

*Original article***LABORATORY INVESTIGATION OF SODIUM FERROCYANIDE AS A CRYSTALLIZATION INHIBITOR TO PREVENT THE DESTRUCTION OF ROCK-CUT MONUMENTS IN PETRA – JORDAN DUE TO THE ATTACK OF SALT MIXTURES**

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Abstract:

Salt weathering is considered one of the most important factors leading to the damage of Petra's monuments. Inhabiting or limiting the crystallization of these salts could therefore prevent/slow down the destruction of Petra's sandstones. Using of sodium ferrocyanide as a salt crystallization inhibitor has been proved in the past as a prospective treatment measure against salt weathering. This study is the first to investigate the effectiveness of salt crystallization inhibitor on a stone material loaded with a salt mixture. The effect of sodium ferrocyanide on the crystallization of salt mixtures inside sandstone samples from Petra has been studied. The results showed that using of inhibitor changes the crystal morphology of salts from cubic to dendrites, which makes the drying time faster than that of pure salt solution. Therefore, allows the salt to crystallize on the surface of the stone in the form of harmless efflorescence rather than destructive sub-florescence.

1. Introduction

Salt weathering is considered one of the severest threats to the preservation of cultural heritage built from porous materials. The growth of salt crystals inside confined pores of stone is a crucial factor for generates internal forces that damage the stone material due to crystallization pressure [1-3]. A lot of extensive studies have been done during the last decades, in order to understand the process of salt weathering and their impact on stone materials. Most of these studies concentrated on the damage occurred by the action of a single salt. Whereas, a single salt is scarcely found in porous materials as usually salt mixtures are found in the field [2]. Comparing crystallization pressure of a single salt with that of salt mixtures, it's obvious that the salt crystallization pressure of salt mixtures is more destructive and complicated than that of a single salt [2-4]. Resulting in a great damage potential to stone materials [3]. Inhibiting or limiting the crystallization pressure of salt are required, in order to preserve our cultural heritage. Different methods and technique have been proposed in the past, such as using of absorbent poultices, washing the stone monuments with salt free water,

electro migration, dry brushing and the use of sand lime sacrificial render [5-9] with varying degree of success. This study addresses the ancient city of Petra – Jordan. The archaeological city of Petra is of outstanding universal value; in 1985 it was registered on the UNESCO list of world heritage site. In 2007 it was elected to be 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. The region of Petra is mainly composed from sedimentary rock of the early Paleozoic age. Cambrian Umm Ishrin sandstone formation (middle and upper part) and the Ordovician sandstone formation (Disi Sandstone) are the relevant stratigraphy with respect to the rock cut monuments of the area [10]. All rock-cut monuments show weathering damage, partly to a very high extent. The weathering process in Petra is varied and complicated, many factors work together on the rock monuments

