

Introduction

Since the first international agreement in 1997 (the Kyoto Protocol) the reduction of greenhouse gas emission has a key role in the European Union's energy and climate change policy. Following the Directive 2009/31/EC we are experiencing a significant change in the Hungarian national activity. Since the harmonization procedure which was completed in May 2012, the national regulation obligates the competent authority to collect and regularly update all geological complexes that are potential for CO₂ geological storage.

In Hungary the most abundant potential storage formations are mostly saline aquifers of the Great Hungarian Plain (SE-Hungary), with sandstone reservoir and clayey caprock (Falus et al., 2011). Present work is focused on the mineralogy of the most potential storage rock and its caprock and their expectable geochemical reactions for the effect of scCO₂. It provides an indispensable knowledge for the possible future planning processes of geological storage of CO₂ in Hungary.

Geological background

The Neogene basin of the Great Hungarian Plain was subsided and then filled by a prograding delta system from NW and NE during the Late Miocene, mostly in the Pannonian. The most potential storage rock was formed as a fine-grained sandy turbidite interlayered by thin argillaceous beds in the deepest part of the basin. It has relatively high porosity, depth and more than 1000 m thickness. Providing a regional coverage for the sandy turbidite, a 400-500 m thick argillaceous succession was formed in the slope environment. The composition, thickness and low permeability is expected to make it a suitable, leakage-safe caprock of the storage system. This succession is underlain by argillaceous rocks that were formed in the basin, far from sediment input and overlain by interfingering siltstone, sandstone and claystone succession formed in delta and shoreline environments and in the alluvial plain (Juhász, 1992).

Samples and methods

We have investigated reservoir and caprock samples from different well bores at the Great Hungarian Plain. All samples originate from depths between 1250 and 2230 m.

Storage rock

From the potential reservoir rocks samples (sandstone) thin sections were made to determine the mineral composition, pore distribution and grain size of the samples. The volume ratio of the minerals was calculated using pixel counter. To have more accurate mineral composition XRD measurements were performed and SEM-BSE images were acquired.

To get a picture about the geochemical behavior of the potential CO₂ storage system, geochemical models were made for the reservoir rocks. For the equilibrium geochemical model, PHREEQC 3.0 was used applying LLNL database. The data used in the model are real pore water compositions from the studied area and an average mineral composition based on polarization microscope and SEM images. In the model we considered the cation-anion ratio (<10%) and the CO₂ partial pressure. First of all, we were interested in the direction of the geochemical reactions during an injection process.

Caprock

The caprock samples involved in the study can be divided to mudstone and shale samples. To determine the original mineral composition of these samples, XRD analysis has been carried out. The rock samples have been micronized to increase their specific surface area (SSA) for batch reactions. The SSA value is then estimated based on laser grain size analysis results. We perform the batch reactions in simplified artificial pore water of 250 mmol/L NaCl and apply a 10:1 brine:rock ratio. The scCO₂ treatments are going on at 130 bar pressure close to the original conditions. The temperature was selected to be higher than the original temperature, i.e. 180 °C to increase the speed of reactions and to reach the given pressure. A small part of the samples are treated in H₂O saturated CO₂.

Preliminary results

Storage rock

Two type of carbonate were present in the sandstone samples, one is monocrystalline, while the other has granular texture. With SEM-EDX they were separated into calcite, dolomite and minor amount of ankerite, which was usually a rim around the dolomite grains. The quartz crystals were generally metamorphosed, moreover plagioclase and K-feldspar were also well distinguishable. Minor amount of kaolinite and limonite occurred too. Mica, biotite and muscovite were also present. Most of the biotite was altered to limonite, chlorite or opaque minerals, which were important for the subsequent modeling progresses because of their different geochemical behavior. In most of the cases organic matter was also found.

The preliminary results of the model using an average mineral composition (**Figure 1**) of the reservoir rock and known water composition from the studied area, shows slight dissolution of plagioclase, K-feldspar, ankerite and strong dissolution of calcite. Furthermore intense dolomite, kaolinite and minor quartz precipitation is predicted.

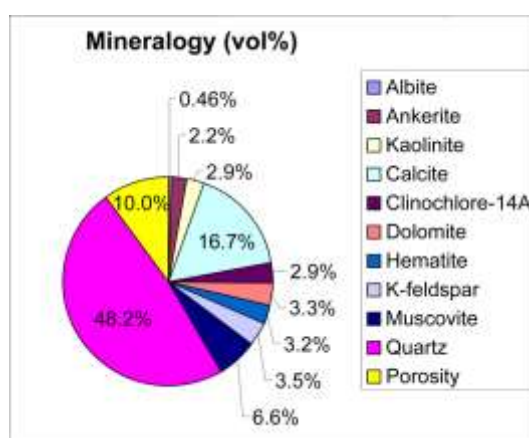


Figure 1 Average mineral composition of the reservoir rock based on optical microscopy and SEM-EDX measurements.

Caprock

We hold a semi-quantitative mineral composition of mudstone samples. The XRD results show the most significant presence of quartz and muscovite (20-30%) in these samples. The amount of clinocllore significantly varies from sample to sample with an average contribution of 15%. Beside these, we found minor amounts (<10%) of albite, kaolinite, microcline, illite, dolomite and calcite.

The micronized samples have about a $0.5 \text{ m}^2 \text{ g}^{-1}$ SSA at the beginning of the batch reactions which indicates a detectable change in the solution composition even in the duration of our experiments. The batch reactions resulting brine and rock samples are under analysis together with undergoing modeling work. However, we experienced the increase of Na-, K- and Mg-ion concentration and the decrease of Ca-ion concentration in the solution for the effect of scCO_2 (in a comparison with non- scCO_2 treatments). The results do not show a significant effect of scCO_2 on the silicate content of the brine.

Summary and further work

In this work we present the most recent knowledge about the potential CO_2 storage formation and its caprock in Hungary for further considerations. Our results do not reject the possibility of a future application of CCS technology within the country. However, they sign out the most important ways to follow in ensuring a safe, long-term leakage safe storage of CO_2 ; namely, the intense study of storage rock and caprock behavior for the effect of a possible injection.

Acknowledgements

We are grateful to Zsolt Bendő, Márton Berta, Ábel Szabó, Maarten Aerts, Beyene Girma Haile, Mufak Naoroz and Rohaldin Miri for their important help in the preparation and analysis of the samples and also to all members of the Lithosphere Fluid Research Lab (LRG, <http://lrg.elte.hu>) for all the help we received during this work. Zs. Szabó is highly thankful for the financial background provided by the Campus Hungary Program, Balassi Institute (TÁMOP 4.2.4.B/1-11/1-2012-0001), the professional support of Szabina Török and Per Aagaard and the help of Gudmund Anders Dalsbø.

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