

# INVESTIGATION ON THE ROLE OF AGITATION IN THE DESALINATION PROCESS OF CERAMICS

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## 1. Introduction

Many of the findings in archaeological sites are ceramic materials. Ancient ceramics have an important role in helping to understand the past from different points of view, such as the history of technology, ethnography and cross-cultural generalization, the environment, and more [1]. Therefore, careful conservation and restoration of these historical objects should be appreciated.

The deterioration of ancient porous materials caused by the crystallization of water-soluble salts is a well-known phenomenon. Salt crystallization is one of the most important factors in the deterioration of ancient ceramics [2] and will almost always cause some degree of damage, ranging from exfoliation of the glaze to complete disintegration of the body [3]. Three essential components in this scenario are water, salt and a host material to be eroded. Important factors are the relative humidity and temperature of the surrounding environment, and the porosity and permeability of the host material. In subflorescence, crystal growth within the pores of the ceramic material causes cracking and spalling. Efflorescence, on the other hand, accumulates on the ceramic surface. The negative effects of efflorescence are not as severe as subflorescence [4].

Two mechanisms for deterioration by salts have been recognized. The first is based on the assumption that expansion and shrinkage, during hydration and dehydration processes, are responsible for the damage. The second is based on a model in which pressure from crystallization causes damage [5]. Desalination is therefore, one of the most important treatments in the conservation and restoration process of ancient ceramics.

Desalination is the process of removing soluble salts from a material. One of the standard treatments consists of immersing the ceramics in a static bath of water and waiting a period of time for the soluble salts to go into solution with a daily change method (i.e. waiting 24 hours for the soluble salts to go into solution) and/or equilibrium method [6].

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One disadvantageous aspect of desalination by immersion is that the low-fired ceramic surface may soften. This can lead to changes in reflectance of the ceramics, with possible disintegration and segregation of the original components in mid to late desalination, possible biodeterioration [6, 7], and rehydration of clay minerals with resultant damage, such as the formation of microcracks and cracks due to the expansion of minerals [2, 8]. These negative aspects, related to desalination by immersion, are furthermore made worse, the longer the contact period is.

An alternative desalination method should consequently be identified to minimize any potential damage to potteries. Jang and colleagues have suggested raising the temperature of the water as an alternative desalination process, in order to avoid potential damage to potsherds [7]. Although this is a more efficient desalination method and can reduce the contact period, it seems that warm water is not safe enough to use. The structure of ancient objects may be damaged with water at 50°C, due to the aggressive action of higher solubility. In addition, using this method in situ at excavation sites is not always easy.

Another suggested method for desalination of porous materials is the use of surfactants in water [9, 10]. Surfactants can enhance the desalination process by decreasing the surface tension of water. However, it seems that more research is necessary to evaluate the potential effects of surfactants or surfactant mixtures on desalination processes [9].

Another suggested method in this field is agitation. There is no systematic detailed study on the role of agitation in desalination processes in the relevant scientific literature [3, 7].

In this study, the importance of agitation in the desalination process has been formulated theoretically and validated by experimental results.

## 2. Theory

The desalination of excavated ancient ceramics such as potteries, is a mass transfer operation. Water, as a solvent, after contacting with entrapped salts in the pores of an ancient object dissolves them as ions. A transport of mass will take place in a fluid mixture of two or more species whenever there is a spatial gradient (concentration, pressure or electric field) in the proportions of the mixture. In a hydrodynamic system there is also a contribution to the species flux due to convection. The flux contributions from diffusion, electromigration, and convection can be linearly superposed, giving the Nernst–Planck equation (equation 1). The corresponding mass transfer flux of *i*-th species is:

$$j_i = -v_i z_i F \rho_i \nabla \phi - D_i \nabla \rho_i + \rho_i u \quad (1)$$

$v_i$  is the mobility of the species *i*

$z_i$  is the charge number of the species *i*

$F$  is Faraday's constant equal to the charge of 1 mole of singly ionized molecules

$\rho_i$  is the density of the species *i*

$\nabla \phi$ ,  $\nabla \rho_i$  are the electrostatic potential and density gradients respectively

$D_i$  is the diffusivity of the species *i*

$u$  is the average velocity of liquid

The Nernst–Planck equation (equation 1) can be used both for describing the desalination flux and also for monitoring desalination by means of an electrical conductivity meter.

