

Salts in Ceramic Bodies I: Introducing Salts into Ceramics

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Abstract

An experimental study was designed to introduce known amounts of soluble salts into ceramic tiles, evaluate the effect these salts have on the ceramic when cycled over a limited range of RH, and eventually desalinate the tiles to quantitatively evaluate the different desalination procedures used. This first part of the study describes the ceramics used and the methodology followed to introduce salts into them. The soluble salts used were NaCl, Na₂SO₄ and CaSO₄·2H₂O, and mixtures of the first with either of the other two. It was found that the method of drying the tiles significantly affected the amount of salt remaining in them and this was salt-specific. Reasons for this behavior are discussed.

Keywords: ceramics, salts, porosity, sodium chloride, sodium sulfate, gypsum, drying method

Salze in poröser Keramik I: Einbringen der Salze in die porösen keramischen Proben

Zusammenfassung

Um bekannte Mengen Salz in keramische Ziegel einzubringen, wurden entsprechende Versuche durchgeführt. Ziel der Studie ist es, den Einfluss, den diese Salze auf die Eigenschaften der keramischen Proben unter zyklischer Veränderung der relativen Luftfeuchtigkeit in einem begrenzten Bereich haben, um schliesslich die Ziegel wieder zu entsalzen, um dadurch die unterschiedlichen verwendeten Methoden quantitativ beurteilen zu können. Im ersten Teil werden die Herstellung der

keramischen Ziegel und die Methode, mit der Salze in diese Proben eingebracht werden, beschrieben. Die folgenden wasserlöslichen Salze wurden verwendet: NaCl, Na₂SO₄ and CaSO₄.2H₂O. Ausserdem wurden Mischungen aus dem ersten mit dem zweiten und mit dem dritten der genannten Salze eingebracht. Es wurde festgestellt, dass die Trocknungsmethode einen deutlichen Einfluss auf die Menge Salz hat, die in den porösen Ziegeln zurückbleibt. Ausserdem hängt diese Menge noch von der Salzart ab. Die Ursachen für dieses Verhalten werden diskutiert.

Stichwörter: Keramik, Salze, Porosität, Natriumchlorid, Natriumsulfat, Gips, Trocknung



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1 Introduction

The deleterious effect of soluble salts in porous materials is well known, however, the limiting conditions under which this deterioration occurs is not so well understood. Similarly, the evaluation of desalination methods, usually carried out on archaeological or architectural objects, mainly relies on the analysis of the amount of extracted salts. The laboratory study described in this and subsequent papers in this issue, aims to evaluate the role of soluble salts in the deterioration of ceramic bodies that are exposed to minimal changes in relative humidity as well as the effectiveness of subsequent desalination methods. For this purpose, ceramic tiles of different porosity were obtained and impregnated with known amounts of salts. While the behaviour of the test tiles may not precisely replicate real objects the study may prove useful in devising treatments for salt-laden artifacts.

The study used ad hoc prepared ceramic tiles which were impregnated with various soluble salts: sodium chloride (NaCl), sodium sulfate (Na_2SO_4) and gypsum, ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), as well as mixtures of the first with either of the other two. The choice of soluble salts and their mixtures was based on personal experience of the authors and other researchers as to the most frequently found salts in archaeological ceramics from museum collections [1,2]. This first paper describes the tiles used for this experiment and the procedure adopted to introduce the individual salts, or their mixtures into the tiles.

2 Experimental

2.1 Ceramic tiles

Two sets of approximately fifty ceramic tiles each were manufactured. The first was an Ohio Red Art earthenware clay and the second a stoneware clay. The ceramic tiles were manufactured by extruding a 6 x 6 x 6 cm clay slab and then slicing 1.5 cm thick tiles from it. Tiles were identified by numbers scratched into the surface with a dremmel tool after firing.