and damage the structural strength of the stone. In this respect, experts agree that salt is the major contributor of this damage [11-19]. All types of stone detachments are connected to the presence of salts [17,19] resulting in flaking, spalling and salt efflorescences [20]. Results of previous studies concentrated on salts damage at the archaeological city of Petra revealed a wide variety of salts, (NaCl, CaSO₄·2H₂O, KNO₃, KCl, K₂SO₄, CaSO₄, MgCO₃, MgSO₄, Na₂SO₄·10H₂O etc...) [11,17,18]. Occurring as efflorescence, sub-florescence or salt crusts. The highest damage potential is attributed to the subflorescence. Because of the internal stress which they exceed the strength of the stone material and leads surface spalling, scaling and detachment, the internal stress is generated due to volumetric expansion of salt crystals inside the pores [21,22]. Consequently, inhibiting or limiting the crystallization of these salts could slow down and/or prevent the damage of the stone monuments in Petra by the action of salts weathering. A quite new field of research is the use of salt crystallization inhibitor, which has the ability for improving desalination as well as for reducing aggressiveness and damage potential of salt weathering and enhance salt transport from the deep of the porous stone up to their surface, and herewith promote the formation of harmless efflorescence instead of harmful subflorescence [23-28]. Previous research has addressed the treatment of stone by the application of salt crystallization inhibitor [23, 24,29-31]. All of these studies performed their laboratory investigations on stone loaded with a single salt without any consideration to the presence of a salt mixtures inside the stone monuments. In addition, most of these studies performed their investigation by added the solution of crystallization inhibitor to the bulk salt solution prior to samples loaded with salts, thus both are introduced into the sample at the same time during the treatment setup [23, 24,29-31]. While in the real condition salts already exist inside the stone before treatment with crystallization inhibitor. This study is the first to investigate the efficiency of salt crystallization inhibitor on a stone material loaded with a salt mixture. Based on the fact that salts in monuments stone are not exist in a pure state but only as a mixture of different type of salts, this study will examine the effectiveness of one of the most important crystallization inhibitors (Sodium ferrocyanide decahydrate) as a preventive measure against mixtures of salt inside real porous materials, in order to increase the durability of stone materials against the action of salt weathering, and to be as close as possible to the actual condition in the field. Sodium ferrocyanide (Na₄Fe(CN)₆·10H₂O) is a well-known anti caking agent used for sodium chloride. It has a very strong anti-caking effect; it inhibits nucleation and crystal growth of salts, as well as it modifies the crystal habit of sodium chloride. Sodium chloride is growing in the form of dendrites instead of cubic form, even in the presence of an extremely small amount of sodium ferrocyanide [2,32]. The mechanism action of ferrocyanide ions in the inhibiting of sodium chloride is that ferrocyanide ions ([Fe(CN)₆]⁴⁻) displace the chloride ion (Cl⁻) on the surface of sodium chloride. That's leads to one cyanide group replaces the chloride ion, resulting in substitution the

sodium chloride lumps on the surface and block any additional growth because of the different in ion charge [2,32, 33]. In monumental stones this mechanism promotes the ferrocyanide ions to increase the evaporation rate of the salt solution inside the pore structure, and on permitting the harmless efflorescence to be formed instead of harmful sub-florescence [4,28,34]. This study addresses the application of so-called salt crystallization inhibitor on the rock-cut monuments in the ancient city of Petra – Jordan, in order to reduce the aggressiveness and potential damage of stone monuments by the action of salts mixture.

2. Materials and Methods

2.1. Samples

Disi sandstone formation (Ordovician) were collected from the area around the archaeological city of Petra specifically from little Petra (Al-Beidha), because it was not possible to take the samples directly from the archaeological city. Cubes of 6×6×6 cm³ were cut from the blocks. In addition, block of Umm Ishrin sandstone formation (Cambrian) 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 blocks had been gathered for a previous research project in the ancient city of Petra – Jordan (1996-1999). Drill core samples of different length were cut from the blocks. The physical properties: water absorption at atmospheric pressure, water absorption at vacuum, porosity, saturation coefficient and water absorption coefficient for all the samples were measured. After the physical properties were measured, the samples were classified according to their physical properties, in order to use the similar samples in the same test phase to make the results more realistic, tab. (1). To estimate the same behaviour in the real field and to allow unidirectional solution movement from bottom of the sample and drying from the top of the sample during the experiment setup, the samples were sealed with Tesa tape on all side except the top and the bottom of the samples.

Table (1) treatment plan for the samples contaminated with salt mixtures of NaCl, KCl and KNO₃ (composition, 4 m: 1 m: 0.5 m)

Inhibitor concentration		
0.1%		1%
Sample 3-1		Sample 3-2
Sample 5-1		Sample 5-2
Sample 6-3		Sample 6-4
Sample 7-1		Sample 7-4
Sample 9-2		Sample 9-3
Sample 11-37		Sample 11-20
Sample 11-19		Sample 11-10

2.2. Salts

Three types of salts have been introduced to the samples, NaCl, KCl and KNO₃ in ratio of 4m: 1m: 0.5m by capillary rise. This ratio was an estimation from real data of Dr. Kurt Heinrichs from the department of Engineering Geology and Hydrogeology – RWTH Aachen University, from his previous work results in the archaeological city of Petra (2005 and 2008) [19,35]. In addition, these salts were determined in the sandstone monuments at the archaeological

city of Petra, and are considered significant salts causing damage to Petra's sandstones [11,13,17]. The samples were dried under controlled condition (60°C and almost 5% RH). During the drying process, to force the evaporation of the salt solution to occur only through the surface of the stone sample in order to simulate the real field as closely as possible, the base of the samples was sealed. The solution evaporation was periodically measured by weighting the samples two times a day until they reached a steady weight.

