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IMPLICATIONS FOR UNDERGROUND HYDROGEN STORAGE CAPROCK INTEGRITY**

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HYDROGEN-INDUCED CALCITE DISSOLUTION IN AMALTHEENTON FORMATION CLAYSTONES: IMPLICATIONS FOR UNDERGROUND HYDROGEN STORAGE CAPROCK INTEGRITY

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Abstract

With the rising potential of underground hydrogen storage (UHS) in depleted oil and gas reservoirs or deep saline aquifers, questions remain regarding changes to geological units due to interaction with injected hydrogen. Of particular importance is the integrity of potential caprocks/seals with respect to UHS. The results of this study show significant dissolution of calcite fossil fragments in claystone caprock proxies that were treated with a combination of hydrogen and 10 wt% NaCl brine. This is the first time it has been experimentally observed in claystones. The purpose of this short communication is to document the initial results that indicate the potential alteration of caprocks with injected hydrogen, and to further highlight the need for hydrogen-specific studies of caprocks in areas proposed for UHS.

Keywords

- Underground hydrogen storage
- Caprock integrity
- Calcite dissolution
- Hydrogen

1. Introduction

Secondary storage of gases in the subsurface has been proposed as a way to help reduce global carbon emissions while continuing to meet global energy demands. Sequestration of CO₂ in the subsurface can be used to reduce emissions of CO₂ to the atmosphere, while underground hydrogen storage (UHS) may facilitate the use of a carbon-free energy source derived from renewable processes [1–3]. Depleted oil and gas reservoirs and deep saline aquifers have been proposed for UHS [1,4,5]. Caprock integrity is critical for safe and effective secondary hydrogen storage [5–7]. The textural and mechanical changes that may take place with the addition of secondary storage gases

such as hydrogen, and how those changes may affect the integrity of the caprock, need to be understood. In this study we present the first results from a series of hydrogen treatments applied to caprock-proxy claystones collected from outcrop.

2. Materials and Methods

To determine textural changes due to hydrogen exposure, claystone samples from the Lower Jurassic Amaltheenton Formation, collected from a claystone pit in Unterstürmig, Germany, were subjected to various static treatments then analysed via broad ion beam-scanning electron microscopy (BIB-SEM). The maximum burial depth of the sampled material was estimated to be 1700 m [8]. The sample material is thinly bedded, though not fissile. A small, single block of outcrop material was dry-cut into four pieces with final parallel sides using a Buehler IsoMet low speed precision cutter. One of four treatment options was then applied to each individual sample: (i) untreated (reference), (ii) hydrogen gas treated (dry-H₂), (iii) NaCl brine treated (brine), and (iv) NaCl brine and hydrogen treated (brine-H₂). All samples were treated for 30 days at room temperature. Treatment options with hydrogen were undertaken in Berghof BR-25 high-pressure laboratory reactors with a hydrogen pressure of 150 bar and brine options were treated in a synthetic 10 wt% NaCl solution. To be suitable for placing under vacuum for BIB-milling and SEM analysis, the brine and brine-H₂ samples were dried for 24 hrs at 25°C in a drying cabinet after treatment. BIB-milling was performed using a Hitachi ArBlade 5000 system (3h at a milling energy of 8kV). Samples were then coated with gold using a Cressington Sputter Coater 108auto (30s sputtering time). BIB-SEM image acquisition was done using a TESCAN CLARA field emission (FE) microscope equipped with the TESCAN Essence Image Snapper software version 1.0.8.0, which allows capturing and stitching of high resolution images. Both backscattered (BSE) and secondary (SE) electron image maps were obtained. Images were taken at 10kV electron energy. The collected images were analysed for differences in texture in the samples arising from the different treatment types.

3. Results and Discussion

3.1. Petrography

The SEM images of the analysed samples show a typical grain size of approximately 25 μm in a finer clay matrix. Based on BSE images and SEM energy dispersive spectroscopy (EDS) the detrital grains are interpreted as quartz, calcite and feldspar in a clay matrix. Calcite is present as bioclasts. Minor amounts of organic matter are present and authigenic pyrite is observed, typically within fossil fragments. Original porosity is present as both intergranular porosity between detrital grains as well as some intragranular porosity within fossil fragments. Some areas of higher intergranular porosity are observed in the untreated sample (Fig 1A) and are likely pellets or due to bioturbation.