The earthenware tiles were fired at 800°C (cone 015). After firing, the red coloured tiles measured an average of 5.7 x 5.6 x 1.4 cm and had an average weight of 71.61 grams. Characterization of the pore size by optical microscopy in thin section showed that the main pore sizes ranged from 0.05 mm² to 0.0001 mm² with nearly half of the measured pores having areas below 0.01 mm². All of the pores in the earthenware tiles were small and their shapes generally depended on their size. Pores with an area between 0.05 mm² and 0.0025 mm² were oblong in shape as a result of the extrusion manufacturing process. Smaller pores, with an area under 0.0025 mm², had a more circular shape. Further information on the ceramic composition can be found elsewhere [3].

The stoneware clay tiles were fired at 1230°C (cone 06). The yellow-pink stoneware tiles had average dimensions of 5.3 x 5.4 x 1.4 cm and an average weight of 76.90 grams. More pores, as compared to the earthenware tiles, were long and narrow reflecting the extrusion manufacturing process. However, some pores were significantly larger, having an area above 0.1 mm². There were few medium-size pores with areas between 0.05 mm² and 0.01 mm². Nearly half of the measured pores had areas smaller than 0.01 mm². Further information on the ceramic body composition can be found elsewhere [3].

A review of the literature shows that the ranges of open porosity found in both archaeological and architectural ceramics results largely from differences in material and manufacturing processes. The most common range falls around 10-20% that is similar to the porosities of the tiles used in this experiment.

The amount of moisture held by these tiles when dried and weighed in the laboratory was about 0.4% for the earthenware and less than 0.02% for the stoneware ones.

2.2 Open porosity and drying curves

The open porosity of the tiles was determined by total immersion in deionized water following the two immersion methods described in ASTM C67-97 [4]. These use immersion times of twenty-four hours in cold water and five hours in boiling water. The results are presented in Table 1.

Complementing the above method, the water absorption curves of totally immersed tiles were obtained following the NORMAL 7/81 procedure [5]. Figure 1 shows typical water absorption curves - up to the asymptotic region - for both types of tiles. During the initial water absorption stage stoneware tiles had a greater dispersion of data than earthenware tiles. This reflects the influence of the larger pores they contain.

Table 1: Open porosity of the ceramic tiles measured by total immersion in deionized water: 24 hours in cold water and 5 hours in boiling water (ASTM C67-97). Standard deviation is given in brackets.

	24-hour immersion (cold water)	5-hour immersion (boiling water)
Earthenware	17.7 % (±0.8)	19.1 % (±0.8)
Stoneware	5.1% (±0.3)	7.8% (±0.3)

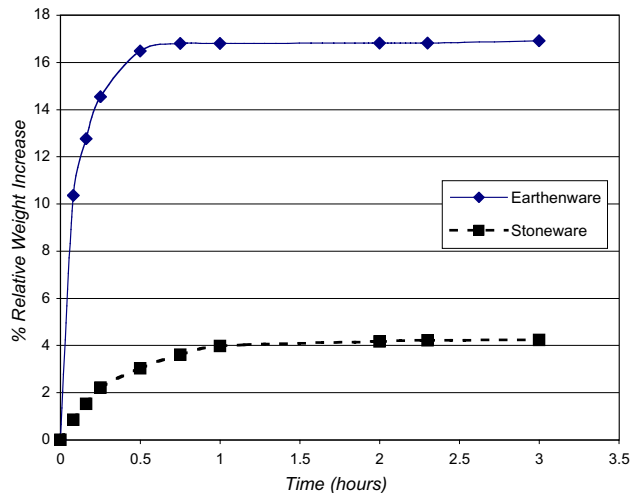


Figure 1: Initial section of typical water absorption curves by total immersion for both earthenware and stoneware tiles.

The drying behaviour of the tiles was determined following the NORMAL 29/88 procedure [6]. From the drying curves obtained, shown in Figure 2, the critical moisture content for the earthenware and the stoneware tiles was estimated to be about 8% and 2.5% respectively. Although stoneware tiles have a slightly slower drying rate they reach the critical moisture content faster than the earthenware ones - approximately in half the amount of time - mainly because of the lower amount of water they absorb (see Figure 1). The slower drying rate of these tiles is also evident in the time they take to reach the final horizontal section of the curve where the evaporation mechanism is controlled only by water vapour diffusion.