2.3. Crystallization Inhibitor

0.1 % and 1% of inhibitor solution $[\text{Na}_4\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ was prepared and introduced into the salinated samples by capillary rise. The used concentration has been selected based on earlier works carried out by several scholars who declared that using sodium ferrocyanide as a salt crystallization inhibitor could reduce the potential damage of salts [23,24,26,27,29]. To prevent the introduced salts from being mixed up during the treatment setup, each sample was placed in a separate box and treated independently. The weight and the height of the inhibitor solution were periodically measured until the solution reached the surface of the sample. Because of the drying surface is the wetting surface as mentioned by G. Borsoi et al [36], after saturation the samples were covered on the reverse side, turned upside down in order to allow water to evaporate from the same area which absorbed the inhibitor solution, then they were placed in a chamber for drying. The samples were dried at 35°C, to be as close as possible to the real condition in the site, the weight of the samples was registered periodically during the drying process. The efflorescences which developed on the surface of the samples during the drying process were frequently documented by photos. Those efflorescences were collected at the end of the drying process. The methodological approach of this study has been taken from the previous work of the author [28]. Figure (1) demonstrates the methodological approach of the treatment setup. The ultrasonic technique is used in this study to determine the behavior of salt distribution inside the studied samples before and after inhibitor treatment. The diagram of the setup is given in the previous article of the author [28]. This technique can evaluate the capability of the crystallization inhibitor to slow down the stone weathering by the action of salt. Moreover, it evaluates to which extent the crystallization inhibitor can pull out the salts from the back to/or near the surface of the stone. Therefore, making it effortless to remove later, by using spraying or poultices for example.

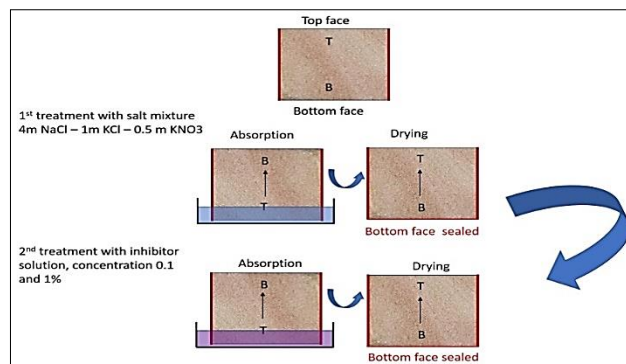


Figure (1) scheme of the experiment designed to treat the samples (Modified After: Abu Alhassan et al 2020)

3. Results

After salination of the samples, the salt content in each sample was calculated by measuring the weight difference of the sample before and after salt insertion. Table (2) shows the salt contents inside the samples. At the end of drying process, the efflorescence which was formed on the surface of the stone samples was collected and weighed. Figure (2-a & b) illustrates the efflorescence formed at the surface of the studied stone samples at the end of drying procedure.

Table (2) salt contents inside the studied samples

Salt mixtures salinated samples	
Sample	Initial salt contents (g)
3-1	6.78
3-2	7.12
5-1	4.56
5-2	4.01
6-3	5.36
6-4	5.52
7-1	6.08
7-4	6.03
9-2	6.09
9-3	6.10
11-10	8.14
11-19	8.18
11-20	8.08
11-37	9.30

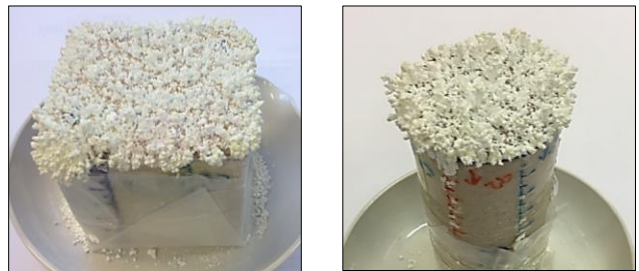


Figure (2) efflorescences formed at the end of drying process on sample 11-37 salinated with salt mixture NaCl-KCl-KNO₃ a. treated with 0.1% inhibitor solution, b. on sample 9-3 treated with 1% inhibitor solution

