EÖTVÖS LORÁND UNIVERSITY
FACULTY OF SCIENCE

Geochemical investigation of geological formations from the perspective of hydrogen storage potential

by

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Theses of the Ph.D. dissertation

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DOI: 10.15476/ELTE.2024.342

Budapest

1. Introduction and aims

Transformation of the global energy sector from fossil-based to renewable energy sources is generally called the energy transition, a process that is shaping the beginning of the 21th century. In contrast with conventional hydrocarbon-based energy production, the major renewable energy production is intermittent since its vast majority comes from solar and wind sources (Simon *et al.* 2015). Within this context, the European Union, including Hungary, faces a fundamental moment in reshaping its energy system to drive the transition toward a sustainable and circular economy. Power-to-gas technology, which converts surplus electrical energy into gas storage, is one of the available methods aimed to balance the gap between production and consumption (Lehner *et al.* 2014). Hydrogen could play a central role in future energy systems since it can be used as a storage material of excess renewable energy via the conversion of electric energy to hydrogen gas.

The role of geologic formations (depleted gas reservoirs, rock salt formations and saline aquifers) in the energy transition is unequivocal, since they are the storage objects for both methane and hydrogen (Carden and Paterson 1979; Ozarslan 2012; Tarkowski 2017). Taking a closer view at our region, the Hungarian part of the Pannonian basin system is filled with thick (3-6 km) Neogene sediments, and its stratigraphic features indicate potential in subsurface gas storage (Király *et al.* 2010). Beside siliciclastic sedimentary rocks, Transylvanian basin, the easternmost subbasin of the Pannonian basin, is characterized by significant rock salt occurrences, and it is the nearest remarkable evaporite formation to Hungary.

The understanding of geochemical interactions between hydrogen, pore water, and the rock forming minerals during underground hydrogen storage is a huge priority of applied geochemistry (Flesch *et al.* 2018; Yekta *et al.* 2018). The main objective of this study is to identify possible abiotic reactions in the rock–porewater–hydrogen system with the detailed investigation of mineral–hydrogen interaction and their extent in aqueous environment. The thesis covers the complex experimental and modeling study of three common rock-forming minerals, namely calcite, K-feldspar and pyrite (Figure 1). In addition, a key goal was to build an experimental lab dedicated to geochemical research for underground hydrogen storage in the frame of PhD research.

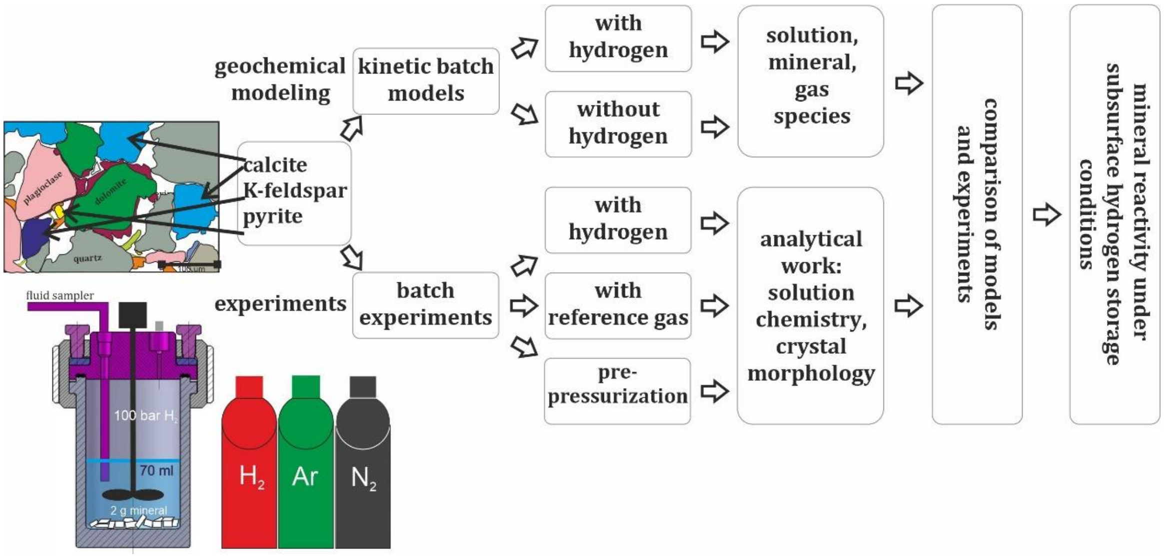

Figure 1. Overview of the doctoral study. Rock-forming minerals were examined with two different approaches. Laboratory experiments combined with geochemical modeling were used to understand mineral reactivity under high pressure H_2 and reservoir temperature. Several analytical techniques were applied to detect changes in solid and liquid phases.