#### Desalination flux

In ordinary desalination processes, the electric field is absent; therefore, the corresponding mass transfer flux of *i*-th species can be calculated from the modified Nernst–Planck equation, equation (2) by ignoring the contribution of the electric field gradient in equation (1).

$$j_i = -D_i \nabla \rho_i + \rho_i u \quad (2)$$

Equation (2) is called Fick's first law of diffusion and it shows the mass transfer due to the concentration gradient.

The first term in the right hand side of equation (2) shows the molecular diffusion, but the second term shows the advective mass transfer.  $D_i$  is the diffusivity of the species *i*.  $D_i$  is the molecular diffusion coefficient in a stationary liquid, but in an agitated liquid it modifies to  $D_e$ , the eddy diffusion coefficient.  $D_e$  can be as high as orders of magnitude of  $D_i$  in a well agitated liquid.

Advective mass transfer can be enhanced by inducing convection. Convection flow can be produced by both pressure gradient and surface tension gradient. The flow due to the surface tension gradient is usually termed the Marangoni effect. Mineral salt increases the surface tension of water; therefore, the surface tension of water in the pores is greater than the bulk water; this surface tension gradient smoothes the progress of the water downwards into the pores. The Marangoni effect improves desalination.

Convection flow can also be improved by decreasing the surface tension of the washing water. This is possible either by increasing temperature [7] and/or using surfactant agents [9, 10].

### 3. Experimental method

Three industrial brick samples were chosen with nearly similar weight and volume (Table 1). The firing temperature of the samples is about 950- 1000°C. The presence of hematite in the matrix of the samples was detected by Polarizing Microscope (Pol. Microscopy, PM-240 SA Iran). This finding indicates that the kiln had an oxidation atmosphere. The porosity of the samples was calculated with ASTM designation C20 and also helium porosimetry (Helium Porosimeter, POROPERM, core diameter: 1" and 1.5", core length: 0.75" to 3", maximum pressure: 10000 psi).

Table 1. Sample characterization

Sample Number	Shape	Weight (g)	Weight after salt absorption (g)	Volume (g/ml)	Porosity (%)	Water Absorption (%)
1	Cone	115.295	116.0	61.969	52.31	28.11
2	Pyramid	108.602	109.14	58.37	51.29	27.57
3	Cylinder	171.87	172.95	92.38	48.67	26.16

To investigate the matrix of the samples, thin section petrography was performed

using polarizing microscopy. It was known that the matrix of the samples is argilliferous-calcareous (Figure 1). The tempers are quartz and fragments of granitic stones with different sizes and shapes (mostly sub-angular); in some cases grog was detected. Pyroxenes (augite and diopside), micas (muscovite and biotite) and plagioclases were other observed minerals in these matrices.

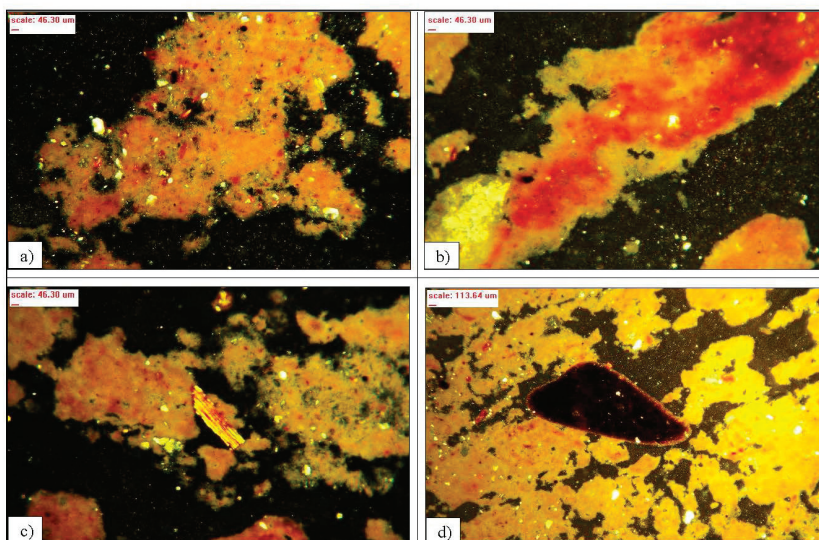


Figure 1. Thin section petrography of samples; a) general argilliferous-calcareous matrix of samples with quartz, micas, etc. (sample no. 1), b) oxidation condition evidenced by formation of hematite in argil, c) muscovite in the texture of samples, and d) grog in the texture of samples (sample no. 3).

