# **Supplementary Document A**

## **Detailed methodology**

### Sampling of salt core

Two borehole cores held within the National Geological Materials Collection (NGMC) collection at BGS, Keyworth were sampled (Table 1). These borehole cores were both drilled through Triassic halite in the NW of England (formed ~245 Mya): The Arm Hill No 1 borehole core (Lat. 53.9119788196, Long. -2.99077338532) in the Preesall Saltfield in Lancashire and which has a drilled length of 609 m, with 341 m through the Lancashire Preesall Halite; and the Northwich Victoria Infirmary borehole core (Lat. 53.2568729118, Long. -2.52039762053) in the Cheshire Basin, which has a drilled length of 129.5 m through the Northwich halite. The Preesall Halite and Northwich halite are lateral equivalents (Wilson and Evans, 1990; Wilson, 1993) and these lithologies were selected as both have been used, or are being considered, for gas storage (Evans and Holloway, 2009; Evans, 2016). From the core, two adjacent lengths of core (each 100 mm long) were selected to capture each lithological variation. This was to ensure that the two samples were as alike in fabric as is feasible. The diameter of the Arm Hill and the Northwich cores varied (85 and 120 mm respectively), but otherwise the dimensions of the experimental core blocks were identical. Five key salt end-member fabrics (refer Hough et al., 2011) were identified, ranging from almost pure halite (cumulate and primary founded mat, to a high mud content (>80%: haselgebirge), with intermediate chicken-wire fabric containing anhydrite and clays. The final fabric is a sheared salt, which we refer to here as ‘mylonite’.

**Table 1 - Experimental samples**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Borehole** | **Formation** | **Location** | **Texture\*** | **Experiment A (brine)** | **Experiment B Seawater** |
| Arm Hill | Preesall Halite | Lancashire | M |  | x |
| Arm Hill | Preesall Halite | Lancashire | M | x |  |
| Arm Hill | Preesall Halite | Lancashire | PFM | x |  |
| Arm Hill | Preesall Halite | Lancashire | PFM |  | x |
| Arm Hill | Preesall Halite | Lancashire | CW | x |  |
| Arm Hill | Preesall Halite | Lancashire | CW |  | x |
| Northwich | Cheshire Northwich | Cheshire basin | C | x |  |
| Northwich | Cheshire Northwich | Cheshire basin | C |  | x |
| Northwich | Cheshire Northwich | Cheshire basin | H | x |  |
| Northwich | Cheshire Northwich | Cheshire basin | H |  | x |
|  |  |  |  |  |  |
| *\*M = mylonite, PFM = primary founded mat, CW = chicken wire, C = cumulate, H = Haselgebirge* | | | | | |

### Experimental set-up

The experimental setup is shown in Figure 2A and B of the paper. The cores were pre-drilled in the centre with a four mm diameter pilot-hole. This pilot-hole is in part analogous of the pilot borehole, present within a full-scale cavern. The solution was injected into the pre-drilled hole from the top by a peristaltic pump at a constant flow rate of 0.58 ± 0.02 ml/min and a fluid temperature of 23 ±1 oC. Two solutions were used for the experiments: experimental set A used a brine with a concentration of 270 g/l NaCl; and experimental set B used a commercially available artificial seawater (D-D H2O Ocean Pro+ Aquarium Salt: 24 g/l NaCl). Sodium fluorescein was also used in the inlet fluid as a fluorescent tracer dye to monitor the extent of any fluid transport into the salt core.

One salt core of each of the five end-member fabrics was used with each fluid.

To prevent leakage and ensure that the experimental fluid was transported into the pilot-hole, each end of the salt cores was capped with machined clear acrylic (polymethyl methacrylate) end caps and sealed with air cured silicone rubber. Perfluoroalkoxy alkane (PFA) bulkhead compression fittings with an anti-slip ring were affixed to the end caps to hold the tubing (also PFA) in place.

The duration of the experiments varied across the experimental runs: experiments were terminated when the total volume of the initial pilot-hole (~ 1250 mm3) had expanded by at least 10 times from the start of the experiment. Experimental set B were of shorter duration because of the anticipated faster salt dissolution rates related to the more diluted injected sea water solution. For runs longer than 7 hours the pumping of fluid was paused overnight, and the salt core drained and weighted, with the fluid injection being resumed the following day. This allowed tighter control of the dissolution experiment conditions, particularly in case of fluid loss by seepage through the bottom or top caps, or break-out through the salt core itself. The whole salt core assemblage was initially weighed, and then subsequently at the end of each leaching period to estimate the rate of mass loss during the dissolution experiments.

After passing through the salt cores, the fluids at the bottom outlet were collected for analysis in 15ml to 30 ml tubes, using a fraction collector.