2. Study area and samples

The study area is located near Öcsöd village between the Kunság basin and Öcsöd–Martfű structural height, a recently subsiding sub-basin of the Great Hungarian Plain (Hungary). Samples originate from two wells namely from Öcsöd-1 and OGD-Öcsöd-K-2 wells and they were collected with the support of the company O&GD Central Ltd. The reservoir has an extension of ~1300 m in SW-NE and ~600 m in NW-SE direction, respectively. The reservoir is located between depths of 2104 - 2120 m (measured depth). Core samples from Öcsöd-1 and drill cutting samples from 3 intervals from OGD-Öcsöd-K-2 were selected for further detailed analyses.

Natural mineral phases were used for static batch experiments. Calcite (Iceland spar) (BE24569, BE40764, BE40763), K-feldspar (BE40767) and pyrite (BE40766) were provided by the Mineralogical Collection of Natural History Museum, Eötvös Loránd University (ELTE). Prior to experimental work, the homogeneity and chemical composition of the natural samples were analyzed by various methods (e.g., XRD, SEM). The single crystals were crushed and powdered to the size (100 and 200 µm) of reservoir rock-forming minerals.

3. Methods

Petrographic features of samples were observed with two methods: optical microscopy in the Lithosphere Fluid Research Lab, Faculty of Science, ELTE and Hitachi TM4000Plus electron microscope available at Research and Instrument Core Facility, Faculty of Science, ELTE.

Major and minor element analyses of the rock-forming minerals (feldspars and carbonates) from cuttings of OGD-Öcsöd-K-2 were conducted using a JEOL JXA-8230 SuperProbe at the Institute of Earth Sciences, University of Iceland.

Chemical composition analyses on solutions were carried out with inductively coupled plasma-optical emission spectrometer (ICP-OES), HORIBA Jobin Yvon® ULTIMA 2C instrument, at an accredited laboratory of Supervisory Authority of Regulatory Affairs Hungary.

X-ray photoelectron spectroscopy (XPS) analysis was carried out at the Research Institute for Technical Physics and Materials Science, HUN-REN Centre for Energy Research, Hungarian Research Network using an Escalab Xi+ (Thermo Fisher). Compositional changes on the surface of pyrite grains due to exposition to hydrogen under reservoir conditions, was studied.

Static batch experiments were carried out with the three selected mineral phases which are common constituents of reservoir rocks. The experimental setup followed similar procedure with each mineral. In a typical experiment, 2 g mineral and 70 mL of distilled water were placed into the reactor. The reaction mixture was then heated up to 105 °C and the total system pressure was set up to 100 bar. Stirring was continuous by a four-bladed turbine stirrer with an RPM of 345 min^{-1}. At given reaction times (3, 24, 76 hours), ca. 2 mL of liquid samples were taken via dip tube into the sample holders for off-line analysis to detect the changes of ion concentration in the solutions. The experiments were repeated with reference gases (nitrogen or argon).

Geochemical modeling was carried out using the PHREEQC ver. 3 geochemical software (Parkhurst and Appelo 2013). I used kinetic modeling to understand reaction kinetics and their results are comparable with short-term laboratory experiments. I also used equilibrium modeling to assume the long-term effect of gas injection (e.g., H_2, CO_2) into porous media (Hassannayebi *et al.* 2019).

4. Scientific outcomes (theses) of the doctoral study

1. I defined an experimental process suitable for studying the effect of hydrogen on minerals under subsurface storage conditions. I also built kinetic models, which results are comparable with those of experiments. This combination of geochemical modeling and experimental work is a more effective way to predict hydrogen behavior than using only geochemical modeling. I stated that modifications of geochemical model databases backed by experimental results are recommended to better constrain the abiotic carbonate-hydrogen reactions in the models, since underground hydrogen storage should generally not assume significant interactions with carbonates (Gelencsér *et al.* 2023).