All samples were initially immersed in distilled water before the saturation step to remove already existing soluble salts in the structure of the specimens. The required soaking time in this stage was found to be about 72 hours. The specimens were then dried in an oven at a temperature of  $(105 \pm 5)^\circ\text{C}$  until a constant mass was reached (about 10 hours). They were then allowed to cool to room temperature and weighted to  $\pm 0.001$  g.

The saturation process entailed the use of a 3.5% solution of sodium chloride. In this step, samples were completely immersed and covered with the NaCl solution to a depth of 30 mm above the top of the specimens for 96 hours at  $(20 \pm 1)^\circ\text{C}$ . There were 30 mm between each specimen and at least 30 mm between the specimens and the sides of the container. To reduce the rate of evaporation, the immersion bath was kept covered. After immersion, the samples were removed from the solution and dried in ambient temperature for 24 hours and then left in the oven at  $50^\circ\text{C}$  for 8 hours.

Progress of the desalination process was monitored by measuring the electrical conductivity of the washing water at certain times. In the international system of units (SI) electrical conductivity is expressed in Siemens per centimeter (Siemens which is the reciprocal of resistance in ohm).

The desalination test was done in three stages. In each stage, the dried samples

were placed in separate 1000 ml containers (one sample in one container) with 800 ml distilled water of  $6 \mu\text{S}\cdot\text{cm}^{-1}$  EC (Electrical Conductivity Meter, inoLab 740, WTW, Germany). All containers were covered to reduce evaporation rate. The washing waters were changed after 72 hours (in the first stage), and after one week (168 h, at the second stage) for each sample. Conductivity of each sample, in the first 72 hours, was examined at 1, 2, 4, 6, 7, 8, 9, 24, 48 and 72 hours. In the second week conductivity of the samples was recorded at 24, 48, 72 and 168 hours. In the final stage EC was measured after 24 and 48 hours.

To differentiate the effect of eddy diffusion on mass transfer, EC measurements were done without mixing washing water samples, except for sample no.1 at the seventh hour and sample no. 2 at the eighth hour. Sample no. 3, without any mixing, was used as a blank.

In the first run of tests, the samples were agitated before the EC reading (except no. 3, blank sample). In the second run of tests, after a week, the EC of each sample was measured both before and after agitation of the washing water. The agitation rate was 50 rpm (revolutions per minute) for 100 seconds. The EC measurements were done after a minute of agitation stop to obtain a stable EC reading.

#### 4. Result and discussion

Figure 2 shows the cumulative EC of two samples versus time in the first day. Weight and volume of samples are approximately the same.

