Desalination of Limestone Using Agarose/Ion-Exchange Resin Hydrogel: An Analysis Using the NMR-MOUSE Spectrometer to Preserve Cultural Heritage

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Introduction

A major concern in the field of cultural heritage is the degradation caused by soluble salts in porous materials, such as stone. Exposure to fluctuating environmental conditions, like humidity cycling, causes salts to dissolve and recrystallize within the pores.[1] The recrystallization can cause internal stress leading to delamination, powdering, and flaking of the surface (Fig. 1 and 2). To prevent further damage, art conservators desalinate objects as part of the treatment process. One promising technique uses an agarose and ion-exchange resin hydrogel to extract the soluble salts.[2]

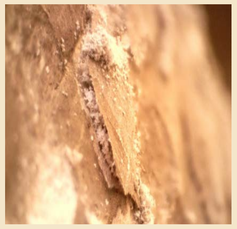

Fig. 1: Microscopic image of flaking on Egyptian limestone artifact.

Fig. 2: Ancient Egyptian column with powdering and delamination.

Figures courtesy of the Walters Art Museum, Baltimore.

The Profile NMR-MOUSE spectrometer (Fig. 3) was used to study the efficacy of this hydrogel treatment. Measurements for the NMR-MOUSE are noninvasive and *ex situ*, taking place outside the magnet within a sensitive slice above the probe head.[3] This configuration, combined with a strong, constant gradient, affords depth profiling, measurements of diffusion coefficients, and relaxation (T_1 and T_2^*) for liquids and unmodified porous materials. This non-destructive design is critical for cultural heritage as it allows for artifacts to be studied without removing a sample, affecting the material make up, or disrupting the pore structure of the object.[4] This preliminary desalination study utilized depth profile and T_2^* (spin-spin) relaxation experiments to monitor the bulk diffusion of soluble sodium chloride (NaCl), and the efficacy of the agarose and ion-exchange resin hydrogels during the treatment process.

Fig. 3: Kea2 Spectrometer (left) & PM5 NMR-MOUSE (right)

Methodology

The stone samples were prepared by heating the stones under vacuum at 110°C for 24 hours and soaking them in a 30% (w/v) NaCl solution for 48 hours. Bio-Rad Macro-Prep DEAE Media weak anion exchange resin was washed following the preparation protocol from the manufacturer. Benchmark molecular biology grade agarose and the ion-exchange resin were used to prepare the hydrogels, as can be seen in Fig. 4. The hydrogel was used to desalinate the saturated samples for 12 hours (Fig. 5).

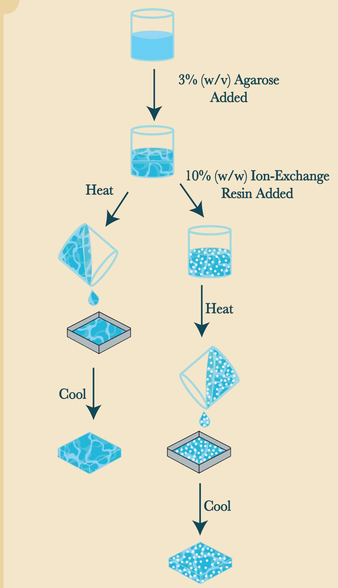

Fig. 4: Preparing the hydrogel.

Fig. 5: Hydrogel application and direction of diffusion.

The treatment process was monitored with a PM5 NMR-MOUSE connected to a Kea2 spectrometer operating at 18.9MHz (1H). A 5mm penetration coil was used without spacers for all measurements. To track changes within the hydrogel, the spin-spin relaxation times (T_2^*) were acquired using a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence of 2048 echoes, an echo time of 60 µs, and 64 scans. The depth profile was run at 20 minutes intervals over the treatment period, utilizing a CPMG of 256 echos, an echo time of 60 µs, and 16 scans. The data was processed with Prospa V3.39.

Results & Discussion

The relaxation of pore fluids is determined by bulk, surface, and diffusion effects. Within the hydrogel, water is characterized as $T_{2\ long}^*$, attributed to mobile water, and $T_{2\ short}^*$, attributed to bound water that interacts with the pore structure through hydrogen bonding or chemical interactions.[5] After a 12 hour desalination period, the 3% agarose hydrogel showed an increase in proton density (Fig 6). $T_{2\ long}^*$ relaxation also increased after the desalination (Fig 7). The shift in T_2^* relaxation towards longer relaxation times correlates to an increase of NaCl concentration within water samples, shown in Table 1. This shift in $T_{2\ long}^*$ indicates the bulk diffusion of the NaCl into the hydrogel. The $T_{2\ short}^*$ was also seen to increase. This suggests an introduction of NaCl to the system allows for more movement of the bound water.

