

Salts in Ceramic Bodies IV: Considerations on Desalination

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Abstract

Several factors that affect the efficiency of salt(s) removal from ceramic materials during desalination treatments were investigated. The results show that before a suitable desalination method is chosen, the role of the porosity of the material, the solubility of the contaminating salt(s), the kinetics of the dissolution process and the mobility of the ions have to be evaluated. A method to calculate the maximum amount of salt remaining in the object after repeated washings, based on the amount of salt extracted, is presented in order to address the fundamental question of defining an acceptable salt content for long term conservation.

Keywords: desalination, ceramics, porosity, solubility, diffusion, sodium chloride, gypsum, sodium sulfate

Salze in poröser Keramik IV: Überlegungen zum Entsalzen

Zusammenfassung

Mehrere Faktoren, die die Wirksamkeit der Verfahren zur Entfernung von Salzen aus porösen keramischen Werkstoffen beeinflussen, wurden untersucht. Die Ergebnisse machen deutlich, dass vor der Wahl eines Verfahrens zum Entsalzen der Einfluss der Porosität eines neuen Werkstoffes, die Löslichkeit der zu entfernenden Salze, die Kinetik des Lösungsvorganges und die Innenbeweglichkeit bestimmt werden müssen. Eine Methode zur Berechnung des maximalen Salzgehaltes, der nach

mehrmaligem Waschen in einer Probe zurückbleibt, wird vorgeschlagen. Die Berechnung geht von der Menge Salz aus, die entfernt wurde. Damit wird die grundsätzliche Frage aufgeworfen, wie ein annehmbarer Salzgehalt für eine lange Aufbewahrung festzulegen sei.

Stichwörter: Entsalzen, Keramik, Porosität, Löslichkeit, Diffusion, Natriumchlorid, Gips, Natriumsulfat



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1 Introduction

It has long been known that the amounts of salts removed during desalination by total immersion in a static bath depend on the solubility of the salt(s), the distribution of the salt(s) within the porous body, the size and mobility of the ions to be extracted, the porosity of the material, the concentration gradient developed between the object and the bath, and the temperature [1,2]. However, few studies have analyzed these aspects in depth [3,4,5] or evaluated desalination methods based on samples containing known amounts of salts [6]. There are even fewer studies that have dealt with the fundamental question of defining an acceptable level of residual salt in the object for long-term preservation [7,8]. One of the problems is that these studies are carried out on real objects where the actual amount of salts can at best be estimated.

The aim of the present paper is to further elucidate the role of the possible mechanisms at work during desalination of porous ceramic bodies, using the experimental data presented in a previous paper [9]. For this purpose, ad-hoc prepared ceramic tiles, both earthenware and stoneware, were impregnated with sodium chloride, NaCl, sodium sulfate, Na₂SO₄, and calcium sulfate, CaSO₄, saturated solutions, these being the salts most frequently found in both archaeological and architectural ceramics and stone in the authors' experience. The tiles were also used to investigate the influence of minimal changes in relative humidity, or to determine the sorption curves, that induced some efflorescence and movement of salts as described previously [10].

Desalination of the tiles was carried out by total immersion in a static bath, either by long-term immersion or by repeated washings. The data obtained are analyzed taking into consideration the main transport mechanism, diffusion, and the influence that the porosity of the tile, the solubility of the salt in question, and the mobility of the ions among other parameters, have on desalination.

2 Experimental

The experimental procedure will be briefly summarized, since a detailed description can be found elsewhere [9]. Desalination was carried out by three methods: prolonged immersion, repeated washings, and by intermittent washings.

The first and second methods used both 150-ml and 300-ml of deionized water for immersion. The third method used only 150-ml since no significant difference was obtained with the change in volume.

For the repeated washings method the wash solution was changed every hour for the NaCl-impregnated tiles and every two hours for those containing sulfate salts. In the case of the intermittent washings, the solution was changed as pre-

viously but the tiles were allowed to dry for four hours in between successive washings.