2.3 Salt solutions

Saturated solutions of the following salts were prepared:

- Solution a: NaCl
- Solution b: Na₂SO₄
- Solution c: CaSO₄.2H₂O
- Solution d: mixture of NaCl and Na₂SO₄
- Solution e: mixture of NaCl and CaSO₄.2H₂O

The saturated solutions of the individual three salts, solutions a-c, were prepared by mixing the corresponding amount of salt into 1.5 liters of distilled and deionized water and then adding an excess of some 10-15 grams to ensure saturation.

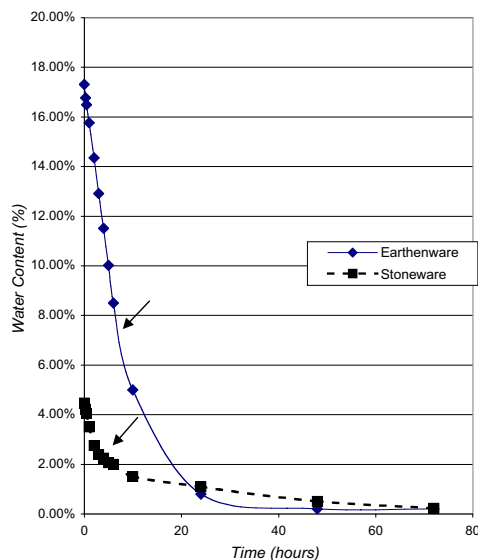


Figure 2: Typical drying curves for both earthenware and stoneware tiles. Arrows point out the respective critical moisture contents.

The solutions were left for a week to ensure excess solid was present, and if necessary, more salt was added.

To prepare solutions d and e, equal amounts of solutions a and b and a and c, respectively, were mixed, extra amounts of both salts were added and the mixture was left to equilibrate for a week. The solid residue was checked for both chloride and sulfate ions and if necessary, more salt was added to ensure saturation with regards to both salts.

2.4 Impregnation of tiles with salts

Each tile, previously dried and weighed, was wrapped in cheese cloth, sets of three wrapped tiles were suspended from glass stirring rods so that they were totally immersed in the prepared salt solutions. Most tiles were immersed for at least 23 hours, but some were left up to 96 hours. No influence on the soaking time was observed on the amount of salt retained by the tiles.

After soaking the tiles for about a day, they were removed, dried in the oven at 105°C, and re-weighed after cooling for 20 hours in a desiccator at 0%RH. The tiles were then subjected to a second drying at 105°C for 24 hours and re-weighed. This procedure induced hairline cracks in a few earthenware tiles (1 out of 8 immersed in NaCl and 1 out of 7 immersed in the NaCl + Na₂SO₄ solution) and faint efflorescences on others (1 out of 6 earthenware and 2 out of 9 stoneware tiles immersed

in Na_2SO_4 solution). A room-drying period (6 hours, the time needed to reach the critical moisture content in the earthenware tiles, see below) plus pre-drying at 50°C in the oven for 2 hours before drying at 105°C eliminated the appearance of hairline cracks and visibly reduced the appearance of efflorescences. In those few cases where efflorescences were noted, they were brushed off before weighing.

During the experiments, described in the following paper [7], it was observed that some tiles, particularly stoneware ones treated with the $\text{NaCl} + \text{Na}_2\text{SO}_4$ mixture, had not dried completely. To obtain the weight of salt introduced into them, these samples were dried again after the experiments were ended.

