | 8-1 | Drill core Length: 11cm Diameter: 4.5cm | | |
| White, medium-grained, massive sandstone - planar or trough cross-bedding - partly with gravel layers and scattered quartz pebbles | | | | Drill cores Length: 12.5cm Diameter: 4.5cm | |
| Disi Sandstone Formation (DI) | stone ion - large-scale cross-bedding - partly with gravel layers and scattered, well- rounded quartz pebbles - significant grain-size variation | | 11-7 11-28 11-31 11-42 11-50 11-51 | Cubes Edge length: appr. 6cm | |

Table 1. Lithology and description of the studied samples

| Correct | | Inhibitor concentration | | | | |
|-------------------------------------|-----------------------|-------------------------|-------|-------|-------|--|
| Group | 0.0% | 0.1% | 1% | 2% | | |
| 1 | 0 | | 1-3 | 2-4 | 1-4 | |
| (Contaminated with NaCl) | Sample | 11-28 | 3-3 | 7-5 | 3-4 | |
| | | | 5-4 | 5-3 | 11-42 | |
| | | | | 11-31 | | |
| 2 | le | | 1-1 | 1-2 | 2-2 | |
| (Contaminated with salt mixtures of | salt mixtures of KCl) | 11-7 | 2-1 | 8-1 | 3-6 | |
| NaCl and KCl) | | | 3-5 | 9-1 | 4-2 | |
| | | | 11-50 | | 11-51 | |

Table 2. Grouping and the treatment plan for the samples

Figure 1 illustrates the methodological approach of treating the samples with salt and an inhibitor.



Fig. 1. Scheme of the experiment designed to treat the samples

After each treatment, with salts and inhibitor, the salt and inhibitor content inside each sample was calculated by measuring the weight difference of the samples before and after treatment. Table 3 shows the salt contents inside the studied samples.

| NaCl salinated samples | | NaCl – KCl salinated samples | | |
|------------------------|---------------------------|------------------------------|---------------------------|--|
| Sample | Initial salt contents (g) | Sample | Initial salt contents (g) | |
| 1-3 | 1.94 | 1-1 | 2.74 | |
| 1-4 | 2.31 | 1-2 | 3.38 | |
| 2-4 | 3.26 | 2-1 | 3.61 | |
| 3-3 | 5.69 | 2-2 | 3.51 | |
| 3-4 | 5.45 | 3-5 | 5.53 | |
| 5-3 | 3.23 | 3-6 | 5.31 | |
| 5-4 | 3.55 | 4-2 | 5.10 | |
| 7-5 | 5.37 | 8-1 | 4.84 | |
| 11-28 | 9.73 | 9-1 | 5.95 | |
| 11-31 | 8.86 | 11-7 | 10.34 | |
| 11-42 | 8.23 | 11-50 | 8.18 | |
| | | 11-51 | 8.59 | |

Table 3. Salt contents inside samples salinated with saturation solution of NaCl or with 5M NaCl - 1M KCl salt mixtures

In this study, STEINKAMP Ultrasonic Tester BPV, 45kHz was used to measure each sample three times: before introducing the salt to the samples, after salination and after treating the samples with a crystallization inhibitor. The values of US measurements were calculated in the special formula to draw the salt distribution inside the samples.

Cambrian sandstone samples were divided into 6 measuring paths, while the Ordovician sandstone samples were subdivided into 8 measuring paths, as clarified in the figures 2 and 3.





For ultrasonic measurements, the samples were marked with a permanent pen (every 0.25mm) from all sides in order to measure the ultrasonic velocity in the same points (before and after salination the samples), which allows the detection of the salt distribution inside the samples [1].

The ultrasonic technique is used to study the behavior of salts distribution inside the stone before and after treatment of the samples with the inhibitor. The technique can evaluate the ability of the inhibitor to decrease the stone weathering due to salt attacks. In addition, it

assesses to which extent the inhibitor can extract salts from the back to/ or near the surface of the stone thus making it easier to remove later, for example, with the use of poultices or by spraying [1].

Results and Discussion

In all samples, the presence of salts (single salt or salt mixtures) decelerated the drying rate compared to loaded water samples.