Ultrasonic velocity technique has been used to establish an evaluation model by a special computer program under Excel, to assess the salt distribution inside the stone samples before and after using the salt crystallization inhibitor. The technique could lead to developing the success rate of using the inhibitor solution to extract salts from deep of the samples to/or near the surface of the stone in order to make the salts easily removable [28]. Figures. (4 & 5) illustrate the distribution of salts by using this technique. The influence of treatment with crystallization inhibitor on the salinated samples is presented in fig. (6-a). The results show that the formation of efflorescence and the total removability of salts were considerably high. Figure (6-b) summarize the main results of salt removability after treatment. The following figure outlines the total removability of salts from the samples after being treated with a salt crystallization inhibitor, where (A) is the mass of salts dissolved in the course of treatment setup, (B) is the inhibitor introduced to the

sample, (C) is the formed efflorescence at the end of drying, Thereafter, the total removability of salt can be calculated according to the following formula: Removability of salt =

(A+C) - (B) [28]. Table (3) summarizes the effect of sodium ferrocyanide on the removability of salts from the samples salinated with both single and mixtures of salts.

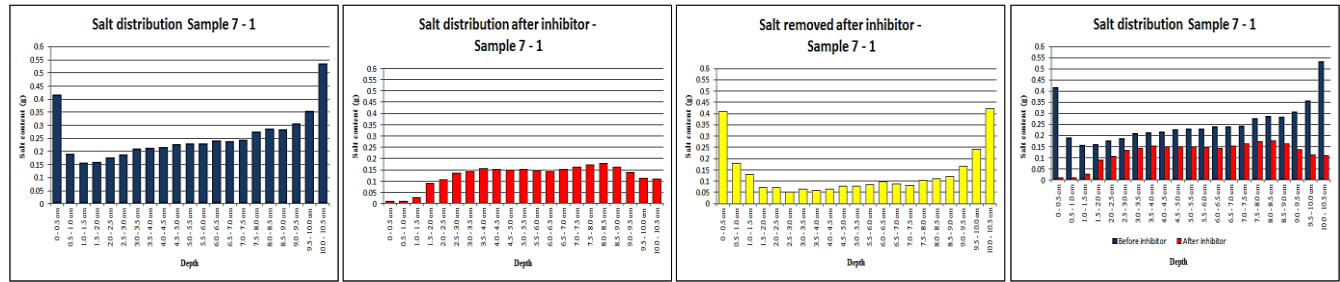


Figure (4) salt distributions for a representative sample 7-1 salinized with NaCl-KCl-KNO₃ and treated with 0.1% inhibitor solution

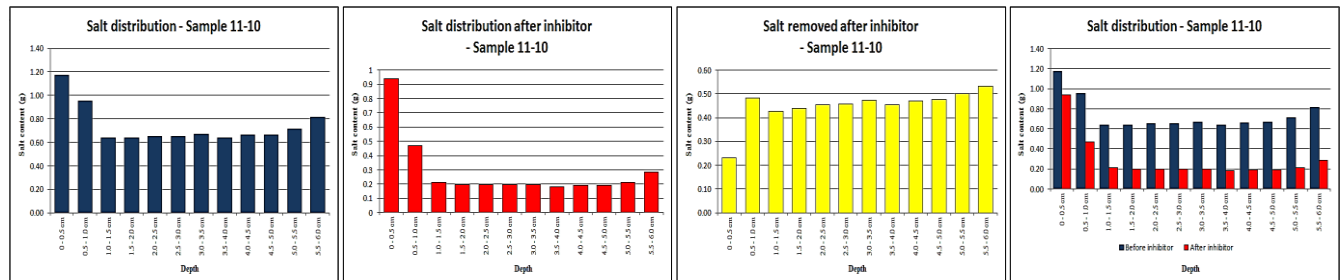


Figure (5) salt distributions for a representative sample 11-10 salinized with NaCl-KCl-KNO₃ and treated with 1% inhibitor solution