2.5 Drying curves for tiles with salts

The drying curves for tiles with salts were obtained following the NORMAL 29/8 procedure slightly modified by reducing the previous immersion time to 1 hour to minimize salt loss with the drying carried out in laboratory conditions. Drying curves for the earthenware tiles impregnated with NaCl and its mixture with gypsum are shown in Figure 3. The amount of salt remaining in the tile after the 1 hour

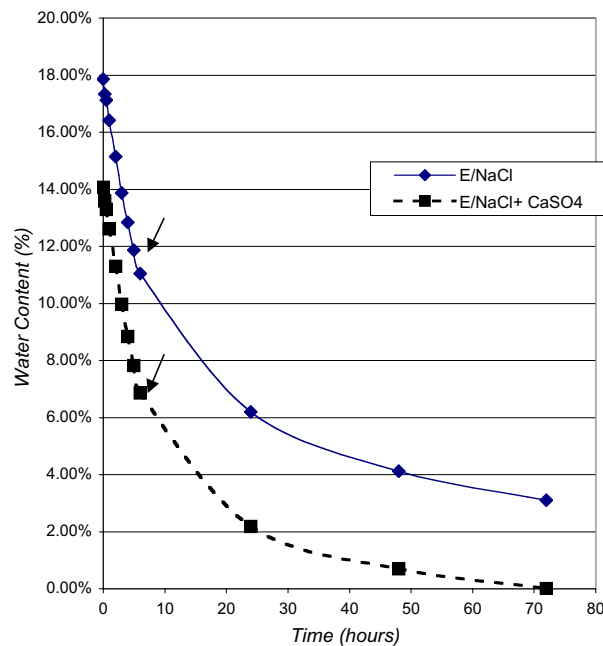


Figure 3: Typical drying curves for earthenware tiles containing NaCl [original amount 3.06 g, after immersion ~ 1.5 g] and $\text{NaCl} + \text{CaSO}_4$ [original amount 3.17 g, after immersion ~ 2.5 g]. Arrows point out the respective critical moisture contents.

immersion can be estimated to be 50% for NaCl and approximately 80% for the NaCl + CaSO₄ mixture, based on subsequent desalination experiments [8]. Finally it should be noted that during the 3 days of drying, no efflorescences were noted on the tiles.

It is interesting to note that the critical moisture content is reached by all tiles, including control runs under the same conditions, at about the same time, some 6 hours for earthenware tiles and between 2 and 3 hours for stoneware tiles.

The water uptake after 24 hours total immersion, the critical moisture content and the residual moisture after 3 days drying for both earthenware and stoneware tiles are presented in Table 2.

Table 2: Water content after 24-hour total immersion, critical moisture content and residual moisture content, all expressed in kg/m³, of earthenware (E) and stoneware (S) tiles impregnated with salts. The data for the control tiles are also included.

		Water Content [kg/m ³]	Critical Moisture [kg/m ³]	Residual Moisture [kg/m ³]
E	Control	290	140	< 0.2
	NaCl	330	200	3.2
	Na ₂ SO ₄	280	150	< 0.2
	CaSO ₄	270	120	< 0.2
	NaCl + Na ₂ SO ₄	250	120	< 0.2
	NaCl + CaSO ₄	240	120	< 0.2
	S	Control	84	47
NaCl		72	46	20
Na ₂ SO ₄		98	64	15
CaSO ₄		96	63	4.6
NaCl + Na ₂ SO ₄		88	61	19
NaCl + CaSO ₄		95	55	18

3 Results and Discussion

The results obtained show that the critical moisture content is affected by the presence of salts, however, the time necessary to reach this moisture content depends mainly on the porosity of the material (see Fig. 2).

While for earthenware tiles the critical moisture content is increased by the presence of NaCl, for stoneware tiles the increase was induced by the presence of the sulfate salts, by themselves or in conjunction with NaCl. This may be related to the different porosities of earthenware and stoneware tiles and the preferential location of NaCl in smaller and Na₂SO₄ in larger pores [9].

A similar pattern was observed for the residual moisture after 3 days. Earthenware tiles containing only NaCl retained more moisture, but not when it was present in conjunction with other salts. On the other hand, stoneware tiles retained more moisture for all salts, except CaSO₄, indicating that practically none of this salt was introduced into these less porous tiles.

