

## EFFECTS OF SUPERCRITICAL CARBON DIOXIDE ON ROCKS HAVING CARBON DIOXIDE STORAGE POTENTIAL

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One of the most important problems of our society is the rising CO<sub>2</sub> concentration of the atmosphere supposed to be a reason of the climate change. The Carbon Capture and Sequestration (CCS) may be a temporary solution for this problem. CCS is the technology when the CO<sub>2</sub> is separated from the local CO<sub>2</sub> sources, and is injected at least 800–1000 m deep where, because of the high pressure and higher than ambient temperature, it will be supercritical (scCO<sub>2</sub>). We need to study what are the geochemical changes induced by scCO<sub>2</sub> to use safely this technology. This was the main motive why we started to make experimental and analytical methods on real core samples from exploration drilling. We added scCO<sub>2</sub> to sandstone core samples in brine and very high purity calcite samples in 5 w/w% NaCl solution in 70–220 bar pressure interval and in 55–65 °C temperature interval in a high pressure resistant bomb and autoclave. After experiments the brine and solution samples were analyzed by ICP-MS and the core samples by XRF and SEM. The results indicated significant alteration in the concentration of Na, Ca, Mg, K, Fe and Sr ions concentration before and after the addition of scCO<sub>2</sub>. After adding scCO<sub>2</sub> the concentration of Ca grew in the brine and was reduced on the surface of the sandstone. The XRF results indicated a very high dispersion of the elements on the surface of the samples. The SEM images show Ca soluble-cuts and solution of the surface.

**Keywords:** Carbon-dioxide Capture and Storage; CCS; reactions in CO<sub>2</sub>; long-term CO<sub>2</sub> storage; calcite dissolution

### Introduction

Europe's efforts to cut Green House Gas (GHG) emissions, as well as the EU directives are major policy drivers in all the countries of the EU. The final solution of the increased CO<sub>2</sub> emission will be the use of the renewable energy sources. Today these technologies are not economical, thus we should use temporary solutions to avoid the continuous accumulation of CO<sub>2</sub> in the atmosphere. In Hungary Carbon Capture and Sequestration (CCS) is considered to be a viable possibility to reduce CO<sub>2</sub> emissions mostly in the energy sector. The major storage potential of Hungary is in deep saline aquifers (2000 Mt) and hydrocarbon reservoirs (400 Mt), therefore a potential site for CO<sub>2</sub> storage can be a regional saline aquifer in the northeastern part of the Great Hungarian Plain [1].

The main concept, behind the technological process, CO<sub>2</sub> is separated from the flue gas of local sources like energy power plants. The separated CO<sub>2</sub> is compressed and transported to the injection site, where it is injected

to at least in 800 m deep in to an adequate storage volume. Here the CO<sub>2</sub> becomes supercritical (scCO<sub>2</sub>), because of the elevated pressure and temperature. One part of the scCO<sub>2</sub> injected in the reservoir dissolves in the pore water and converts to H<sub>2</sub>CO<sub>3</sub>. The H<sub>2</sub>CO<sub>3</sub> dissociates, therefore lowers the pH of the brine. The acidic pH changes the geochemical equilibrium between the pore water and rocks. Finally, the result may be a change in porosity and permeability of the CO<sub>2</sub> storing lithologies. Also, it may influence the stability of the storage and cap rocks, meanwhile the efficiency and safety of the CO<sub>2</sub> storing itself.

For millennial timescale must be assured that the injected CO<sub>2</sub> can be stored in the deep reservoir without any harmful effects, or leaking back to the surface. This can only be achieved through multiscale studies involving laboratory tests, real time field experiments and use of natural analogues to inform models that can robustly predict the fate of CO<sub>2</sub> once injected into the ground [2]. In this paper we present the results obtained contacting model brine with rock samples from potential storage formations in scCO<sub>2</sub> and with pure calcite formations, and monitoring the changes in the system by scCO<sub>2</sub>.

## Materials and methods

### Geological background

Preceding studies (e.g., EU GeoCapacity 2006–2008) suggested that the Lower Pannonian stratigraphic system is the most suitable for storage because of generally better reservoir geological parameters than the Upper Pannonian unit. Moreover, the depth of the Lower Pannonian sedimentary sequences corresponds to pressures high enough to maintain the supercritical state of CO<sub>2</sub>.

The thickness of the Algyó Formation at some points of the Pannonian Basin can reach 900 m and it provides a regional cover for the Szolnok Formation (Fig. 1). It is an association of sublittoral and slope facieses of the delta, containing mainly siltstone and clay marl, but there are some bodies of sandstone (Fig. 1). From the aspect of the storage process Algyó Formation is considered to be the sealing formation.