The amount of salt extracted was evaluated by conductance methods, both through calibration curves and direct conductometric titrations. A complete description of the methodology can be found elsewhere [11].

3 Results and Discussion

3.1 Influence of the desalination method

A typical desalination curve obtained with the prolonged immersion method is shown in Figure 1.

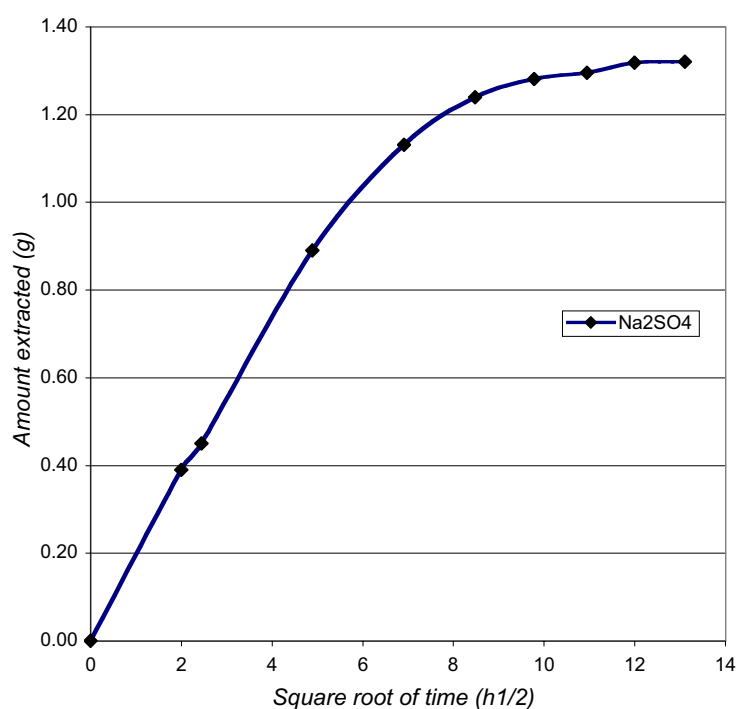


Figure 1: Desalination curve plotting grams of salts removed as a function of the square root of time ($h^{1/2}$) for prolonged immersion in 300-ml of water of an earthenware tile containing 1.71 g of Na_2SO_4 .

The curve shows, at first, a linear slope in which the extraction of salts is governed by diffusion and follows Fick's law. As the concentration gradient decreases, the amount of extracted salt decreases, as shown by the curved section, reflecting that diffusion in the bath is no longer the limiting step. Other factors, such as the concentration gradient established within the tile, may be controlling the process. The curve tends to a limiting value in the final horizontal section, where the salt concentration in the bath is close to the salt concentration in solution found in the pores of the object, and no further salt is extracted. At this point, the total amount of salt extracted, for the case of small objects such as the tiles under study, is close to the amount of salt originally present, since the volume of water is sufficient to dilute the salts to a maximum under practical conditions. Hence, theoretically, a larger amount of water in the bath should extract more salt, but as shown in the present experiments the increase is not significant for the case of these small objects, given the relatively low amounts of salt in them.

For larger objects the distribution of the salt within the porous material is critical in determining how much salt will be removed. And, if more than one salt is present, their distribution will determine which one will be removed first [4,5].

It has generally been assumed that repeated washings are more efficient than one single wash prolonged over a long time, since the water change will reestablish the largest concentration gradient possible between the tile and the water bath increasing the extraction rate. This has been proved so for the case of both tile types impregnated with the NaCl: earthenware (open porosity 17.7%) and stoneware (5.1%). However, when extracting sulfate salts, this is not the case. Table 1 summarizes the relevant results from the experiments described in more detail in the previous paper [9].

As the differences in washing efficiency between the two methods—indicated in bold in the table above—are around 5% and considering that the average standard deviation in the data is around $\pm 3\%$, it can be safely concluded that the amount of CaSO_4 removed from either type of ceramic, or of Na_2SO_4 from the less porous ones, does not increase as expected when the wash-water is changed. This implies that diffusion is not the only mechanism influencing the movement of ions out of the tile and that most probably solubility and dissolution kinetics, also play a role.

