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**The Influence of NaCl Concentration on Salt Precipitation in Heterogeneous Porous
Media**

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Abstract

Evaporation of saline solutions from porous media is governed by the complex interactions between the transport properties of the porous media, the evaporating solution and the external boundary conditions. In the present study, we have investigated the effects of salt concentration on the evaporation process from porous media in the presence of a sharp textural discontinuity; a common heterogeneity in natural porous media formed due to the weathering or formation of soil horizons, wind deposition and erosion. We have conducted a comprehensive series of macro- and micro-scale experiments to delineate how the precipitation pattern is modified as salt concentration varies from relatively low values to a concentration close to the solubility limit. For concentrations much less than the solubility limit, the precipitation begins at the coarse-textured part of the heterogeneous porous media (which is a counter-intuitive result considering the preferential evaporation of water from the fine-textured part of the heterogeneous surface). However, when the concentration is close to the solubility limit, precipitation initiates preferentially at the fine-textured part of the heterogeneous porous surface. This behaviour results from the interaction between the transport properties of the porous media and the properties of the evaporating solution which must be considered. Additionally, using pore-scale images obtained by X-ray micro-computed tomography (CT), we have visualized the dynamics of precipitation in the presence of heterogeneity at high spatial and temporal resolution. The pore-scale results corroborate the mechanisms controlling the precipitation patterns in the presence of textural discontinuities inferred from the macro-scale experiments.

1. Introduction

Evaporation from salty solutions in porous media is of major importance in various engineering, environmental, and hydrological applications such as CO₂ sequestration [Peysson et. al., 2014, Ott et al., 2015, Jambhekar et al., 2015, 2016], where salt precipitation reduces the permeability near the wellbore, soil salinization [Prasad et. al., 2001, Jardine et. al., 2007, Russo, 2013] where salt adversely influences the vegetation and crop production, and the preservation of building materials [Pel et. al., 2004, Shahidzadeh and Desarnaud, 2012, Gupta et. al. 2014, Derluyn et. al., 2014] where precipitation of salt causes serious damage to the porous materials. This has motivated many researchers to study the complex interactions between the evaporating solution and the porous media under various external conditions, all of which influence the evaporation process.

During evaporation from porous media, large pores at the surface are infiltrated first by the air phase, while smaller pores remain saturated due to their higher capillarity threshold (in a manner similar to drainage from an initially saturated porous medium). The evaporative demand imposed by external gradients is supplied by capillary-induced liquid flow from within the porous medium to the evaporating surface. The process occurs during the so-called stage-1 evaporation during which liquid vaporisation occurs primarily from liquid-filled pores at the surface. When salt is present in the evaporating solution, the vapour pressure and consequently the driving force for evaporation is reduced. Solute is transported to the evaporation surface and gradually concentrates as liquid evaporates. When the salt concentration at the evaporating surface exceeds a critical value precipitation ensues. The higher the initial salt concentration in the solution, the sooner precipitation begins. Salt precipitation patterns on an evaporating surface significantly influence subsequent evaporation rates[Sghaier and Prat, 2009; Eloukabi et al, 2013; Bergstad and Shokri, 2016],

hence it is important to distinguish the effects of various processes and conditions on the precipitation rates and patterns. Here we focus on differences in evaporation dynamics and rates from porous media having different capillary characteristics and the effect of initial salt concentration. We have selected a system where evaporation occurs from surfaces of hydraulically connected vertical texturally contrasting regions (comprising fine and coarse textured sands) that span a range of evaporation dynamics [Lehmann and Or, 2009].