3.2. Fractures and Bedding

Petrographic analysis of the SEM images of the four samples shows that the three treated samples have some open cracking parallel to bedding (Fig 1). Whereas bedding is apparent in the untreated sample, significant opening is not observed. When removed from the treatment vessels, brine and brine-H₂ samples had split along bedding into several pieces, but the dry-H₂ sample remained intact and cracking was not observed at the macroscopic level. Despite the broken nature of the brine and brine-H₂ samples, pieces remained sufficiently intact for BIB-SEM preparation and imaging. EDS imaging of Na and Cl shows significant salt precipitation along bedding and in some pores in the brine and brine-H₂ samples (Fig 1 C&D, Fig 3F).

The observed cracks are interpreted as artefacts of shrinking-swelling during moisture changes and are not representative of in-situ changes expected for underground storage. The sensitivity of shales and mudstones to changes in moisture content and subsequent changes in strength are well understood and documented [9–11]. BIB-SEM imaging has the advantage of being able to make visual observations of very fine-grained rocks at high magnification. This allows for meaningful observations to be made despite non-representative experimental changes to the samples, such as cracking and salt precipitation, which may not be corrected for in quantitative, non-visual methods.

3.3. Dissolution

The brine-H₂ sample shows significant etching and dissolution of grains that is not observed in the other samples (Figs 1D and 2D). Figure 3 shows examples at various scales of the grain dissolution observed with the brine-H₂ treatment. Based on the morphology of the grains and the EDS, which shows high calcium at these locations, the etched and dissolved grains are calcite fossil fragments. Intragranular porosity is observed in calcite fossil fragments of all samples (Fig 2). It is likely that in the brine-H₂ treated sample dissolution was initiated in the intragranular porosity of the fossil fragments due to the higher internal surface area for dissolution reactions to occur.

Although this is the first experimental result showing calcite dissolution with brine and hydrogen treatment in claystones, dissolution of calcite under hydrogen treatment is not unprecedented. Similar autoclave studies of reservoir sandstones by Flesch et al [6] showed that, when present, anhydrite and calcite cements undergo dissolution under the influence of brine and hydrogen mixtures. Furthermore, PHREEQC modelling by Bo et al [12] indicates that calcite dissolution due to hydrogen dissociation may occur in UHS conditions. The results from the current study indicate that despite the low permeability of the claystones, calcite fossil fragments in potential seal rocks are subject to dissolution in the presence of brine and hydrogen. Liquid metal injection experiments by Klaver et al [13] on the Posidonia Shale, which stratigraphically overlies the Amaltheenton Formation, indicate that porosity in fossil fragments is one of the major components responsible for pore fluid transport in the shale samples. This supports the current study in which brine with hydrogen would be accessible to fossil fragments and lead to their dissolution.

In addition to calcite reactions, other modelling and experimental studies [7,14,15] presented the likelihood of pyrite and/or goethite alteration to pyrrhotite in the presence of brine and hydrogen. Although pyrite is present in our samples, there is no textural evidence that it was altered under our experimental conditions (Fig 3E). The experimental results of Truche et al [15] indicate that the pyrite to pyrrhotite reduction in potential UHS settings would be significant at temperatures above 25°C, a condition not met in this study.

3.4. Experimental Implications

Although altering the saturation state of mudstone samples with brine can be experimentally difficult [9,10], experiments require both brine and hydrogen treatment for dissolution to occur. Under the duration and experimental conditions of this study, dry hydrogen treatment alone did not lead to significant dissolution of calcite (Figs 1B and 2B). Therefore, one could not estimate potential reactions with the experimentally easier dry hydrogen treatments alone. Furthermore, because of the likelihood of experimental damage due to swelling and salt precipitation that are not representative of in-situ storage conditions, a brine only sample should be used as a comparative reference. The brine treated reference sample would be of particular importance for standard, nonvisual measurements such as geomechanical testing or porosity measurements, which could be affected by shrinking, swelling and salt precipitation.

3.5. Underground Hydrogen Storage Implications

In order to safely store hydrogen underground, a robust and reliable seal is required. The potential for increased porosity due to brine-H₂-rock interaction, as shown experimentally by this study and through modelling by Bo et al [12], may compromise the tightness of caprocks. In addition to the potential loss of sealing capacity, an increase in porosity in shales is often related to a decrease in strength [16,17]. The decrease in caprock strength over time due to hydrogen storage could lead to operational complications of UHS systems subjected to cyclic pressure changes during injection/withdrawal. Furthermore, geochemical reactions involving hydrogen in the subsurface may lead to loss of up to 9.5% hydrogen [12], which would have economic impacts for the operator.