Depending on the physical properties of the samples, Cambrian sandstone samples salinated with a saturated solution of NaCl took 993.58 hours to dry while Ordovician sandstone samples saturated with the same salt needed 185 hours to dry out. In the case of samples saturated with NaCl-KCl salt mixture solution; the Cambrian sandstone samples took 378.28 hours to dry out while Ordovician sandstone samples needed 185 hours to dry out, taking into consideration that in the case of water loaded samples, the drying process lasted only 24-48 hours. This effect can be attributed to blocking of the pores inside stone samples by salts which decrease the movement rate of the salt solution through the stone by clogging the pores. In addition, it is attributed to a thin layer of salt crystals which were formed on the surface of the stone samples and reduced the permeability [1]. At the end of the drying process, the salt contents in each sample were calculated by measuring the weight difference of the samples before and after salination.

In order to study the influence of crystallization inhibitor on the drying and crystallization behavior of single salt and salt mixtures, the drying tests with inhibitor solutions were conducted on salinated sandstone samples with different types of salts. The evaporation kinetics of inhibitor solutions were periodically controlled by weighing the samples until they reached a constant weight.

The drying rate of the samples salinated with salts and treated with an inhibitor solution was faster than that of the samples salinated with salts only (Figs. 4 and 5). This might be due to the presence of sodium ferrocyanide which modifies the kinetics behavior of the evaporation rate of salt solutions inside stone samples and changes the crystal morphology of salts from cubic to dendritic. Consequently, it promotes the movement of salt solutions from inside the samples to their surface in the form of harmless efflorescence instead of harmful subflorescence [1]. Efflorescence acts as a saturated network with a very high surface area, which leads to a greater surface area for evaporation, which dramatically increases the evaporation rate. In addition, the evaporation rate was significantly higher in the presence of inhibitors due to the reduction of the surface tension of the salt solution. This caused a reduction of the capillary pressure in a pore radius leading to a faster evaporation rate [1, 8, 21]. At the end of the drying process, the efflorescence formed at the surface of the stone samples was collected and weighed. Figures 6 and 7 shows the efflorescence formed on the stone surface at the end of the drying process. It should be mentioned that the efflorescence starts to form on the stone surface in the earliest stage of the drying process after treatment with an inhibitor. Some samples start to show efflorescence on their surface after approximately 2 hours of treatment.

The results indicate that sodium ferrocyanide acts as a powerful nucleation suppressor. Inside porous materials, this mechanism encourages the formation of harmless efflorescence instead of destructive subflorescence. Efflorescence, in this case, acts as a sink for the salts inside the stone and contributes to reducing the amount of salts inside the stone [1, 21]. Also, the formation of efflorescence prevents the pores inside the stone from clogging, which allows the transport of more salts from inside the stone up to the drying surface [22].

Ultrasonic velocity was used to develop a calculation model by a special computer program under excel, in order to assess the salt distribution inside the samples before and after treatment with a crystallization inhibitor. The technique could lead to establishing the success rate of applying an inhibitor solution in order to extract salts from the depth of the samples to / or near the stone surface to make the salts easily removable. Figures 8 and 9 represent the distribution of salts by using this method [1].



Fig. 4. Drying curve of sample 11-50 salinated with salt mixture and treated with 0.1% inhibitor solution



Fig. 6. Efflorescences formed at the end of drying process on sample 11-50 salinated with salt mixture and treated with 0.1% inhibitor solution



Fig. 5. Drying curve of sample 7-5 salinated with saturated soluation of NaCl and treated with 1% inhibitor solution



Fig. 7. Efflorescences formed at the end of drying process on sample 7-5 salinated with saturated soluation of NaCl and treated with 1% inhibitor solution

The figures 8 and 9 show the distribution of salt before and after treatment with an inhibitor. The figures also illustrate that the salts were removed from each section along the sample, especially from the inner parts of the sample (bottom of the sample). Regarding the salt extraction performance of sodium ferrocyanide, it is clear that it can extract deep-lying salt from a salt mixture better than from a single salt. This of course is good news because salts in the field are usually mixtures of salt and rarely single salts is present

According to our studies, it can be noticed that the total removability of the salts after treatment with a crystallization inhibitor for both single and salt mixtures is controlled by two main factors:

- Dissolution of the salt during the treatment which might be attributed to the crystallized salts near the surface (base) of the sample which partially dissolved and leached out of the sample during the treatment process.
- Formation of removable efflorescences at the end of the drying process.