Drying patterns and dynamics are greatly influenced by the presence of textural discontinuities that may result in preferential drying and promotion of capillary exchange between different regions [Lehmann and Or, 2009]. This type of heterogeneity may arise due to human activities (e.g. agricultural practices) or natural processes such as the weathering or formation of soil horizons, wind deposition and erosion, as well as sequences of freezing, thawing, swelling and shrinking. Previous studies have shown that sharp textural discontinuities in porous media affect preferential evaporation and salt deposition and precipitation patterns [Pillai et al., 2009; Lehmann and Or, 2009; Shokri et al., 2010; Nachshon et al., 2011ab; Veran-Tissoires et al., 2012]. In particular Lehmann and Or [2009] have shown that during evaporation from columns having vertical textural contrast between fine and coarse sand, the fine-textured region (and its surface) remains saturated while the coarse textured domain dries preferentially. The evaporative flux from the fine-textured surface is supported by capillary flow supplied from the adjacent coarse-textured domain, driven by intrinsic capillary pressure differences between these two domains. Lehmann and Or [2009] found that the difference in the air entry value (i.e. the pressure required for evacuating the largest pore of the porous media which indicates the minimum pressure required to begin desaturation) between the two domains is a key factor in determining the magnitude of the capillary transfer from coarse to fine porous media.

Nachshon et al. [2011] studied the consequences of such evaporation patterns and dynamics (from heterogeneous media with vertical layers of fine and coarse sand) on salt deposition (using salt solutions at concentrations close to their solubility limit). They found preferential salt deposition on the fine section of the heterogeneous surface due to the prolonged duration and preferential evaporation from the fine sand domain, during which the coarse sand domain exhibited minimal surface precipitation. Veran-Tissoires et al. [2012] obtained similar results regarding the preferential salt precipitation at the fine-textured part of a heterogeneous porous surface. In their study, the initial salt concentration was also close to the solubility limit. Contrasting results were reported by Bechtold et al. [2011] who performed evaporation experiments with 0.6 wt % KCl solution, where salt was deposited initially at the coarse region of the heterogeneous surface. Bechtold et al. [2011] argued that salt accumulation was not governed by local evaporation from the heterogeneous porous surface and attributed the behaviour to lateral fluxes arising from differences in the hydraulic conductivities of each region.

Our hypothesis is that salt precipitation is determined by a combination of the transport mechanisms in the porous media and the evaporating properties of the solution; both must be considered for the different domains to predict the onset and location of deposition. This could resolve the apparently contrasting observations of Bechtold et al. [2011] reporting precipitation on the coarse domain at low salinity, and Nachshon et. al. [2011] or Veran-Tissoires et. al. [2012] reporting preferential precipitation on the fine-textured region of the heterogeneous surface at high initial salt concentration. Consequently, we have performed evaporation experiments with sand packs containing sharp vertical textural contrasts to investigate the impact of varying salt concentration on the localisation of salt precipitation and the drying rate. Additionally, X-ray micro-tomography has been used to verify the mechanisms governing the saline water evaporation.

2. Experimental Considerations

2.1 Macro scale laboratory experiments

A series of evaporation experiments was conducted in an environmental chamber at constant temperature and relative humidity of 30°C and 30%, respectively. Fine and coarse sands with particle size ranges of 500-700 μm and 1000-1250 μm respectively, were used to prepare a heterogeneous sand pack in a cylindrical glass column (70 mm in diameter and 70 mm in height). The heterogeneous porous medium consisted of a cylindrical fine-sand inclusion (with diameter of 23 mm) in the coarse-sand background. This heterogeneity was made by inserting a tube into the cylindrical column filled with the saline solution and filling the outside with saturated coarse sand and the inside with saturated fine sand. The tube was pulled upward gradually (and gently) during packing resulting in a porous medium containing hydraulically connected vertical domains of fine and coarse sand with sharp textural contrast. During packing, sand grains were immersed in the solution (by always maintaining a few mm of solution above the sand surface) to ensure complete saturation. The capillary pressure-saturation relationship (i.e. the water retention curve or soil water characteristic curve) of each sand was measured using HYPROP (Decagon Devices, USA) (Figure 1) and the parametric Van Genuchten (VG) model (Van Genuchten, 1980) was used to describe the experimental results with the VG parameters presented in Table 1. The air entry value, h_b , was calculated using [Shokri and Salvucci, 2011]:

$$h_b = \frac{1}{\alpha} \left[\left(\frac{n}{n-1} \right)^{2-\frac{1}{n}} - \frac{1}{n} \left(1 + \frac{n}{n-1} \right)^{2-\frac{1}{n}} \right] \quad (1)$$

where α and n are the VG parameters of each sand. We used NaCl to make the saline solutions. Six drying experiments were performed with different concentrations of NaCl