4. Conclusions

Initial autoclave experiments on caprock-proxy claystones from the Amaltheenton Formation indicate that calcite dissolves at room temperature in less than 30 days in the presence of brine and hydrogen. These results are supported by recent geochemical modelling results [12]. The dissolution of calcite in caprock units may have implications for the feasibility of UHS in seal-reservoir systems with high calcite content, specifically increasing the porosity in the caprock. This may (i) increase

permeability and decrease the effectiveness of the caprock to contain hydrogen, (ii) decrease strength and stiffness, with geomechanical implications for the caprock integrity, and (iii) lead to additional loss of hydrogen through chemical reactions. Despite the experimental difficulty of treating shale samples with brine arising from the likelihood of slaking and disintegration of low-maturity claystones, it is nevertheless essential to include an aqueous medium in experiments for dissolution to occur, as dry hydrogen alone did not result in significant dissolution of grains. Furthermore, care must be taken to disregard experimental changes such as cracks formed due to moisture variations, and precipitation of brine salt on fracture surfaces and in pores during subsequent sample drying.

This is the first experimental demonstration of potential dissolution of calcite in claystones, which has important implications for future research in UHS. Although these results are preliminary, they indicate the importance of further research on UHS caprocks. Ongoing research is required to confirm these initial results, as well as to introduce more variables to better understand the brine-H₂-rock interactions that may occur. Future tests required include various treatment times, various temperature controlled reactions, and multigas treatments more reflective of in-situ conditions. Furthermore, as these initial findings are a proof of concept on caprock proxies, similar experiments should be conducted on actual caprocks and formation brine from nominated storage sites.

5. Acknowledgements

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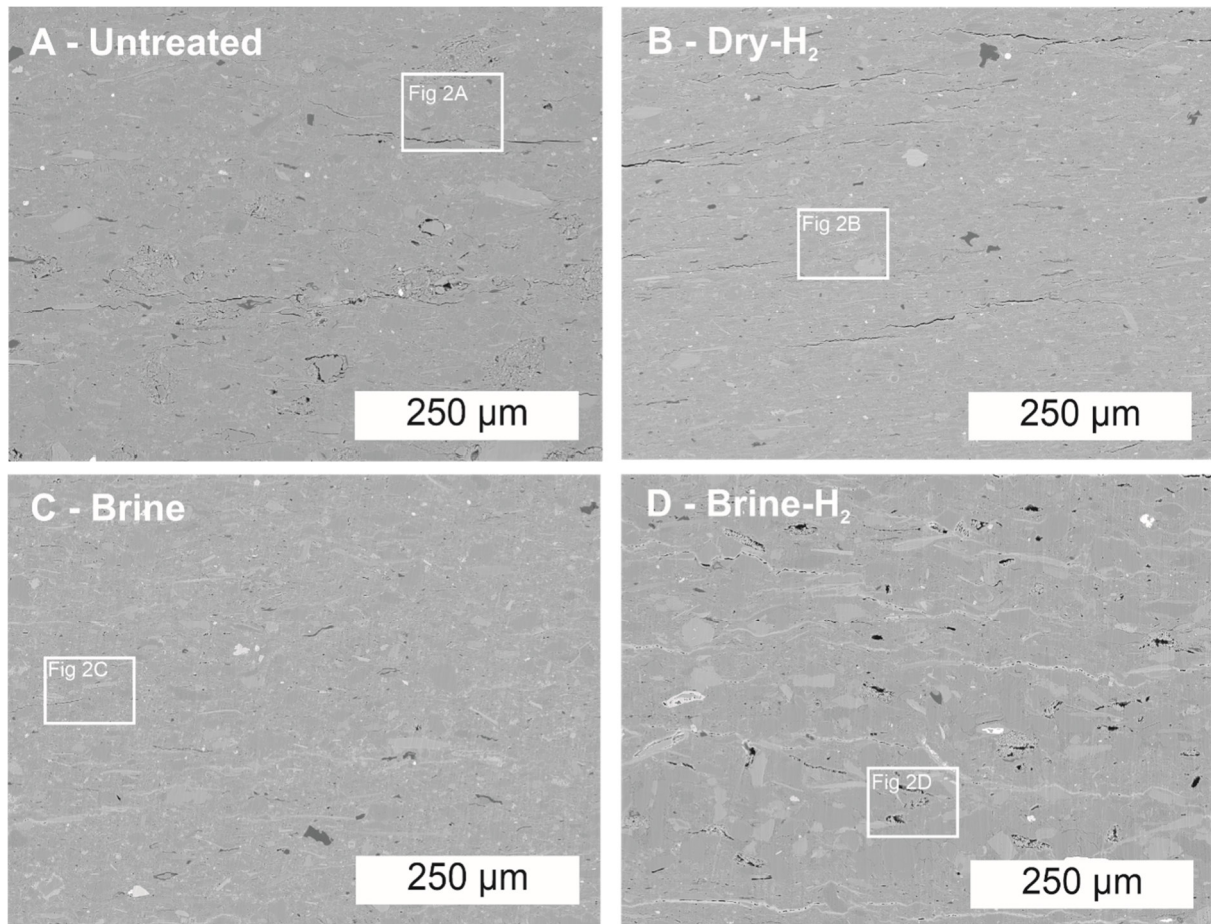