The following figure 10 summarizes the effect of treatment with inhibitor on the mass of the samples

If (A) is the mass of salts dissolved during the treatment with the salt inhibitor, (B) is the mass of the inhibitor and (C) is the mass of salts formed as efflorescences; then total removability of salt can be calculated according to the following formula: Removability of salt = (A + C) - B.



Fig. 8. Salt distributions for a representative sample 11-42 salinated with NaCl and treated with 2% inhibitor solution



Fig. 9. Salt distributions for sample 11-51 salinated with NaCl-KCl salt mixtures and treated with 2% inhibitor solution

The effect of treatment with inhibitor on the mass of the samples is presented in table 10. The results of treated samples salinated with single and salt mixtures show that the formation of efflorescence and the total removability of the salts were significantly higher in the case of salt mixtures than in single salts. Figures 11 and 12 summarize the main results of salt removability after treatment.



Fig. 10. The effect of treatment with inhibitor on the mass of the samples

The formation of efflorescences can indicate the success of the salt removal treatment. In the case of sodium chloride, the average salt efflorescence is about 27%, while in the case of NaCl – KCl mixture the average is 46%. This means that the average formation of efflorescence in the case of NaCl – KCl mixtures is about 70% higher than the formation of efflorescence in the case of single salt, which makes the total removability of salts from samples salinated with NaCl – KCl mixture and treated by crystallization inhibitor 33% higher compared to the application of such a product on samples salinated with NaCl. This could be attributed to the presence of KCl especially K⁺, which improves the ability of sodium ferrocyanide to act as a crystallization inhibitor for sodium chloride salt. In addition, the presence of K⁺ could reduce the cohesion effects of NaCl. It also reduced the interconnection between the NaCl molecules which led to them being easily extracted by sodium ferrocyanide [1].



Fig. 11. Salt removability in (%) of initial salt contents.

Saturated NaCl and treated with inhibitor solution, (0.1%, 1.0% and 2.0%).



Fig. 12. Salt removability in (%) of initial salt contents. Mixture of NaCl - KCl and treated with inhibitor solution, (0.1%, 1.0% and 2.0%)

Table 4 summarizes the effect of sodium ferrocyanide on the removability of salts from the samples salinated with both single and mixtures of salts.

| Salt introduced | Inhibitor concentration | Sample | Drying time (h) | Initial salt contents (g) | Dissolutions in the course of treatment (%) | Efflorescences formation (%) | Total removability (%) |
|--------------------|----------------------------|--------|--------------------|------------------------------------|--|------------------------------------|------------------------------|
| Ū | 0% | 11-28 | 227.00 | 9.73 | 18.49 | 20.54 | 39.03 |
| | 0.1% | 1-3 | 676.70 | 1.94 | 26.13 | 23.19 | 49.00 |
| | | 3-3 | 783.73 | 5.69 | 14.87 | 22.32 | 36.99 |
| | | 5-4 | 1234.43 | 3.55 | 14.16 | 18.00 | 31.99 |
| | | 2-4 | 340.62 | 3.26 | 22.66 | 37.75 | 58.09 |
| Ž | 1% | 7-5 | 331.57 | 5.37 | 16.09 | 33.16 | 47.51 |
| | 1 70 | 5-3 | 1547.25 | 3.23 | 19.81 | 24.49 | 40.03 |
| | | 11-31 | 201.00 | 8.86 | 24.47 | 35.11 | 57.67 |
| | 2% | 1-4 | 765.95 | 2.31 | 30.42 | 23.79 | 48.22 |
| | | 3-4 | 903.45 | 5.45 | 19.56 | 34.34 | 50.1 |
| | | 11-42 | 344.20 | 8.23 | 19.81 | 24.29 | 40.11 |
| NaCI - KCI | 0% | 11-7 | 333.00 | 10.34 | 8.38 | 0.48 | 8.86 |
| | 0.1% | 1-1 | 594.23 | 2.74 | 38.65 | 20.46 | 58.83 |
| | | 2-1 | 329.63 | 3.61 | 12.88 | 57.32 | 70.00 |
| | | 3-5 | 477.67 | 5.53 | 11.07 | 51.68 | 62.58 |
| | | 11-50 | 140.35 | 8.18 | 6.87 | 49.39 | 56.06 |
| | 1% | 1-2 | 735.53 | 3.38 | 24.04 | 28.98 | 50.77 |
| | | 8-1 | 467.42 | 4.84 | 16.24 | 47.30 | 61.87 |
| | | 9-1 | 397 | 5.95 | 6.17 | 51.46 | 55.65 |
| | 2% | 2-2 | 282.72 | 3.51 | 14.12 | 55.81 | 65.64 |
| | | 3-6 | 728.02 | 5.31 | 10.40 | 51.23 | 57.69 |
| | | 4-2 | 479.13 | 5.10 | 24.77 | 52.14 | 73.09 |
| | | 11-51 | 140.35 | 8.59 | 4.79 | 40.07 | 40.66 |