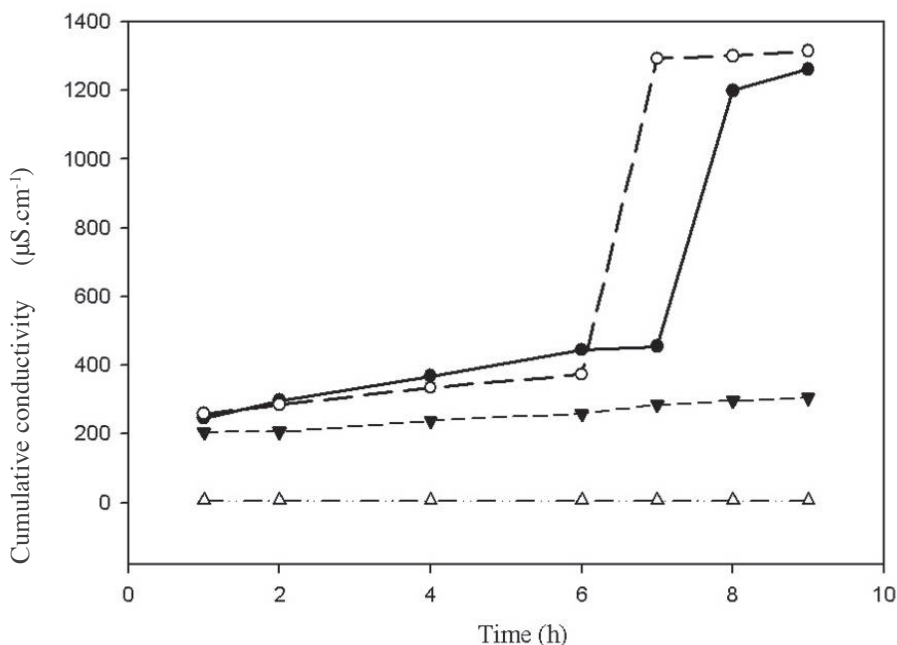


Figure 2. Result of EC measurement for sample no.1 (●), sample no.2 (○), sample no.3 (▼) and distilled water (Δ) in the first day.

There is a progressive trend of EC versus time, but with a sharp change at the 7<sup>th</sup> hour for sample no. 1 and at the 8<sup>th</sup> hour for sample no. 2 where, before each EC measurement, the washing water was agitated. Agitation causes eddy diffusion.

The effect of eddy diffusion on increasing the conductivity of water was discussed in Section 2, "Theory". As mentioned, high EC indicates a high rate of salt extraction (EC increases due to the increase in ions in the immersion bath, as a result of salt transfer from object to washing water).

Figure 3 shows the cumulative EC of the same samples versus time in the first 72 hours. As can be seen, the trend of progressive EC continues after the first day.

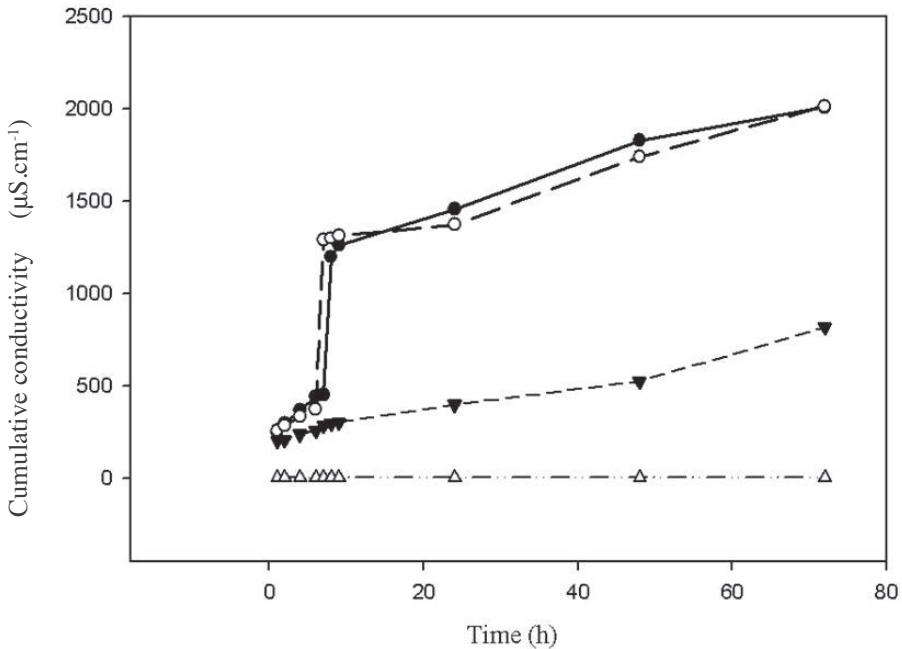


Figure 3. Result of EC measurement for sample no.1(●), sample no.2 (○), sample no.3 (▼) and distilled water (Δ) in the first 72 hours.

The washing water was changed after the first 72 hours and the three samples were immersed in fresh distilled water. In the second week, each EC measurement was read before and after agitating the washing water (Figure 4). It can be observed that agitation has a profound effect on the rate of salt extraction, which is manifested in the EC measurement.

The jump in EC value due to agitation can be explained as follows:

In the bath method (immersion) desalination, diffusion is the main mechanism for mass transfer [11]. However, diffusion is essentially a slow process that depends on the concentration gradient of salt ions in the pores and washing water.