Taking the case of Na_2SO_4 -impregnated tiles, that show a change in behaviour depending on the porosity of the ceramic material, it could be postulated that ready access of fresh water into the more porous ceramic facilitates the dissolution of the salt thus increasing the concentration gradient, and that diffusion is the limiting step in the removal rate. In the less porous ceramics, the water exchange may be slowed down, thus allowing the dissolution rate to be the limiting step. In the case of CaSO_4 , due to its low solubility, dissolution would appear to be the limiting step for its removal from both types of ceramics.

Table 1: Percentage of salts removed during five successive washings with 150-ml or 300-ml of water and for the equivalent amount of time in prolonged immersion in the same amount of water. Numbers in bold mark those data where a prolonged immersion is more efficient than repeated washings.

	Washing		% salts extracted		Washing	
	time (hr)	vol. (ml)	5 washes	prolonged immersion	time (hr)	vol. (ml)
E/NaCl	1	150	62.4 %	~54%	5	150
E/NaCl	1	300	61.5%	~49%	5	300
S/NaCl	1	150	34.5%	~24%	5	150
S/NaCl	1	300	32.9%	~23%	5	300
E/Na ₂ SO ₄	2	150	45.1%	~40%	10	150
E/Na ₂ SO ₄	2	300	51.9%	~35%	10	300
S/Na ₂ SO ₄	2	150	20.0%	~25%	10	150
S/Na ₂ SO ₄	2	300	19.4%	~23%	10	300
E/CaSO ₄	2	150	15.4%	~25%	10	150
E/CaSO ₄	2	300	20.9%	~26%	10	300

Another possible contributing factor that requires further investigation is the different hydrodynamic behaviour of the ions within the pore system [12,13].

Although viscosity differences between the concentrated solution within the pores and the bath water could help explain the loss in efficiency in the repeated washings procedure for the Na₂SO₄ case (the saturated Na₂SO₄ solution has a viscosity of approximately 2 cP) this could hardly be the case for CaSO₄ whose saturated solution has a viscosity close to that of water. Finally, the behaviour of these ions during extraction when present in a mixture with NaCl, which as the most concentrated salt would provide the background viscosity of the mixture, appears to indicate that viscosity is not a key factor in influencing salt removal efficiency.

The extraction efficiency of all ions when originating from a salt mixture, decreases significantly as shown in Table 2.

Table 2: Average percentage of salts extracted by 3 successive intermittent 150-ml washings from tiles containing individual salts or mixtures (see Table 4 in [9]). Washing time was 1 hour, except for tiles containing Na₂SO₄, where it was 2 hours. Successive washings were separated by a 4-hour drying period. "n.d." = not determined.

	% Salts Extracted		
	NaCl	Na ₂ SO ₄	CaSO ₄
E/single salt	65.1%	81.1%	70%
E/NaCl+Na Sulf.	49.4%	49.8%	
E/NaCl+ Ca Sulf.	39.7%		37%
S/single salt	36.9%	21.2%	n.d.
S/NaCl+Na Sulf.	18.1%	21.1%	
S/NaCl+ Ca Sulf.	27.4%		n.d.

The decrease in efficiency for the overall removal of salts could tentatively be attributed to ion association phenomena such as occur in brines [14]. It appears that different ions are extracted with approximately the same efficiency when originating from a mixture such as the ones tested in this experiment. Furthermore, the amounts extracted appear to maintain the same proportion to the amounts found in the original body, as pointed out in the previous paper [8]. This is probably the case for small objects with a uniform salt distribution and could not be extrapolated to larger objects where salt distributions may vary significantly.

3.2 Repeated washings

The effectiveness of repeated washings has been studied in the past by analytical chemists for washing a precipitate free of contaminants. For the washing of an ideal precipitate, the following equation has been proposed [15]:

$$C_n = (V_r/V+V_r)^n C_o \quad (1)$$

where:

C_n = residual amount of contaminant in the precipitate after n washings

C_o = original amount of contaminant in the precipitate

V = volume of wash solution

V_r = volume of solution retained in the precipitate after washing.