2. Through experimental work with calcite, I confirmed that highly limited extent of calcite dissolution is expected under high pressure (100 bar) hydrogen at 105 °C. This results contrast with previous studies, which, solely based on geochemical modeling, predicted significant hydrogen loss and mineral dissolution induced by the reaction of carbonate minerals with hydrogen. My results suggest that carbonate-bearing geological formation should not be excluded from consideration for underground hydrogen storage (Gelencsér *et al.* 2023).

3. I conducted a series of experiments and kinetic modeling with K-feldspar mineral representative of real rock-forming constituents to study the significance of K-feldspar in the reservoir rocks in underground hydrogen storage. The experimental work of this PhD revealed limited effect of hydrogen on K-feldspar compared to reference experiments with nitrogen. However, this effect manifested in an increased release of potassium and the formation of aluminum-bearing phase, compared to reference experiments. Based on the changes in the chemical composition of the solution, this process can be explained by an enhanced exchange reaction between hydrogen and alkali ions at the mineral surface. Subsequently, the Al–O bonds and Si–O bonds are also breaking down, which is followed by the formation of Si-rich precursor complex. In the context of a polymineralic subsurface reservoir environment, the results of this PhD may suggest that hydrogen injection can slightly enhance K-feldspar dissolution, hence supplying ions for secondary mineral precipitations (Gelencsér *et al.* 2024c).

4. To better understand the pyrite reactivity under hydrogen storage conditions, I designed a more complex experimental setup, building on the experience I gained from studying the other two minerals (i.e., calcite, K-feldspar). In particular, a mixture of calcite and pyrite (with 1 to 10 wt.% pyrite) was reacted with hydrogen, representing a typical range of pyrite content in sedimentary rocks. Beyond the well-established procedures of optical microscopy and scanning electron microscopy, I successfully utilized X-ray photoelectron spectroscopy (XPS) to study chemical changes on pyrite induced by hydrogen. The XPS measurements on pyrite surface revealed that pyrrhotite forms on the surface of the pyrite due to the hydrogen treatment. In the reference experiments, pyrrhotite formation was not observed. With angle-resolved XPS measurements I determined the thickness of the pyrrhotite growth on pyrite surface. Calculations give an average of 2 nm, with an error margin of +/−1 nm. This result implies that about 0.02 wt.% pyrrhotite precipitation is expected in system with 5 wt.% pyrite content on a 50 µm-size pyrite grain due to 76-hour H_2 exposure Kinetic geochemical modeling was in complete agreement with my experimental results. Regarding the associated production of hydrogen sulfide, geochemical modeling results indicate that it remains in the solution rather than going to the gas phase under reservoir conditions (105 °C, 100 bar) (Gelencsér *et al.* under rev.2).

5. Hydrogen injection simulation with reservoir parameters of Öcsöd hydrocarbon field indicates subordinate effect of hydrogen on mineral dissolution and precipitation in the reservoir (Gelencsér *et al.* 2024a). Considering the high availability of the studied reservoir rock type, the geological characteristics of the Pannonian basin system are favorable for underground hydrogen storage due to the large volume of porous rocks including several depleted gas fields (Gelencsér *et al.* under rev.1). However, further detailed experimental control is necessary for geochemical modeling. Additionally, the Transylvanian basin has hydrogen storage potential in evaporites as well, which are geochemically neutral with hydrogen. However, the structural stability of salt occurrences in the region could be a geological risk, which needs further analysis (Gelencsér *et al.* 2024b).

5. Conclusions

The geological formations, subjected to hydrogen storage, in the Pannonian basin system was studied geochemically and petrologically. The major goal of my PhD research was to investigate possible abiotic reactions between rock forming minerals and hydrogen under subsurface storage conditions. Combined experimental and geochemical modeling research was carried out on three minerals of the reservoir rock. Additionally, the rock salt of the Transylvanian basin was also taken into the scope of this research.

Based on the results of the rock–water–gas interaction studies, high pressure hydrogen

- has no effect on the dissolution of calcite,
- can promote the dissolution of K-feldspar,
- can enhance the reductive dissolution of pyrite, which lead to the formation of pyrrhotite and hydrogen sulfide.

Geochemical modeling cannot substitute experimental work in understanding the geochemical reactions induced by hydrogen. Furthermore, the deformation rate of the Transylvanian (Praid) rock salt may be acceptable for cavern storage, however this issue requires further studies. To summarize the results, the Pannonian basin system with its geological resources displays positive potential to the challenges of energy transition.

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7. Publications related to doctoral study

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