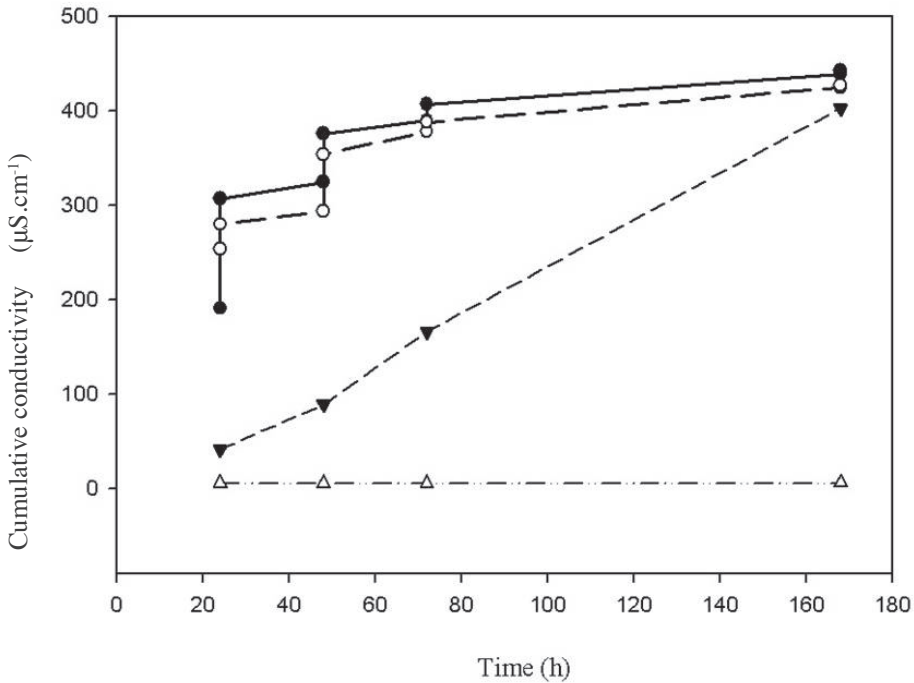


Figure 4. Result of EC measurement for sample no.1(●) sample no.2 (○), sample no.3 (▼) and distilled water (Δ) in the second week.

As a consequence of dissolving entrapped salts in pores, the concentration of solutes at the solid and liquid interface tends to be higher than in the bulk of the liquid. This concentration gradient generates a mass transfer flow from the interface into the bulk of the liquid. As this is a pure molecular diffusion and very slow, there is a build-up of salts in the water immediately surrounding the object. The extracted ions concentrate only in a very thin liquid layer near the interface, called the concentration boundary layer (CBL). This phenomenon is called concentration polarization. The most deleterious effect of concentration polarization is the local increase in osmotic pressure due to the increased solute concentration in the CBL. The result is that the solubility rate of salts in the washing water is gradually decreased because of decreasing the effective driving force. This decrease in the rate of desalination can be seen in Figure 5.

Figure 5 shows the differential conductivity versus time of a two-stage desalination experiment of the sample. The sample was initially immersed in fresh water and after 72 hours the washing water was renewed. The differential conductivity curve, i.e. desalination rate, shows similar trends in both stages: the desalination rate is initially high and decreases with time due to concentration polarization. The initial desalination rate in the second stage is higher than that at the end of the first stage, because fresh water removes the CBL and eliminates concentration polarization. However, the initial rate of the second stage is lower than the initial rate of the first stage due to partial depletion of salt in the sample's porous structure.