The equation is valid for the removal of a uniformly distributed contaminant and when the wash solution has uniform access throughout the precipitate. Although this is seldom the case for soluble salt removal from a porous body, it could be considered the ideal case.

The above equation shows that the residual amount of contaminant in the precipitate is a power function of the number of washings. It also predicts that for equal amounts of water, multiple washings are more effective at removing the contaminant than a single washing. It can also be deduced that the ratio of concentrations between any two successive washings is a constant ($V_r/V+V_p$) that can theoretically vary between 0, i.e., total extraction when an infinitely large volume of wash water is used; to 1, when no extraction occurs and the residual concentrations in two successive washings are equal.

During the analysis of the experimental data, it was observed that the amount of salt extracted during each successive washing decreased, tending to a constant value after several washings. The resulting pattern is similar to that obtained for prolonged immersion (see Figure 1). The data of three particular earthenware tiles, impregnated with NaCl, Na₂SO₄ and CaSO₄, respectively, will be used to further illustrate the point. The amount of salt extracted (C'_n) and that remaining in the tile (C_n) after successive washings with 150-ml of water is reported in Table 3. The relationship between these values is given by the equation:

$$C_n = C_{n-1} - C'_n \quad (2)$$

where:

C_n = amount of salt left in the tile after the nth washing

C_{n-1} = amount of salt in the tile prior to the nth washing

C'_n = amount of salt extracted in the nth washing

Table 3: Amount of salt extracted (C'_n) and amount of salt remaining in the earthenware tiles (C_n), expressed in g, after successive washings with 150 ml of water. Co = original amount of salt in the tile. Note that the amounts of CaSO₄ extracted are close to the detection limit of the conductance method used.

(n) No. Washings	E47 NaCl Co = 3.78 g		E51 NaSO4 Co = 1.60 g		E68 CaSO ₄ Co = 0.13 g	
	C _n (resid)	C' _n (extr)	C _n (resid)	C' _n (extr)	C _n (resid)	C' _n (extr)
1	1.90	1.88	1.18	0.42	0.119	0.011
2	1.73	0.17	1.09	0.09	0.116	0.003
3	1.61	0.12	1.018	0.072	0.114	0.002
4	1.512	0.098	0.950	0.068	0.112	0.002
5	1.421	0.091	0.884	0.066	0.110	0.002

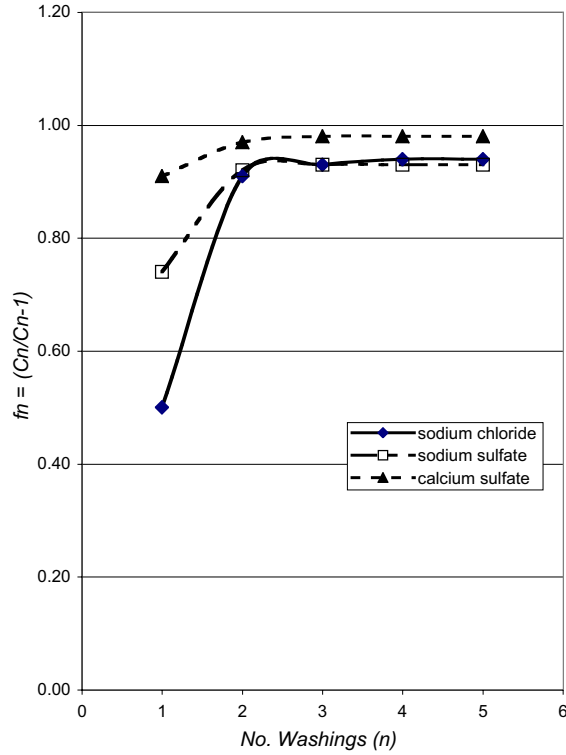


Figure 2: Ratio of remaining salt amounts (f_n) after two successive 150-ml washings of earthenware tiles containing one of the following salts: NaCl, Na₂SO₄ or CaSO₄, plotted as a function of N, the number of washings.