### Analytical Methods

### *Fluid measurements*

Measurements and analysis carried out on the fluids included: chloride concentration, seawater fluid density, volumetric flow rate, and temperature of the solutions. Electrical conductivity was measured for all the seawater experiments, and the primary founded mat and mylonite brine experiments. Methodology is summarised below:

A subset of fluid samples was analysed for chloride concentration to determine the rate of halite dissolution. The fluid density for the seawater experiments was calculated by weighing the fluid in each sampling tube and measuring its volume.

The volumetric flow rate Q (ml/min) during the experiments was obtained by measuring the volume of brine collected in each sampling tube divided by the collection time. Initial velocity Vi was calculated as Q/Ai, where Ai denotes the area of the initial drilled hole section of 1.26 mm2. For the measured flow rate of 0.58 ± 0.02 ml/min, Vi was 44 ± 2 mm/min.

Electrical conductivity and temperature of the solutions at the core inlet and outlet were measured with a Toledo Seven Gro pro SG7 conductivity meter with probe InLab 783 (conductivity range 0.001 to 100 mS/mm). The conductivity of a reference solution saturated in NaCl at the same temperature of the dissolution experiments was also measured.

### *Fluid geochemistry*

Collected fluids were analysed for cations (Ca, Mg, Na, K, Si, Ba, Sr, Mn, Total Fe, P and S, and selected trace elements) by inductively-coupled plasma – mass spectrometry (ICP-MS) using an Agilent 7500CX. Ongoing halite dissolution was measured (Cl-, SO42-, NO3-) for a sub-set of brine samples using a hand-held “chloride ion selective” probe calibrated against analysis of chloride concentrations by Ion Chromatography (IC) on a Thermo-Fisher ICS 5000.

Due to the nature of the samples (high concentrations of Na and Cl in solution) which are at concentrations too high for analysis by IC and ICP-MS to effectively measure and allow good recoveries of the major ions in question, samples were subsequently diluted via a gravimetric method using ultra-pure 18 MΩ “Milli Q” water (Millipore) as the diluent.

A nominal dilution factor of 5000 was set for all samples, however after measuring the weight of the pipetted sample and the total weight including the diluent calculations indicated that the total dilution factor was approximately 4200 (mean value of all 19 samples ± 72.1).

It is to be noted that although the possible effect of the high density of the samples (i.e. Na+ and Cl-) may have been a factor resulting in the lower total dilution values (i.e. 4200), it may be more likely that the viscosity of the waters would be the most likely contributing factor when pipetting out the volumes.

Furthermore, due to high concentrations of Cl- in the samples and the resulting high dilution factor, those anions which would usually be analysed by IC e.g. F-, NO2-, NO3-, Br-, SO42- and HPO42- would be at concentrations too low to be measured.

### *Ion Chromatography*

Anions concentrations in the fluids (including F-, Cl-, NO2-, NO3-, Br-, SO42- and HPO42-) were determined by ion chromatography using a Thermo-Fisher ICS5000 Ion Chromatograph system (S/N 10060887). Instrument operation and data acquisition was controlled by the Chromeleon (version 7) software package. Anion separation is performed using a Thermo-Fisher AG19 guard column and an AG19 analytical column using an injection volume of 10 μl. Three QC standards are prepared from a proprietary mixed anion reference solution traceable to National Institute of Standards and Technology (NIST) standards (SpexCertiprep®) in order to cover the anion calibration ranges. Two standards (10× and 25×) cover the upper and lower ranges of F-, Cl-, NO3- and SO42- and one (100×) covers all anions. A calibration drift check standard, which gives the concentrations within the calibration ranges of each anion, was analysed at the end of each analytical run. The data obtained were accepted within ±10% of the target values. The overall error estimates for anion species were F- 20%, Cl- 10%; NO2- 20%; Br- 20%; NO3- 10%, SO42- 10% and HPO42- 20%.

### *Inductively-Coupled Plasma – Mass Spectrometry (ICP-MS)*

Fifty-seven major and trace elements from the extracted fluids were analysed by inductively-coupled plasma - mass spectrometry (ICP-MS). Analysis were performed using an Agilent 7500cx series (serial number JP51202387) quadrupole ICP-MS instrument fitted with a CETAC autosampler. The instrument was operated using the bespoke Agilent 7500 ICP-MS Chemstation B.03.06 software package.

The instrument was calibrated at the beginning and end of every analytical run using at least three standards and a blank for each trace element, and three standards and a blank for major elements. These are prepared from a proprietary mixed solution traceable to NIST standards. Multi-element QC check standards were analysed at the start and end of each run, and after a maximum of 30 samples.

A Certified Reference Material (CRM: CNRC SLRS-5 trace elements in natural water) was run between each batch of QC standards. Detection limits have been calculated as three times the standard deviation of the 1% nitric plus 0.5% hydrochloric acid blanks inserted at regular intervals during the analysis. The uncertainty associated with the ICP-MS measurements above the detection limit is generally considered to be of the order of ±10%. However, for, Na, Ca, Si, P, S, K, Fe, Zn, Sr and Ba, the overall uncertainty is of the order of ±15%. For Li, B and Al the overall uncertainty is of the order of ±20%.