including 1, 2, 3, 4, 5 and 6 Molal (mole of NaCl/kg of water). This enabled us to investigate the effects of salt concentration on the onset and location (domain) of salt deposition during evaporation from heterogeneous surfaces. At 30°C the solubility limit of NaCl in water is 6.14 Molal. The solutions were prepared by weighing the required amount of NaCl and dissolving it in 1000ml of water to reach a target concentration. The solution was mixed for 1 hour before being used to saturate the sand. The saturated columns containing the different salt solutions were placed on digital balances connected to a computer for automatic recording of the column mass at 5 min intervals. A reference evaporation rate from pure water under similar conditions was measured as 6.4 mm/day. The average amount of salt solution per column was about 108 ml and the initial evaporation rate from the sand packs was about 14 g/day (or 4.5 mm/day). The surfaces of the columns were automatically photographed every hour to visualize the precipitation dynamics. Customized routines were developed in MATLAB following the procedure described in Shokri et al. [2008] to segment the recorded images from which the fraction of the surface covered by precipitated salt could be quantified during the evaporation experiments.

Table 1. Saturated and residual water content (θ_s and θ_r , respectively), shape parameters n and α , fitted to the van Genuchten model to describe the water retention curves of fine and coarse sand used in this study.

Type of sand	$ h_b $ (mm)	α (mm ⁻¹)	n (-)	θ_r (-)	θ_s (-)
Coarse sand	60	0.012	8.150	0.104	0.420
Fine sand	123	0.006	9.50	0.085	0.390

2.2 Pore-scale experiment monitored by X-ray tomography

We used X-ray micro-tomography to observe the 3D pore-scale dynamics of the liquid phase distribution and salt precipitation during evaporation from the heterogeneous porous media directly. We used the same fine and coarse sand used in the macro-scale laboratory evaporation experiments packed in a cylindrical column 20 mm in height and 10 mm in diameter. Similar to the macro-scale experiments, the heterogeneous system included a fine sand inclusion (diameter 3.3mm) within a matrix of coarse sand. The column was packed in the same way as in the macro-scale experiment, saturated with a 3M NaCl solution. To boost the evaporation, a fan was positioned 450 mm away from the drying sample. The temperature and wind speed 20 mm above the sample were 25°C and 1.5 m/s, respectively measured using an Omega HHF-SD2 Anemometer-Thermometer.

The dynamics of the evaporation process and salt precipitation were visualized using a Nikon X-Tek 225kV/320kV customised bay (operating at 80 kV and 250 μ A) housed in the Henrey Moseley X-ray Imaging Facility of The University of Manchester. We acquired pore-scale images at spatial and temporal resolutions of 0.01 mm and 60 min, respectively (each scan took 60 minutes). The duration of the experiment was 24 h. Each 3D scan was computationally reconstructed using a filter back projection algorithm from 2000 radiographs (projections). Each virtual 2D cross section was segmented into solid (sand grains and precipitated salt), liquid and air phases using customised routines developed in MATLAB following the algorithm described in Shokri et al. [2010] and Shokri and Sahimi [2012]. To distinguish between the precipitated salt and the sand grains we have followed the procedure used in Norouzi Rad et al. [2013, 2015] by comparing each 2D cross section with its corresponding image obtained at the beginning of the experiment (when there was no precipitated salt present) with the difference indicating the precipitated NaCl.