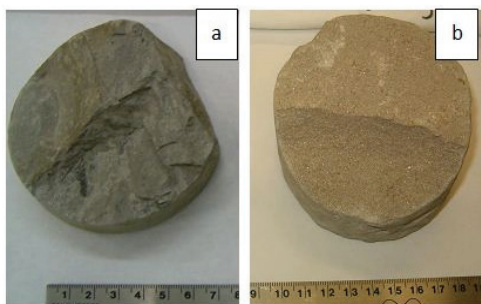


Figure 1: Macroscopic view of characteristic sedimentary rock samples from the Jászág subbasin of a drilling core:  
a) clayey Algyó Formation,  
b) sandy Szolnok Formation

The thickness of the Szolnok Formation in the study area can reach 1000 m (Fig. 2), it is composed mainly by sandstone and rarely siltstone. This formation is a thin-layered, turbiditic series, in which the layers are sharply separated from each other and sometimes contain charred plant pieces [3]. For sequestration purposes it is considered to be used for storage (Fig. 1/b).

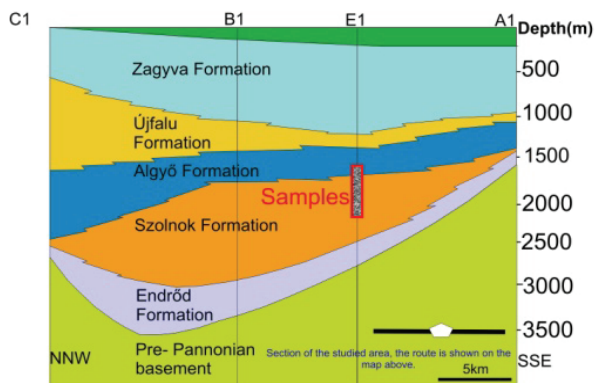


Figure 2: Theoretical cross section of the studied area showing the Jászág subbasin. The colors show the different formations deposited in sequential periods

The red rectangle shows the interval the samples were taken from the clayey Algyó Formation and the sandy Szolnok Formation. The samples from the Szolnok Formation were the target of the current study (Fig 2).

The mineral composition of the rock determined by polarization microscopy corrected by determination of pore volume by water saturation: quartz (40%), calcite (28%), feldspar (7%) and mica (5%), pores (11%), cement (9%). In analytical quantity: rutile, tourmaline, pyrite was also found. The average grain measure 30–90 μm, the porosity is 11%.

### High pressure equilibrium experiments

First the rocks were saturated under vacuum with brine (similar in composition to that observed on the field: 5% NaCl eq.). Autoclave experiments were run to react carbon dioxide with sandstone samples from Szolnok Formation immersed in brine. The experimental time varied within 5–37 days, the temperature was set between 55–65 °C and the pressure range studied was 70–220 bar. Two pieces of core samples were placed in a glass boat and model brine was added. Two boats were placed into the autoclave tube and after setting the temperature it was pressurized with CO<sub>2</sub> (99.7% purity) by an ISCO 260 D syringe pump. The glass boats are necessary to avoid chloride corrosion of the stainless steel autoclave. Before the slow depressurization the autoclave was cooled to room temperature. Liquid samples were taken directly from the residue in the boat, whereas the stone samples were immersed in distilled water prior to surface analysis.

### High pressure kinetic experiments

A set of experiments with pure calcite samples was run by sampling the liquid phase of the solid – liquid – fluid heterogeneous reaction system. The designed reactor setup allows us to take sample from the bottom of the reactor at constant pressure and temperature (Fig. 3).

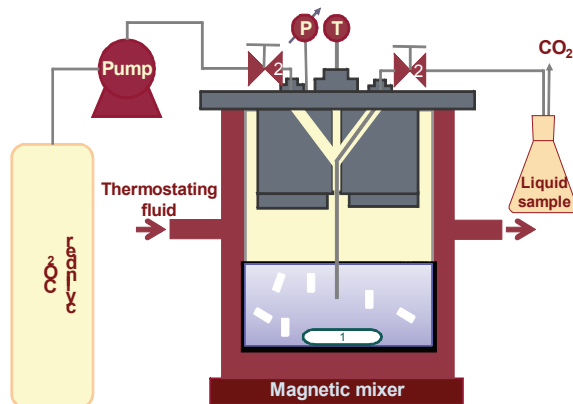


Figure 3: High pressure reactor setup for isobar and isotherm sampling of the liquid phase.