### *2D X-ray radiography*

Post-experiment, all cores except MPLT622A (the first experiment) were analysed non-destructively using 2D X-ray radiography on a GE Inspection ISOVOLT Titan E X-ray generator. The settings used varied slightly due to differences between the core diameters in the Northwich and Arm Hill cores, and the amount of insoluble material (affecting the density) of the sample: X-rays were taken at a distance of 1200 mm, 60 second exposure, 10-15 mA and 90-180 kV. Two side views of the cores were imaged at 90o to each other. This technique allows a rapid assessment of the extent and general morphology of the cavity.

### *3D X-ray computed tomography*

3D X-ray computed tomography imaging (X-ray CT) was carried out on the five different rock types, both pre and post experiment. The rock core samples were prepared for X-ray CT by wrapping in parafilm and mounting to the sample stage. The core was scanned using an XRADIA Versa XRM500 (Carl Zeiss, Oberkochen, Germany) using a source setting of 160 kV and 63 µA, and imaged at an optical magnification of 0.399 (large field of view; LFOV) to achieve a spatial resolution 50 µm. Sample orientation during scanning was defined with reference to the direction of the incident X-rays as follows: ZX parallel and normal (-*y* plane), ZY parallel and horizontally perpendicular (-*x* plane), XY vertically and horizontally perpendicular (-*z* plane). No corrections were required for beam hardening or sample displacement artefacts. Reconstructed projection images were post-processed using Avizo Fire v8.1 (FEI, Hillsboro, Oregon, USA). Image stacks were calibrated for length scale, before running 3 iterations of a standard median filter, following by a 5px majority filter (for de-noising). The cavity and any entrapped air voids were then segmented using the interactive threshold module to produce a binary image stack, followed by conversion to a label field to enable measurement of pore size distributions for the entrapped air voids. This was combined with qualitative visual comparisons by overlaying the pre-treatment image stacks with the post-treatment ones. In order to eliminate edge effects (incurred during X-ray scanning) from the outer wall of the core it was necessary to crop the scans of the post-experimental cavities, in some cases slightly cropping the cavities themselves where they had extended to the outer edge of the core.

### *Photo-stimulated fluorescence scanning*

Laser-stimulated scanning fluorescence imaging (LSSFI) was performed on the flat surfaces of the core-halves using an Amersham Biosciences STORMTM 860 variable mode laser scanning system to determine the location of any fluorescein tracer, and therefore the extent of fluid penetration. This LSSFI scanning system was equipped with both red (635 nm) and blue (450 nm) laser diodes for red- and blue-excited fluorescence, with long-pass filters (optical filters that transmit light of wavelengths longer than a specified cut-off. The filter rejects light with wavelengths shorter than the cut-off), to allow recording of fluorescence emissions with wavelengths >650 nm and >520 nm, respectively. Images were scanned and recorded at a spatial resolution of 100 µm per pixel. Fluorescein has a peak fluorescence excitation absorbance band at 494 nm with peak fluorescence emission at 521 nm. The fluorescence from fluorescein can therefore be excited by the blue-diodes but there is no excitation by the red diodes.

### *Optical imaging*

Offcuts of salt from the five end member fabrics were imaged, both in hand sample and polished thin section pre-experiment, using an Olympus SZX-10 stereo-photomicroscope equipped with a high-resolution Peltier-cooled digital camera. Key characteristics within each fabric were identified. Following X-ray analysis, the post experimental cores were sliced longitudinally and the exposed dissolution cavities were again analysed and imaged. These half cores were also laser-scanned using a NextEngine 2020i laser scanner at a resolution of 17,000 points per inch squared. The resulting point clouds were merged within the included ScanStudio HD Pro software to produce an OBJ model with attached texture. From one half of the core, large format (50 x 76 mm), epoxy-resin (dyed blue to highlight porosity) impregnated petrographic polished thin sections were prepared. These were analysed and imaged on a Zeiss Axioplan 2 polarising microscope with Zeiss Axiocam MRc5 digital camera.

### *Scanning electron microscopy*

Detailed morphological observations were made on the salt blocks using secondary scanning electron microscopy (BSEM) in variable pressure mode. Analysis was carried out using a FEI Company QUANTA 600 environmental scanning electron microscope (ESEM) equipped with an Oxford Instruments INCA Energy 450 energy-dispersive X-ray microanalysis (EDXA) system with a 50 mm2 Peltier-cooled (liquid nitrogen free) silicon drift detector (SSD) X-ray detector capable of operating at very high input X-ray count rates (up to ~106 counts per second). The ESEM was operated in variable pressure mode, with an electron beam accelerating voltage of 15 -20 kV.

**References**

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