3. Results and Discussions

3.1 Drying curves

Figure 2 illustrates cumulative mass losses measured during evaporation from sand columns saturated with different NaCl concentrations. The porous medium and the external conditions were similar for all columns, hence observed differences in drying behaviour are attributed to effects of the salt concentrations (and deposition patterns and dynamics). Generally, the cumulative evaporation decreased with increasing NaCl concentration of the solution. This is attributed to the influence of salt concentration on both the saturated vapour pressure and on the onset of salt precipitation at the surface. The relationship between increasing salt concentration and the depression of vapour pressure is well established. For example, Sghaier et al. [2007] related empirically the equilibrium water vapour partial pressure to salt concentration using $P_v = P_0 \times \exp(A_1 - A_2C - A_3C^2 - A_4C^3)$, $A_1 = 2.49 \times 10^{-4}$, $A_2 = 2.59 \times 10^{-1}$, $A_3 = 7.43 \times 10^{-2}$, $A_4 = 2.66$, where P_v , P_0 and C denote the water vapour partial pressure, vapour pressure for pure water at 30°C and the mass fraction of NaCl in solution respectively. Hence, salt accumulation at the vaporization plane reduces the driving force for evaporation and results in lower evaporation rates (i.e. the slope of the lines presented in Figure 2). Additionally, higher salt concentration is associated with early and rapid salt precipitation that ultimately “seals” the evaporation sites at the surface. Notably, the sand column saturated by 6 M NaCl solution did not follow the above trend, with more evaporation observed in that case.

As illustrated by others [e.g. Bergstad and Shokri, 2016, Eloukabi et. al., 2013, Sghaier and Prat, 2009], the presence of precipitated salt at the surface may initially enhance the evaporation rate due to the enhanced evaporation surface area. In such cases water may flow through the porous structure of the precipitated salt to supply the evaporative demand at the top of the crust. Therefore, the precipitated salt formed at the early stages is wet and does not

necessarily act as a barrier for evaporation, but more like a highly porous “sponge” with strong capillary forces [Sghaier and Prat, 2009; Norouzi Rad et al., 2013]. As evaporation continues, the precipitated salt dries out which adds an additional resistance to vapour diffusion. This reduces the evaporation rate. The inset of Figure 2 shows that although at the early stage of the evaporation process the cumulative mass loss from the column saturated by 6 M NaCl solution is lower than for the other sand packs, it increases after only a few hours from the onset of the experiment. This might be due to the rapid precipitation of salt at the surface of the sand pack that boosts the evaporation compared to other columns. Ultimately, further evaporation seals the pores at the surface as a result of further accumulation of salt. At that point, the precipitated salt acts as a barrier that significantly limits the evaporation rate. Next, we will examine how the salt concentration modifies the precipitation patterns.

3.2. Dynamics of precipitation influenced by concentration of NaCl in the solution

The images recorded by the camera were used to investigate the precipitation patterns and dynamics as influenced by the initial salt concentration. We observed that the fraction of surface covered by precipitated salt crystals (for the same evaporative mass loss) increased with increasing initial salt concentration of the solution. This outcome can be rationalised in terms of mass balance with the higher salt concentration requiring less water evaporation to attain the solubility limit ($\sim 6.1\text{M}$). However, the precipitation behaviour in each section of the heterogeneous sand pack (fine and coarse sand) and the sequence of precipitation in each part is more complex.

Figure 3 depicts typical precipitation patterns and dynamics above sand surface saturated with different NaCl concentrations. When the concentration is below the NaCl solubility limit ($\sim 6.1\text{ M}$), salt precipitation begins in the coarse part of the surface and the precipitation in fine domain occurs later. For experiments with 1 or 2 M NaCl solution, salt precipitation in

the fine textured region begins long after most of coarse sand is covered by a salt crust. The result is counter-intuitive considering previous studies [Nachshon et al., 2011a, 2011b and Veran-Tissoires et al., 2012] that have shown higher cumulative evaporation from the fine sand and thus higher potential for salt precipitation. Our results, suggest that these earlier observation (of preferential deposition on the fine region) are associated with the initial solute concentration being close to the solubility limit. For the range of salt concentrations used here, we observe the opposite behaviour (i.e. preferential precipitation in coarse sand followed by precipitation in fine-textured region) as illustrated qualitatively in Figure 3.

A similar behaviour is observed when salt precipitation patterns above each sand column are compared at similar evaporative mass losses. For example, in Figure 4 the cumulative evaporation mass loss is 10 g in all cases but the precipitation pattern is significantly influenced by the initial salt concentration, and similar to Figure 3, when concentration is less than 6 M, more (and earlier) precipitation is observed at the surface of coarse sand. The opposite behaviour is observed for initial salt concentration close to the solubility limit (~ 6.1 M), with more extensive (and earlier) precipitation occurring in the fine section.