When the ratio between the amounts of salt remaining within the ceramic body after successive washings, $C_n/C_{n-1} = f_n$, is calculated and plotted as a function of N, the number of washings, the curves shown in Figure 2 are obtained.

The fact that f_n is not a constant indicates that diffusion is not the only mechanism controlling the extraction. Similar patterns were obtained for the three salts. The most significant difference occurred in the first washing where the largest amount of salt was extracted, because in general salts tend to accumulate in the surface/subsurface region due to the evaporation of water from the surface. This was clearly shown in the discussion of the influence of the tiles previous history on the amount of salt extracted presented in the previous paper [8]. However, as the number of washings increase, f_n tends to a constant close to 1, the point at which a mini-

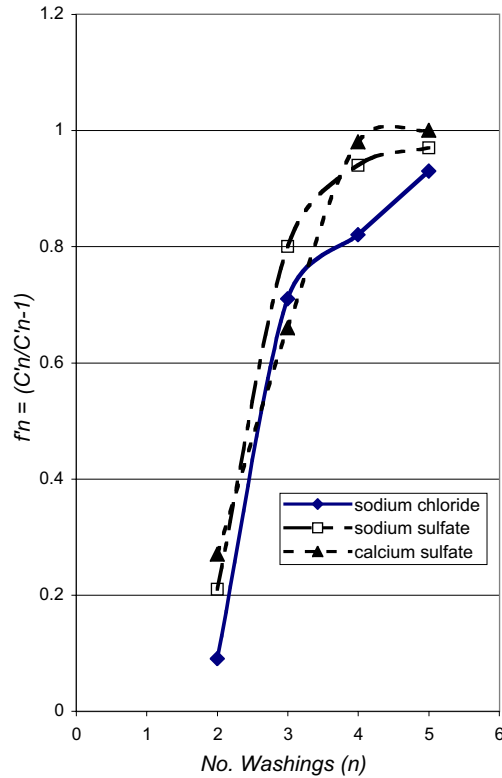


Figure 3: Ratio of the extracted salt amounts (f_n) in two successive 150-ml washings for the same tiles used for Figure 2. The lower ratio obtained for CaSO_4 is probably due to the fact that the amounts extracted were close to the detection limit.

mal amount of salt is extracted and the washing efficiency is reduced to a minimum. The constant value reached appears to be a function of the solubility of the salt and the porosity of the tile. The more insoluble the salt, the closer f_n is to 1.

Similar plots are obtained when calculating the ratio between the amounts of salt extracted in two successive washings, $C'_n/C'_{n-1} = f'_n$ as shown in Figure 3.

As the number of washings increase, the amount of salt extracted between two successive washings tends to a minimum and f'_n tends to 1, as is the case for f_n , when N tends to infinity. The implication is that when this "constant extraction stage" is reached it is certain that f_n is already a constant and that the extraction efficiency has reached a minimum. At this point, the remaining amount of salts in the ceramic body could be estimated using the measured limiting f'_n value as an approximation for f_n , assuming f_n and f'_n will converge when N tends to infinity.

In the case considered, f_5 barely reaches this stage and further washings would be required to get a more accurate value.

For the salts in earthenware tiles used in the experiment, f_5 ranges from 0.93 for Na_2SO_4 to 0.97 for CaSO_4 , while f_5 ranges from 0.92 for NaCl to 1.00 for CaSO_4 . For stoneware tiles, f_5 is 0.99 for both NaCl and Na_2SO_4 while f_5 ranges from 0.91 for NaCl to 1.00 for CaSO_4 . From these values, an overall estimate of $f_5 = 0.95$ can be considered valid, based on the average measured f_5 , having an uncertainty of (± 0.03) and (± 0.04) for the earthen- and stoneware tiles, respectively.