The amount of salt introduced into the different tiles by the various salt solutions and the different methods, is presented in Table 3. For gypsum solutions, the salt remaining in the tiles could be the hemihydrate, CaSO₄·H₂O, and/or the anhydrous calcium sulfate, CaSO₄, the thermodynamically stable form at the drying temperature used in the experiment. Since the phases were not characterized within the porous system, the discussion will always refer to the anhydrous form given the small difference in molecular weight between the two forms. Only the anhydrous salt precipitates out from a mixture with NaCl under the experimental conditions. For comparison, the theoretical amount of salt that could be introduced into these tiles is also reported. For this purpose, the porosity of the tile measured after 24-hour immersion in cold water was used, the solubilities of the individual salts at 20°C (approximately 36g/100 ml for NaCl, 19g/100 ml for Na₂SO₄ and 0.2g/100 ml for CaSO₄), and those of the mixtures at 25°C (5.6 mol/kg for NaCl and 0.6 mol/kg for Na₂SO₄ [10] and 6.2 mol/kg NaCl and 0.04 mol/kg for CaSO₄ [11]). It should be remembered that the solubility of sodium sulfate changes significantly between 20°C and 25°C (19 g/100 ml and 28 g/100 ml, respectively).

For the individual salt solutions the amount of salt introduced into the tiles is directly proportional to the type of tile, i.e., to its porosity, and to the solubility of the salt in question. For NaCl, the amount introduced is practically equal to the theoretical amount, but for Na₂SO₄, it is about half as much and this could be due to several factors. Among these is the viscosity of the respective saturated solutions, which is in the order of 1.66 cP for NaCl and 2.05 cP for Na₂SO₄; the tendency of this salt to concentrate in larger pores, as compared to the NaCl [9]; and, the dehydration mechanism of this salt and its tendency to effloresce, as discussed later.

Table 3: Amount of salt introduced per tile (E: earthenware, S: stoneware), reported as % w/w, for the different salt solutions. Standard deviation is given in brackets. "No." indicates number of tiles tested. The theoretical amount of salt that could be introduced into the tiles is also indicated.

Salt Sol.	NaCl		Na ₂ SO ₄		CaSO ₄		NaCl + Na ₂ SO ₄		NaCl + CaSO ₄	
	No.	%	No.	%	No.	%	No.	%	No.	%
E	8	5.25 (±0.76)	6	2.68 (±0.90)	7	0.13 (±0.05)	9	5.39 (±0.47)	7	3.61 (±0.49)
Theor.		5.5		4.7		0.05		7.3		6.5
S	7	1.44 (±0.35)	9	0.69 (±0.25)	8	0.01 (±0.003)	6	1.55 (±0.15)	7	0.96 (±0.08)
Theor.		1.6		1.3		0.01		2.1		1.9

Given the low solubility of CaSO₄ the amounts introduced into the tiles were very small, close to the sensibility of the balance used, resulting in the largest relative experimental error.

The salt mixture situations are not as straightforward. Although in general the solubility of the more soluble salt, i.e., NaCl, is not affected by the presence of the less soluble salts, a decrease in solubility for the less soluble salt, Na₂SO₄ due to common ion effect is to be expected for the NaCl + Na₂SO₄ mixture. Hence the slight increase in amount of salt introduced by this mixture as compared to the amounts introduced by the individual salts. However, the actual amounts introduced are less than the theoretical ones, which can be attributed in part to the dehydration mechanism of Na₂SO₄, and in part to the fact that the calculations were based on the available solubility data at 25°C.

In the NaCl + CaSO₄·2H₂O mixture, the solubility of gypsum is slightly increased due to the increased ionic strength of the solution, but the overall amount of salt introduced into the tiles is less than that of the more soluble salt, NaCl, by itself. The actual amount introduced is about half of the theoretical value and, in this case, may be related to the anomalous behavior gypsum induces in porous materials [12].

Some interesting trends were observed regarding the amount of salt introduced in the samples depending on the drying procedure used. For solutions of individual salts, the amount remaining in the tiles is a function of the porosity, as previously mentioned, as well as the solubility of the different salts. However, the actual

amount introduced into each tile appeared to be affected by the conditions under which the tiles were dried, while the length of soaking time in the saturated solution, which varied from 23 to 96 hours, was not critical presumably because the small size of the tiles ensured their total saturation within 23 hours. While previous studies have tried to increase the amount of salt retained in a body by using slow impregnation, starting with a capillary rise and ending in total immersion [13], no references to the effect drying might have on the amount of salt retained have been found.