Figure 1: Large-scale BSE image mosaics of each of the four samples of this study. White boxes denote areas presented in detail in Figure 2. Porosity shown by pure black portions appears much greater in brine-H₂

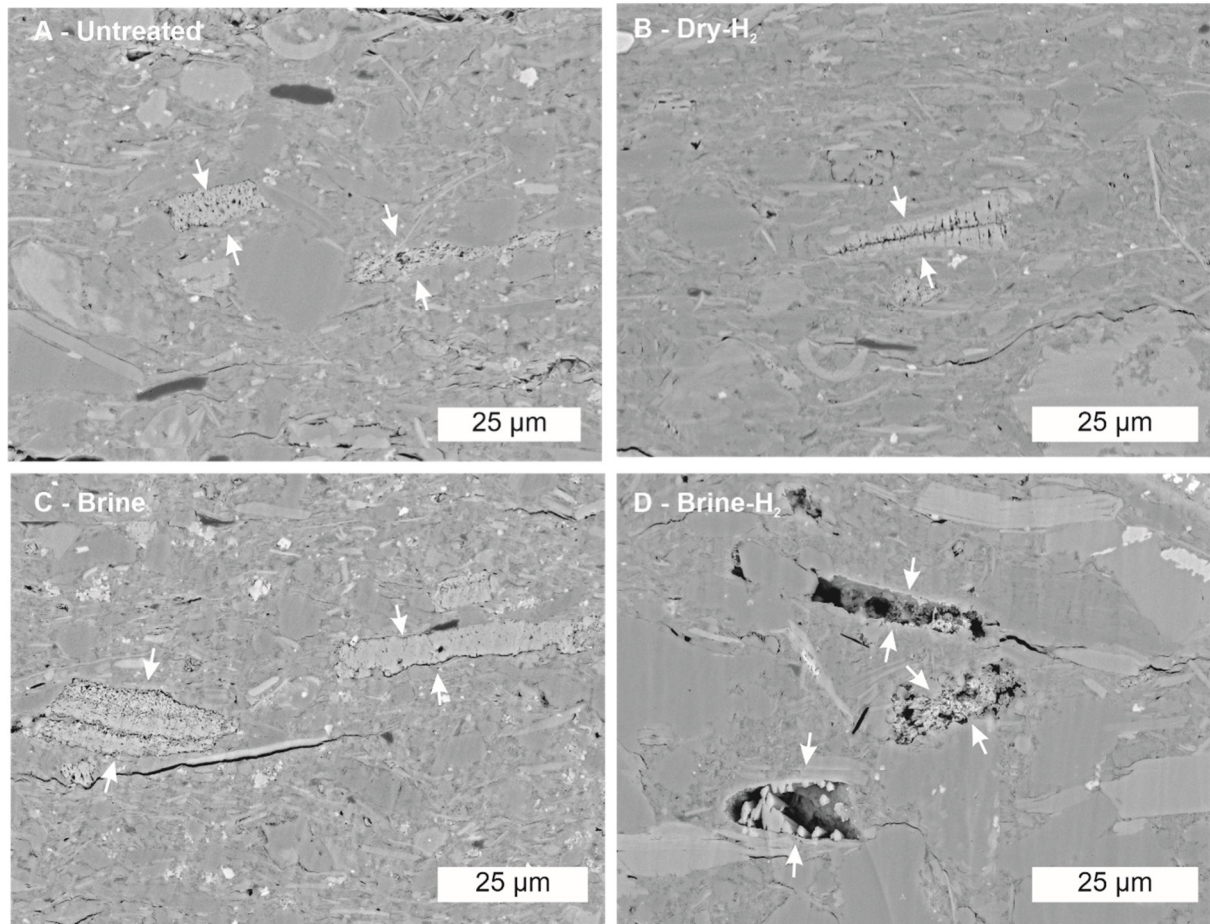


Figure 2: Detailed BSE image for each of the treated samples. The detailed areas show typical fossil fragments (white arrows). The fossil fragments were dissolved by the brine-H₂ treatment (D). Note that intragranular porosity is present in all fossil fragments.