We quantified the surface area covered by precipitated salt in the fine and coarse regions of the columns using image analysis. The results summarized in Figure 5, suggest that lower initial salt concentration delays the onset of salt precipitation and deposition in the fine compared to coarse domain. Our results show that one must consider the proximity of the evaporating solution to the solubility limit to properly predict the precipitation patterns in the presence of vertical textural heterogeneity. This aspect has not received attention in previous studies [Nachshon et al., 2011a, 2011b and Veran-Tissoires et al., 2012] as discussed below.

3.3. Pore-scale mechanisms governing preferential salt deposition on heterogeneous surfaces

Since the coarse region has a lower air entry pressure compared to the fine region, $h_{bc} < h_{bf}$ (Figure 1), at the onset of evaporation from the heterogeneous sand pack it is preferentially invaded by air while the fine region remains saturated. This results in the formation of wet patches (or clusters of liquid-filled pores) at the surface of the coarse domain which are separated by dry regions. Due to the preferential invasion of the coarse domain, the distance between liquid clusters in the coarse domain supplying the evaporative demand (via capillary induced liquid flow) is larger than the ones in fine-textured domain. The spacing between the liquid clusters at the surface influences the diffusive evaporative flux per pore (thus the precipitation behaviour) which is discussed next.

As described by Shahraeeni et al. [2012], in the presence of isolated liquid patches at the evaporation surface, the initial stratified vapour concentration field above the wet surface evolves into a collection of vapour density shells (as a result of the water vapour concentration gradient forming a 3D structure around the pore due to lateral diffusion) [Bange, 1953] over the remaining active pores at the surface. This is illustrated schematically in Figure 6(a). When wet patches are distantly distributed, the vapour shells are spherical. However, when they are closely distributed the vapour shells are not fully formed due to interference from the vapour shells of adjacent pores (Figure 6(a)). When two such shells interact, the lateral component of diffusion is reduced adding additional resistance (hereafter represented by R_{VS}) for vapour diffusion per pore (Holcman and Schuss, 2008; Assouline et. al., 2010; 2011; Shahraeeni, et. al., 2012; Assouline and Or, 2013). Additionally, the stationary air above the surface limits the vapour diffusion via the so-called boundary layer resistance, R_{BL} . Following Lehmann and Or [2015], the vapour diffusion flux per pore in such cases can be described by:

$$e_p = \frac{C_s - C_\infty}{R_{BL} + R_{VS}} = \frac{D(C_s - C_\infty)}{\frac{\delta}{s^2} + \frac{1}{4r} - \frac{1}{\pi s}} \quad (2)$$

where r (m) is the radius of the pore, s spacing between adjacent wet patches, $R_{BL} = \frac{\delta}{s^2 D}$ (s/m³) is the boundary layer resistance, $R_{VS} = \left(\frac{1}{4r} - \frac{1}{\pi s}\right) \frac{1}{D}$ (s/m³) is the vapour shell resistance, δ (m) is the thickness of the boundary layer, D (m²/s) is the diffusion coefficient in air, C_s (kg/m³) is the saturated vapour density, which depends on the NaCl concentration in the evaporating solution, and C_∞ (kg/m³) is the vapour density in the surrounding air (at 30% relative humidity and 30°C). We applied Eq. (2) to evaluate the magnitude of the vapour flux in the fine and coarse domain within a pore of identical size of 0.33 mm (which is roughly equal to 1/3 of the mean particle size of the coarse sand used in our experiment [Glover and Walker, 2009]). In our calculation, we considered $\delta=5.5$ mm estimated using the measured potential evaporation rate (e_0) using $\delta = \frac{(C_s - C_\infty)D}{e_0}$. The obtained result is presented in Figure 6(b) showing reduction of the vapour flux per pore as the spacing between the liquid-filled pores decreases.