1: stir bar, 2: valves,  
P: pressure transducer, T: thermocouple

The constant pressure was maintained by CO<sub>2</sub>. In the kinetic experiments calcite samples of 0.2–0.3 mm diameter size were mixed in 5 w/w% NaCl solution as model brine.

### Analytical methods

The surface analysis of the core samples were made by scanning electron microscopy (SEM) and X-ray fluorescence (XRF). The average surface concentration of the following elements was possible to be detected by XRF: Br, Ca, Cl, Co, Cr, Cu, F, Fe, K, Mn, Mo, Nb, Ni, P, Rb, S, Si, Sr, Te, Ti, V, Y, Zn, Zr.

The concentration of Ba, Ca, Co, Fe, K, Mg, Mn, Na, Ni, Sr, Zn in the liquid samples were analyzed by inductively coupled plasma – mass spectroscopy (ICP-MS), and flame emission analysis.

### Results and discussion

The sandstone samples showed significant changes even at short contact time (several days). Result of surface analytics (SEM, XRF) and analysis of liquid samples are in good agreement.

Concentrations of Ca and Mg in the liquid samples increase with reaction time. Quantification of minor elements suggests also dissolution from the pores (Fig. 4, where the A and B samples are parallel experiments; note that the diagram is in logarithmic scale).

Large standard deviation was observed by XRF measurements on sandstone samples. SEM images confirmed that there is a significant increase of the specific surface for the XRF during the scCO<sub>2</sub> reaction. It is noticeable in Fig. 5, where the dissolution of the calcite created deep lanes in the originally smooth surface.

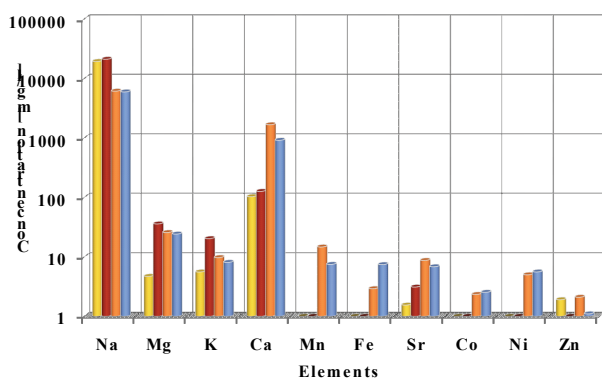


Figure 4: Minor cations of the liquid samples.

The 1<sup>st</sup> columns show the composition of the model pore fluid, the 2<sup>nd</sup> columns the concentration values of pore fluid which is in equilibrium with the core samples in atmospheric pressure. The 3<sup>rd</sup> and 4<sup>th</sup> columns show the composition of the pore fluid after reacting the sample with CO<sub>2</sub> (A and B indicate parallel samples): 163 bar, 55 °C, 14 days

To analyze the time scale of the dissolution of calcite in order to reach a new equilibrium, pure calcite samples of controlled particle size were immersed in brine and reacted with CO<sub>2</sub>. The surface of the calcite grains showed again erosion like picture (Fig. 6). The erosion phenomenon was dependent on the reaction time of the scCO<sub>2</sub> exposure (Fig. 6 and Fig. 7). The most reactive minerals are the calcite and feldspar. There is no visible change on the surface of the quartz as expected (Fig. 5).

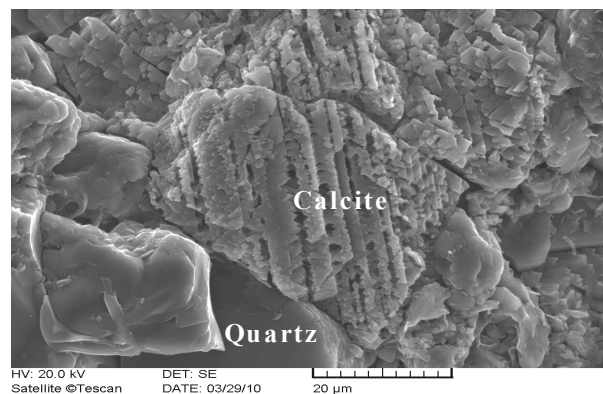


Figure 5: “Erosion lanes” on the surface of calcite observed after 14 days long reaction with scCO<sub>2</sub>

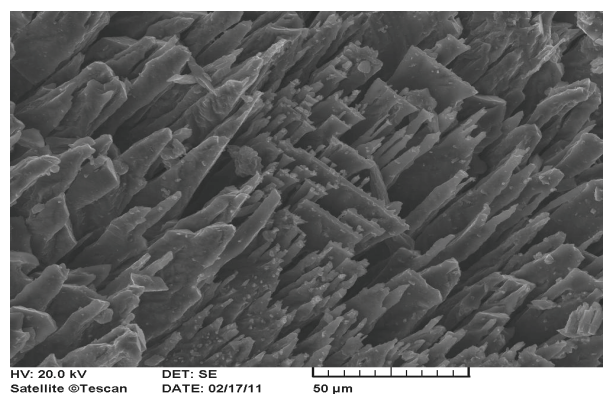


Figure 6: Calcite erosion by the scCO<sub>2</sub> contacting (contacting time: 4 days)

On Figs. 6 and 7 we can also observe that the evolving calcite peaks show a trend in either way.