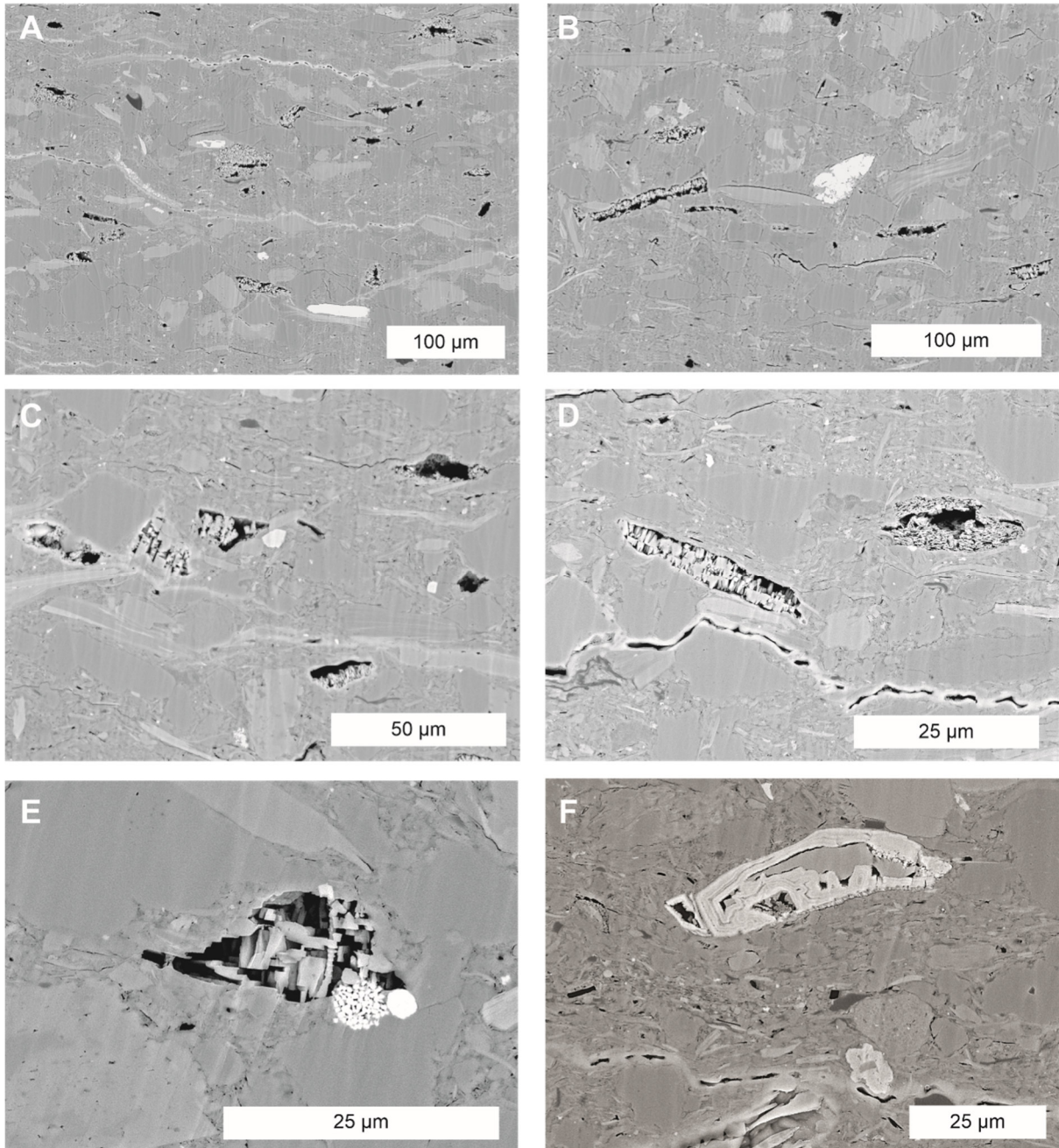


Figure 3: Multiple BSE images from the Brine-H₂ treated sample showing details of grain dissolution. Figs A and B show the general distribution of porosity due to dissolution by brine-H₂ treatment. Images C and D show details of the grain dissolution. Image E shows a dissolved grain with adjacent fine grained pyrite. Image F shows a dissolved grain that was subsequently filled with salt precipitated from the brine in post-treatment drying.