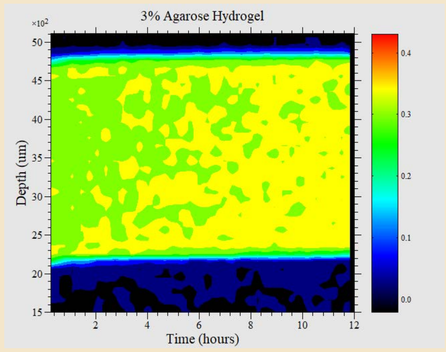

Fig.6: 3% Agarose hydrogel depth profile over 12 hours.

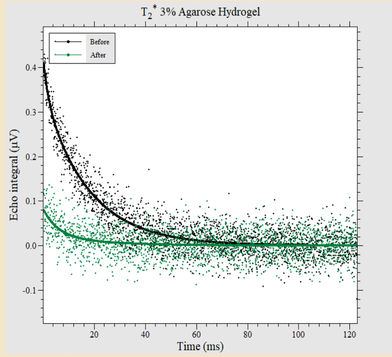

Fig.7: T_2^* relaxation measurement of 3% Agarose hydrogel over 12 hours.

Before $T_{2\ long}^*$ = 17.7 ms $T_{2\ short}^*$ = 2.1 ms
After $T_{2\ long}^*$ = 19.3 ms $T_{2\ short}^*$ = 5.0 ms

Table 1: T_2^* Relaxation Trend

% (w/v) of NaCl Solution	0 (DI Water)	5	10	15	20	25	30
Avg. T_2^* Relaxation (ms)	28.1	29.5	32.3	32.6	35.2	38.1	42.8

The 3% agarose and 10% ion-exchange resin hydrogel also showed an increase in proton density during the 12 hour desalination period. Settling of the ion-exchange resin within the hydrogel could be seen in Fig. 8, indicated by the more intense signal at approx 1x10³ µm. The $T_{2\ long}^*$ relaxation of the hydrogel showed a decrease over the desalination period. This would suggest that little to no NaCl was drawn into the hydrogel, possibly due to the ion-exchange resin hindering the bulk diffusion of NaCl. The $T_{2\ short}^*$ also decreased over the desalination period, suggesting the bound water became more restricted over time.

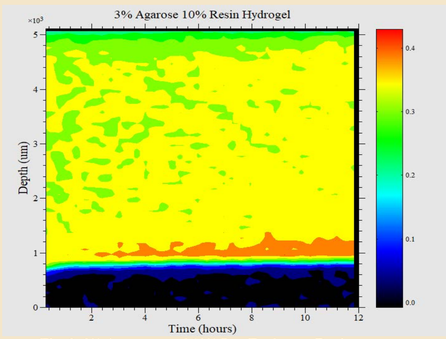

Fig. 8: 3% Agarose and 10% Ion-Exchange Resin hydrogel depth profile over 12 hours.

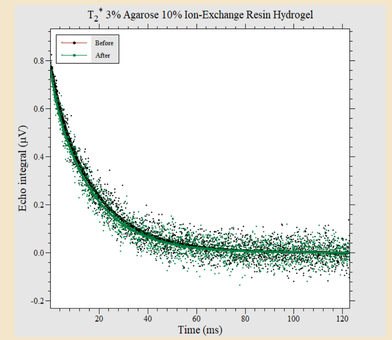

Fig. 9: T_2^* relaxation measurement of 3% Agarose 10% Ion-Exchange Resin hydrogel over 12 hours.

Before $T_{2\ long}^*$ = 18.1 ms $T_{2\ short}^*$ = 4.4 ms
After $T_{2\ long}^*$ = 16.8 ms $T_{2\ short}^*$ = 2.1 ms

Conclusions

The degradation caused by soluble salts in porous materials makes monitoring the desalination process an important aspect of the treatment process. This preliminary study shows the utility of the NMR-MOUSE to monitor the agarose and ion-exchange resin hydrogels, finding that an increase in $T_{2\ long}^*$ indicated the bulk diffusion of salts into the hydrogel. Additionally, the presence of the ion-exchange resin within the hydrogel was observed to hinder desalination. Further measurements are underway to calculate the bulk diffusion rate as expressed as the amount of salt moved per time and to determine the influence of agarose concentration, ion-exchange resin, and/or porosity of the stone on the desalination rate. Additional research is needed to understand the interaction of the NaCl with the agarose and the ion-exchange resin and elucidate the mechanism observed by T_2^* relaxation shifts.

References

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