The effect of pre-drying the samples prior to drying them out completely in the oven, resulted in slightly varying amounts of salts remaining in the tiles, in some cases it was more and in some it was less. This depended on the nature of the salt, as shown in the data presented in Table 4 below. For CaSO_4 the amounts remaining behind were so low that no conclusions could be drawn. For mixed solutions, the pattern observed followed that of NaCl , since this is the most soluble salt.

Analysis of variance of the results presented above show that, except for the stoneware tiles impregnated with the Na_2SO_4 solution, a significant difference is observed between the two drying procedures at the 90% confidence level. The data suggest a trend that needs to be further explored.

To develop experiments to further investigate this trend the following working hypothesis has been developed. When a wet tile just removed from the salt solution, i.e., NaCl , is dried quickly by heating, an important thermal gradient is established in the tile.

Table 4: Amount of salt remaining in the tiles (E: earthenware, S: stoneware) depending on the drying method and the type of salt. Numbers between brackets are the standard deviation.

Tile Type	Solution Drying	NaCl		Na ₂ SO ₄	
		No.	%	No.	%
E	105°C	3	4.70 (±0.60)		3.47 (±0.06)
	pre-dried	5	5.58 (±0.68)	3	1.90 (±0.43)
S	105°C	3	1.19 (±0.19)	3	0.81 (±0.25)
	pre-dried	4	1.63 (±0.33)	6	0.64 (±0.26)

Fast evaporation at the outer surface forces, in part, a convection movement of the solution from the interior to the exterior so that part of the salt will crystallize at the surface without necessarily remaining attached to it and thus reduce the amount of salt that crystallizes within the tile. The movement of the solution towards the surface will be favoured by the creep properties of this salt in which the solution moves ahead of the crystallization front [14]. When the tile is dried at a slower rate, evaporation starts at the surface and continues by the moving of the evaporation front towards the interior. Therefore more salt will crystallize within the body of the tile.

Tiles immersed in Na_2SO_4 solutions follow an opposite pattern. The reason can be found in the deliquescent nature of this salt. The first salt to crystallize from a saturated solution at room temperature is the decahydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, mirabilite. When the tile is dried quickly, the same mechanism described above applies. The salt starts crystallizing as mirabilite on the surface, then quickly decomposes into the anhydrous salt, thenardite. The efflorescences in this case might remain attached to the tiles as was noted for some of them. If the drying occurs at a slower rate, since evaporation of Na_2SO_4 solutions is slower than for NaCl ones [9], crystallization will also occur in the interior of the body and the first salt to crystallize is mirabilite. This deliquescent hydrate has the capacity of "dissolving" in its own crystallization water thus re-gaining mobility and moving towards the surface. The re-dissolved salt will reprecipitate partly as mirabilite and partly as thenardite. The former will again migrate while the latter presumably is the salt that finally remains in the ceramic body. This multi-step recrystallization process has been described in a previous study [15] and together with the observed "floating" of solid crystals on solution films [16] could explain why less salt remains in the interior of the tile body when it is dried at a slower rate.

Both mixtures of salts follow the trend of the NaCl where slower drying increases the amount of salt remaining in the tile, which results from the larger proportion of this salt in either mixture. What is interesting though, is the fact that the presence of gypsum appears to hinder the amount of salt remaining in the tiles as mentioned previously.

4 Conclusions

The study's goal was to research trends in the behavior of salts within porous bodies. The results obtained in this first part show that the amount of salt remaining behind in a porous material is strongly dependent on its porosity, the nature of the salt in question and the drying conditions after soaking in a salt solution. The observed trend suggests that the dynamics of the salt within the porous structure is an important factor in determining the amount of salt that will remain within the material as well as the movement of moisture within the porous body.

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