Table 4. The impact of sodium ferrocyanide on the removability of salts from the samples salinated by NaCl or NaCl-KCl solutions

In the case of sample 11-28, which was salinated with a saturated solution of sodium chloride and sample 11-7, which was salinated with a mixture of NaCl-KCl, and treated with 0% of inhibitor concentration, a salt crust was formed on the surface of the stone. This crust leads to a detachment of the stone materials in the form of flaking, scaling and granular disintegration. Consequently, the salt crust will disintegrate into powder, especially if the stone surface is very brittle and weak. In addition, the salt crust can block the stone surface and prevent water vapor diffusion [17, 22, 23].



Fig. 13. Salt crust and efflorescences formed at the end of drying process on sample 11-28 salinated with saturated solution of NaCl treated with 0% inhibitor solution



Fig. 14. Salt crust and efflorescence formed at the end of drying process on sample 11-7 salinated with salt mixture and treated with 0% inhibitor solution

However, this phenomenon did not take place when a crystallization inhibitor was applied. Additionally, when the desalination process performed without salt inhibitor, the efflorescence strongly stuck to the stone surface, while when the samples were treated with an inhibitor the efflorescence was loose and powdery material. This suggests that using sodium ferrocyanide to prevent salt damage to stone monuments is superior to using water to mitigate the impact of salt weathering [1]. Figures 13 and 14 show the formation of a salt crust on the stone surface at the end of the drying process after treatment with water only.

Conclusions

The existence of salts has a crucial effect on changing the drying rate of porous stone materials. From the drying behavior of porous stone materials salinated with single and salt mixtures with and without inhibitors, the presence of salts (single and salt mixtures) in all samples slows down the drying rate compared to the samples loaded with water only. For the samples salinated with salt and salt mixtures and treated with crystallization inhibitors with different concentrations (0.1%, 1.0% and 2.0%), it is apparent that their drying rate was much faster than that of the samples salinated with salts but not treated with an inhibitor. The faster drying rate could be linked to the presence of sodium ferrocyanide, which modifies the kinetic behavior of the evaporation rate of salt solutions inside porous stone materials.

Within the scope of this study, it has been confirmed that using sodium ferrocyanide decahydrate (Na₄Fe(CN)₆·10H₂O) as a salt crystallization inhibitor for sandstone monuments in Petra – Jordan, acts as a preventive measure for the improvement of desalination processes as well as the reduction of aggressiveness and damage potential of salt weathering regimes against both single and mixtures of salt, even when used in a very low concentrations.

Comparing the extraction of salts from stone samples with traditional methods using distilled water and by the application of a crystallization inhibitor, it can be concluded that using sodium ferrocyanide as a crystallization inhibitor for both preventive measures of salt

weathering and extraction of salts, is superior to using pure water to mitigate the salt-induced damage to porous materials.

In the real field, weathering of monumental stones is caused by the presence of a complex composition of mixtures, for example, it may include NaCl, $CaSO_4 \cdot 2H_2O$, KNO_3 , MgCl₂, Na₂SO₄, KCl, NaCO₃ and K₂SO₄. The existence of several different types of salts together could lead to the formation of complicated salt compounds in these materials. The damaging actions of such compounds need to be studied in more details, in order to understand the weathering mechanisms of such compounds. Therefore, the application of sodium ferrocyanide as a crystallization inhibitor and its influence on other salt mixtures, for example (NaCl, KCl and KNO₃), (NaCl, KCl and CaSO₄·2H₂O) and (NaCl, CaSO₄·2H₂O, KCl and Na₂SO₄) needs to be studied in more details in bulk and porous materials, to provide a basis for complex experiments on porous materials.

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