The practical consequence of this estimation is that earlier precipitation in coarse domain would occur due to the higher evaporative flux per active pore (due to larger spacing between active surface pores). This results in faster salt accumulation at the active pores in the coarse domain that triggers earlier precipitation (before the domain is disconnected by the characteristic evaporation length – or the drying front depth). As evaporation proceeds, salt precipitation spreads laterally over the surface of coarse sand. However, for 6 M concentration, precipitation starts slightly earlier in the fine section of the heterogonous sand pack followed immediately by precipitation in the coarse domain. The origins of this small difference in the onset of initial deposition in the fine and coarse section is not clear; it may be because of preferred crystal nucleation in the fine domain or due to slightly different

energy balance (longwave interception over the fine inclusion). In any case, the difference in the time for onset of salt precipitation was not too large (an hour or two as opposed to days) and the process was dominated by proximity to the solubility limit.

To summarize, although the main part of the evaporative demand is supplied by capillary-induced preferential evaporation from the fine section of the heterogeneous surface [Lehman and Or, 2009], this does not necessarily guarantee preferential salt precipitation over the fine texture domain. In addition to the presence of textural heterogeneity, one must take into account the salt concentration of the evaporating solution and the pore-scale interactions at the surface to be able to describe the selective precipitation patterns. It is the interplay between the presence of heterogeneity and salt concentration that defines the NaCl precipitation patterns and dynamics. In order to have a closer look at the internal phase distribution during the evaporation process as well as to quantify the amount of precipitated salt as drying proceeds we have utilized X-ray micro-tomography technique. This enabled us to visualize the dynamics of evaporation and salt precipitation in a heterogeneous sand pack and verify some of the assumptions mentioned above.

3.4. Pore-scale visualization of salt precipitation dynamics in heterogeneous sand pack

We have analysed the pore scale images obtained by X-ray micro-tomography to delineate the liquid phase distribution, as well as the amount of precipitated salt in each section of the heterogeneous surface (see Figures 7 and 8). Note that the data presented in Figure 5 only indicates the area covered by salt and provides limited information about the mass or volume of precipitated salt. We could extract this information from the pore-scale images.

Figure 7 shows that the coarse region in the sand pack desaturated immediately after the onset of the experiment whereas the fine region remained fully saturated at the early stages of the process due to smaller pores of fine sand (regions with higher capillary pressure)

compared to the coarse sand (regions with lower capillary pressure). This facilitates preferential invasion of air into the coarse sand. This observation is in line with the results presented in Lehman and Or [2009] and Shokri and Or [2013]. Preferential desaturation of coarse sand is followed immediately by earlier precipitation above the surface of coarse sand while there was no salt precipitation above the surface of fine section during the early stages of the evaporation process (Figure 8). The preferential desaturation of the coarse background continues until the pressure required to invade the remaining liquid-filled fine pores of the coarse background is higher than the pressure required for desaturating the largest pores in the fine sand. At that point air invades the fine section followed by salt precipitation above the fine sand. The data presented in Figure 8 shows that the majority of the total cumulative salt is precipitated above the coarse section of the heterogeneous surface which is in line with our macro-scale experiments.

4. Summary and Conclusions

Evaporation experiments from heterogeneous porous media containing a sharp vertical textural contrast saturated with NaCl solution of variable initial concentrations were conducted. The surface of sand was imaged during evaporation in order to investigate the salt precipitation dynamics. Additionally, pore-scale imaging was performed using X-ray micro-CT techniques with high temporal and spatial resolution. Analysis of the obtained results enabled us to investigate the mechanisms causing preferential salt precipitation on the heterogeneous porous surface during evaporation as influenced by the initial salt concentration and the presence of vertical textural interface.

We found that preferential salt deposition on the fine-textured domain of the heterogeneous surface occurs only when the salt concentration is close to the solubility limit. This is in agreement with the commonly accepted scenario in literature [Nachshon et al., 2011 and

Veran-Tissoires et al., 2012], i.e. preferential evaporation from fine-textured porous medium leads to preferential salt precipitation above the fine section of the evaporating heterogeneous surfaces. However, our results showed that this conclusion cannot be generalized as the initial salt concentration of the evaporating solution plays a key role on the precipitation patterns.