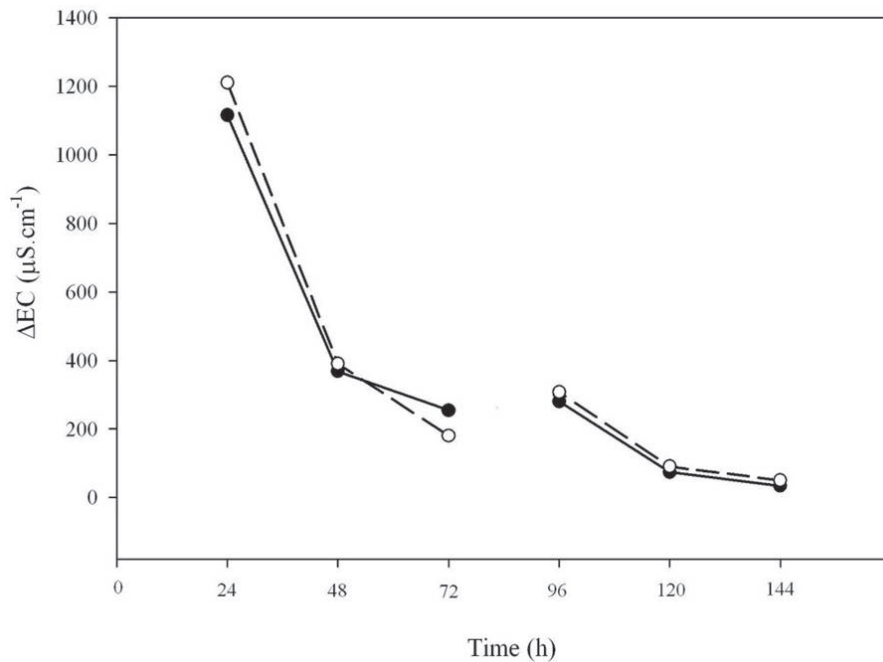


Figure 5. Differential EC ( $\Delta EC$ ) vs. time for sample no.1(●) and sample no.2 (○) during two stages of desalination.

The extent of concentration polarization depends on the hydrodynamics and geometry of the system [12, 13]. Agitation reduces concentration polarization by increasing the flow around the object and magnifying convective mass transfer. This high increase in mass transfer rate is observed in the EC reading jump.

The sharp increase in the conductivity reading after every agitation validates the potential efficacy of this method for accelerating the desalination process without any need to use harmful methods, such as hot washing water.

Figure 6 shows the conductivity data of all stages. It is a good indication of completion of the desalination process in ceramics by aqueous soaking while the salinity of the washing water is between 75 to 100  $\mu\text{S}\cdot\text{cm}^{-1}$  as reported by Koob and Ng [14]. However, conductivity in this work was always less than 100  $\mu\text{S}\cdot\text{cm}^{-1}$  in the final stage.



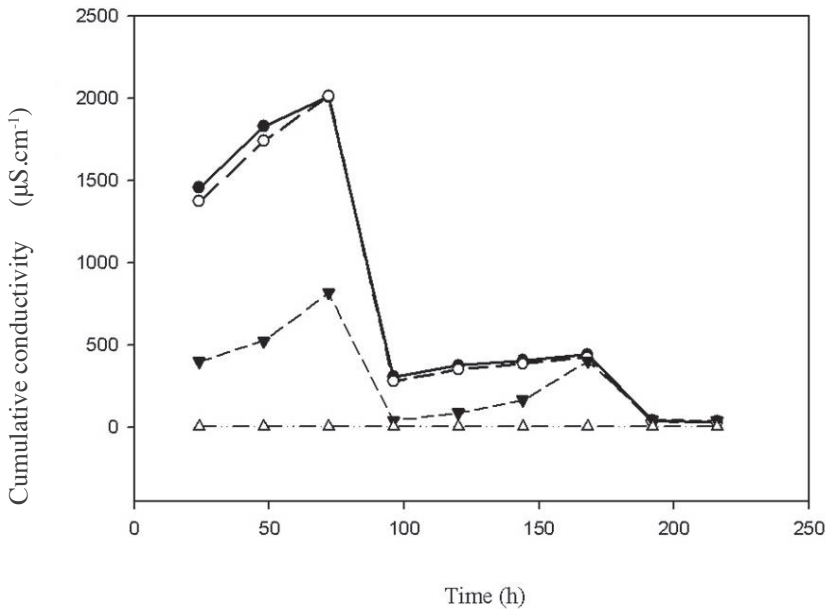


Figure 6. Result of EC measurement for sample no.1(●) sample no.2(○), sample no.3(▼) and distilled water (Δ) in all stages from 24 h in the first week to the 216 h at third week.

## 5. Conclusion

One of the main disadvantages of desalination by immersion is the long duration of contact time between the washing water and the ancient ceramics. This study highlighted the influence of concentration polarization on reducing ion extraction with this method (by decreasing the concentration gradient in the water layer closest to the object). The results of the experiments indicate that agitation has a high potential for avoiding long time contact by minimizing concentration polarization. This gain is achieved by decreasing the concentration of ions in the CBL, resulting in a high increase in the concentration gradient and rate of salt removal. Therefore agitation, in comparison to other methods for enhancing the efficiency of desalination processes such as raising the temperature of washing water or using surfactants, is a much safer method without any possible harmful side effects.

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