With the estimated f_5 and the measured amount of salt extracted in that washing, C'_5 , the amount of salt present in the ceramic before that washing, i.e., C_4 , can be calculated as follows:

$$C_5 = f_5 C_4 = C_4 - C'_5 \quad (3)$$

$$C_4 = C'_5 / (1 - f_5) \quad (4)$$

The results of these calculations are presented in Table 4.

Table 4: Comparison of the measured and calculated amounts of salt present in the tiles prior to the fifth washing using an estimated $f_5 = 0.95$ with an uncertainty ranging from (± 0.03) to (± 0.04) for earthen- and stoneware tiles, respectively. The uncertainties for the calculated values are indicated in brackets. All values are expressed in grams.

Tile	Wash Volume	C_4	
		Measured	Calculated
E/NaCl	150 ml	1.512	1.82 (± 0.6)
E/NaCl	300 ml	1.480	1.80 (± 0.6)
E/ Na_2SO_4	150 ml	0.950	1.32 (± 0.6)
E/ Na_2SO_4	300 ml	1.294	1.92 (± 0.6)
E/ CaSO_4	150 ml	0.112	0.04 (± 1.1)
E/ CaSO_4	300 ml	0.107	0.08 (± 0.85)
S/NaCl	150 ml	0.726	0.16 (± 0.92)
S/NaCl	300 ml	0.819	0.26 (± 0.87)
S/ Na_2SO_4	150 ml	0.485	0.12 (± 0.96)
S/ Na_2SO_4	300 ml	0.510	0.12 (± 0.96)

The high uncertainties for the stoneware tiles contaminated with CaSO_4 reflect the high relative errors in the experimental procedure when low concentrations of salts are measured. In spite of these uncertainties, the method provides a means of roughly estimating the amount of salt remaining in small objects where it can be assumed that the distribution of salts is homogeneous when the "constant extraction stage" is reached by repeated washings. Since the method uses concentration ratios, these can be replaced by the conductance ratios, limiting the determination of the actual amount of salt extracted to the last washing. The method has been proven applicable to ceramics contaminated with individual salts, or simple mixtures, such as the ones tested, where one salt is the major constituent in the mixture. For more complex systems, further testing would be required.

Application of these calculations, in conjunction with studies to determine the adequate level of washing for the stability of the object, as described by Beaubien [7,8] could serve to determine a priori the amount of salts that will not prove harmful in a ceramic of given porosity provided it is kept in a controlled environment.

4 Conclusions

This study discussed the role that the porosity of the material, the solubility of the salt, the viscosity of the solution, the kinetics of the dissolution process and the mobility of the ions may have on the efficiency of the desalination method used. It was shown that the concentration gradient established first between the tile and the bath and later within the pores of the ceramic body play an important role. For the less soluble salts, the kinetics of dissolution may be the rate-limiting step in the desalination process. The viscosity of the concentrated solution within the pores does not appear to be play an equally important role.

Prolonged immersion, thought to be a less effective method when compared with repeated washings, was found to be as or even more efficient depending on the porosity of the ceramic and the solubility of the salt in question. These findings reinforce the importance of identifying the salts present and the overall porosity of the ceramics before a decision is made on the procedure to be used for the removal of contaminating salts.

A more complex situation was observed when salt mixtures were extracted from the ceramic tiles. The decreased extraction efficiency observed, when compared to the results obtained for tiles containing a single salt, could be due to ion pair formation influencing ionic mobility. Furthermore, it was shown that for the case of a uniform distribution of salts, the various ions were extracted with approximately the same efficiency. Further studies on the behavior of porous ceramic materials containing known amounts of different single salts and mixtures would be necessary to determine the influence of ionic mobility in the dynamics of desalination processes.

A method to calculate the maximum amount of salt left in the object after the repeated washing procedure reached the minimum extraction efficiency, was presented. This was an attempt to address the fundamental issue of defining a remaining salt content that is acceptable for the long-term conservation of the object. The results obtained so far are only applicable to small objects containing uniformly distributed salts in their pores; further testing is needed to evaluate the eventual practical application to more complex situations.

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