Using the macro- and micro-scale data presented in this manuscript, we found the preferential salt precipitation on the coarse-textured part of the heterogeneous porous media. The lower air-entry value of the coarse-textured domain compared to the fine-textured sand results in preferential air invasion of the pores in the coarse section. This results in formation of wet patches separated by dry regions at the surface of the coarser-textured domain. The spacing between the wet patches at the surface plays a key role on the diffusive vapour flux per pore. Larger spacing results in higher fluxes. This leads to a higher evaporation rate per pore in the coarse domain compared to the fine-textured domain which results in an earlier precipitation on the coarse section of the heterogeneous surface (when salt concentration is less than the solubility limit). Additionally, since the fine region remains liquid saturated, it takes longer to reach the solubility limit in the fine sand which results in later precipitation. This is an important conclusion because in most natural cases the salt concentration is much less than the solubility limit thus based on the results presented in this study one could expect preferential salt precipitation on the coarse-textured region.

This study reveals the necessity to consider simultaneously the effects of the presence of textural contrast and the initial salt concentration for accurate description of salt precipitation in heterogeneous porous media during evaporation. In addition to the hydrological and environmental applications, the findings of this paper will be useful for the design of porous materials to control salt precipitation in a desired way. This gives us the ability to localise salt precipitation, which could be relevant to preservation of building materials or historical monuments.

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Table 1. Saturated and residual water content (θ_s and θ_r , respectively), shape parameters n and α , fitted to the van Genuchten model to describe the water retention curves of fine and coarse sand used in this study.

Type of sand	$ h_b $ (mm)	α (mm ⁻¹)	n (-)	θ_r (-)	θ_s (-)
Coarse sand	60	0.012	8.150	0.104	0.420
Fine sand	123	0.006	9.50	0.085	0.390

Figure 1. Relationships between the capillary pressure (head) and the water content measured using HYPROP (Decagon Devices, USA) under hydrostatic conditions. The curves were fitted according to the Van Genuchten model for the fine and coarse sand used in the drying experiments. h_b represents the air entry pressure. Subscript f and c represent fine and coarse sand respectively.

Figure 2. Evaporative mass loss for heterogeneous porous media saturated with different NaCl concentrations (the inset illustrates the same data for the first 24 hours of evaporation).

Figure 3. Evolution of precipitation patterns at the surface of heterogeneous porous media (diameter 70 mm) at different concentrations, C_0 (mol/l) and time from the onset of the experiment. Note that the inner and out parts of the heterogeneous porous media comprise fine and coarse-textured sand regions, respectively.

Figure 4. Precipitation patterns at the surface of sand pack saturated with NaCl solution with concentration of (a) 3M, (b) 4M, (c) 5M and (d) 6M. Note that in all cases the cumulative mass loss is 10 g.

Figure 5. (a) Fraction of total surface of sand pack covered by the precipitated salt. The legend indicates the initial NaCl concentration. (b) and (c) illustrates the fraction of the fine (F) and coarse (C) region of the sand pack covered by salt during evaporation. The legend indicates the initial salt concentration. (d) the total cumulative evaporative mass losses from the column, M (g) (solid lines), and time, T (day) (dashed lines), at the end of onset of precipitation on the fine and coarse domain of the sand pack. Note the lower the concentration, the later the precipitation starts at the fine-textured part of the heterogeneous surface.

Figure 6. (a) Spherical diffusion shell and the interference between two diffusion shells when the wet patches at the surface are closely distributed (adopted from Sinha [2004]). R_{VS} and R_{BL} are the diffusion resistances due to presence of vapour shell and vapour shell interactions and external boundary layer, respectively (b) diffusive flux per pore as a function of spacing s between pores for 1M and 6M NaCl concentration in the evaporating solution.

Figure 7. Liquid saturation profiles delineated from the pore-scale images obtained by X-ray tomography in the coarse (a) and fine (b) section of the sand pack. The legend indicates the elapsed time from the onset of the experiment. Note that the sand pack was initially saturated by NaCl solution but the evaporation process started a bit earlier before the first scan was taken. This is why the region close to the surface is not fully saturated in (a) when the first scan (0 hrs) was taken. The Y-axis indicates the depth below the top of the column. The top 2 mm was not filled with sand.

Figure 8. Mass of precipitated salt delineated from the pore-scale images obtained by X-ray tomography as a function of elapsed time from the onset of imaging formed above the fine and coarse-textured parts of the surface together with the total amount of precipitated salt.