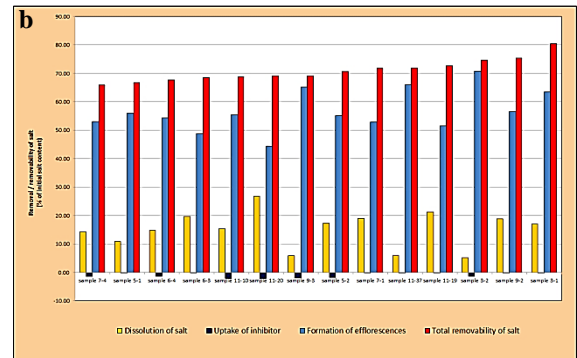
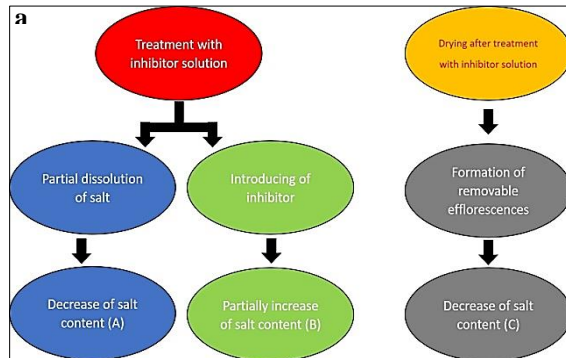


Figure (6) a. the removability of salts after the application of crystallization inhibitor (Modified After: Abu Alhassan et. al 2020), b. salt removability in (%) of initial salt contents. Mixture of NaCl - KCl - KNO₃ and treated with inhibitor solution, (0.1% and 1%)

Table (3) The effect of crystallization inhibitor on the removability of salts from the samples salinized by NaCl - KCl - KNO₃ solution

Sample	Initial salt contents (g)	Inhibitor conc. (%)	Dissolutions in the course of treatment (%)	Efflorescences Formation (%)	Total removability (%)
3-1	6.78	0.1 %	17.15	63.42	80.41
5-1	4.56		10.94	55.92	66.70
6-3	5.36		19.74	48.88	68.48
7-1	6.08		19.02	52.96	71.81
9-2	6.09		18.88	56.65	75.39
11-19	8.18		21.33	51.59	72.71
11-37	9.30		6.04	66.02	71.89
3-2	7.12	1 %	5.15	70.79	74.64
5-2	4.01		17.31	55.11	70.57
6-4	5.52		14.73	54.35	67.70
7-4	6.03		14.32	53.07	65.85
9-3	6.10		5.85	65.25	69.17
11-10	8.14		15.38	55.53	68.80
11-20	8.08		26.82	44.43	69.16

4. Discussion

The influence of salt crystallization inhibitor on the drying behavior of the samples was obvious, since it was faster than that of the samples salinated with salt mixtures. Which is clearly depends on the existence of crystallization inhibitor which change the kinetics behavior of the evaporation rate of salt solution inside the studied samples and modifies the crystal morphology of salts from cubic to dendritic shape. Accordingly, it allows the transportation of salt solution from inside the samples up to their surface, resulting in the formation of harmless efflorescence instead of damaging subflorescence. The results are in line with findings of previous works by [23,27,28]. In addition, Efflorescence in this case works as a saturated network with a very high surface area, that's works on a greater surface for evaporation, leading to increase of the evaporation rate. Furthermore, the evaporation rate was noticeably higher in the presence of crystallization inhibitor because of the reduction of the surface tension of the salt solution, which generate a reduction of the capillary pressure inside a pore radius resulting in a faster evaporation rate [2,23,37]. The results prove that using sodium ferrocyanide as a crystallization inhibitor works as a powerful nucleation suppressor. This mechanism inside stone materials encourages the formation of non-destructive efflorescence rather than destructive subflorescence. Efflorescence, in this case works as a basin for the salts inside the stone and contributes to decreasing the amount of salts inside the stone material [23,28]. In addition, the formation of efflorescence avoids the clogging of the pores inside the stone, which permits the transfer of more salt from the deep of the stone up to their drying surface [38]. Based on the results of this study, fig. (4 & 5) present the distribution of salts before and after treatment with crystallization inhibitor. They also clarify that the salts were extracted from each section along the sample, especially from the deep parts of the sample. This indicates that using sodium ferrocyanide as a crystallization inhibitor can extract deep-lying salts from a complex salt mixture from the inner parts of the sample, which is considered a promising result with respect to the salt weathering reduction. The total removability of salts in this study is controlled by two main factors:

- *) Dissolution of the salts in the course of treatment setup, which might refer to the crystallized salts near the bottom of the sample which partially dissolved and leached out of the sample during the insertion of the inhibitor*
- *) Formation of removable efflorescence at the end of the treatment process.*

According to Abu Alhassan, et. al (2020) [28], the formation of efflorescence plays an important role in the success of the treatment. He mentioned that in the case of using crystallization inhibitor on a salinated samples with a single salt only (sodium chloride) the average of efflorescence formation was 27%, while in the case of NaCl-KCl mixture the average was 46%, which means that the formation of efflorescence in the case of NaCl-KCl in (%) was 70% higher. In this study, the average of efflorescence formation is 56.7%. This means that the average formation of efflorescence in the case of NaCl-KCl-KNO₃ is about 86.4%

higher than the formation of efflorescence in the case of NaCl-KCl mixture, that makes the total removability of salt from the samples salinated with NaCl-NaCl-KNO₃ and treated with sodium ferrocyanide 77.71 % higher compared to the application of crystallization inhibitor on the similar samples salinated with NaCl-KCl mixture. The total removability in this study is 70.95% while in the case of the similar samples salinated with NaCl-KCl (According to Abu Alhassan et. al (2020) [28] was 55.14 %. This could be attributed to the presence of K⁺ in KCl and KNO₃, which enhance the ability of sodium ferrocyanide to work as a crystallization inhibitor for NaCl. In addition, it reduces the cohesion impacts of sodium chloride and decrease the interconnection between NaCl molecules which make them easily extracted by sodium ferrocyanide [2].

5. Conclusions

The greater part of sandstone monuments in the ancient city of Petra are highly subject to salt weathering. Consequently, a crucial action should be taken into consideration to prevent the severe damage of salt crystallization pressure. The methodology which was carried out for this study proved that the application of sodium ferrocyanide as a crystallization inhibitor for sandstone samples from the ancient city of Petra reduces the aggressiveness and damage potential of salt weathering regime (salt mixtures) as well as for the improvement of desalination processes. The crystal morphology of salts changes from cubic to dendrites in the presence of sodium ferrocyanide which makes the drying time faster than that of pure salt solution. Which makes the drying rate faster because of the branches which provide a track for the salt solution to spread over a larger surface area. In porous materials, this effect allows the salt to crystallize on the surface of the stone in the form of harmless efflorescence rather than destructive subflorescence. Important conclusions can be outlined from the experiments presented in this research. Nevertheless, it must not be ignored that the laboratory tests deliver significant and useful suggestion, nonetheless they cannot provide final results. The final results will only be achievable when the materials are analyzed under real natural condition in the field. However, the problems of conservation of our cultural heritage could not be resolved based on laboratory experiments alone. Accordingly, field testing program should run at the same time to the laboratory testing program. Therefore, the results gained and reported in this research are introductory and need to be subjected to further experiments in the real field. Although the results of this study provide very important sings that are of practical value for determining the influence of applying salt crystallization inhibitors to prevent the archaeological city of Petra from the action of salt weathering. Thus, some questions remain that need to be addressed in more details in the future. Can repeat of the treatment improve the removability of salt? If so, to what degree? How long will the crystallization inhibitor be present and useful inside the stone? Can the inhibitor which was left in the samples has a preventive impact in the case of repeated the salination? If so, to what degree? Is it possible to use another inhibitor or a combination of different inhibitors and use them as a preventive measure against the action of salt weathering due to salt mixtures? Further laboratory tests are needed to address the above-mentioned questions.

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