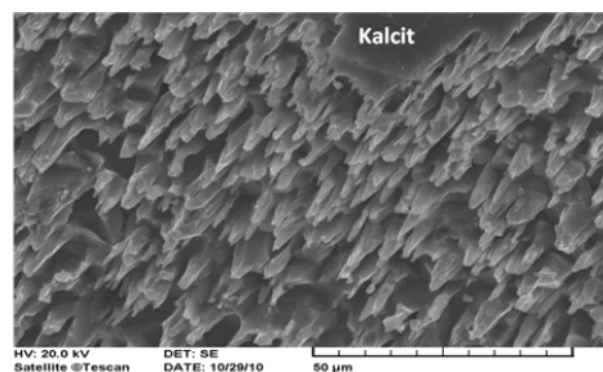


Figure 7: Strong calcite erosion at longer reaction time (15 days)

The surface of the sample remained intact (unchanged) if it was only contacted with the CO<sub>2</sub> phase without brine being present (this case is relevant for rock close to the injection site). On Fig. 8 there is a drop of solution on the surface of the calcite sample. One may notice the calcite erosion and solubility within the borders of the brine drop, but there is no dissolution visible outside.

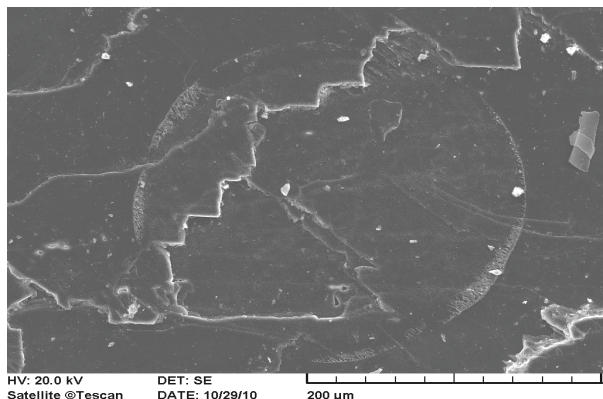


Figure 8: A former NaCl-water solution drop on the calcite surface

Time-dependent liquid phase Ca concentration is shown in Fig. 9. The samples were taken from one batch and analyzed by ICP-MS. The heterogeneous system, even with mixing to reduce the mass transfer limitations (250 rpm), did not reach the equilibrium in 4 days. Ca concentrations in the liquid phase increased with more than 3 orders of magnitude during the experiment, high above the atmospheric saturation concentrations.

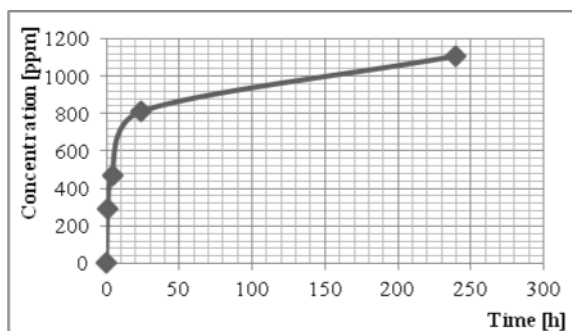


Figure 9: Calcite dissolution curve at 89 °C, 150 bar.

## Conclusions

Hungary has significant regional saline aquifers, mainly those that were formed in the Middle to Late Miocene. Among these the most adequate for CO<sub>2</sub> storage purposes is the Szolnok Formation as the main limit for the safe and economical storage is the adequate reservoir rock. It is highly important to understand the geochemical reactions (e.g., dissolution, alteration, crystallization) occurring in the minerals composing the potential future reservoir rock. Our results show that there are significant changes already in short experimental times (i.e., few days or weeks). These changes may affect the long term safe storage potential even by increasing safety or by rising concerns. Among the major constituents of the studied sandstone samples the most reactive mineral is calcite but feldspar is also slightly affected. Short experiments offer preliminary results however, this field needs further research to achieve the required accuracy of experimental results for reliable modeling of the time scale of geological times.

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