



Short communication

Effect of hydrogen on calcite reactivity in sandstone reservoirs: Experimental results compared to geochemical modeling predictions

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ABSTRACT

Geologic reservoirs including calcite bearing sandstones are among the highest potential structures that can serve as sites for underground hydrogen storage (UHS). However, to confirm the viability of sandstone reservoirs, better knowledge about rock–porewater–hydrogen gas (H_2) systems is needed. Previous geochemical modeling studies predicted significant H_2 loss induced by the reaction of carbonate minerals with H_2 . Our recent combined experimental-modeling study investigated the geochemical impact of H_2 on calcite ($CaCO_3$), a characteristic rock forming mineral in potential hydrogen storage reservoirs. Static batch reactor experiments were conducted in the pressure and temperature range (100 bar, 105 °C) of UHS to track the effect of H_2 on calcite. The experiments demonstrated the non-reactive behavior of calcite as there were no signs (chemical and morphological) of increased calcite dissolution in H_2 atmosphere compared to results with inert gas (N_2). On the contrary, the kinetic PHREEQC model, using a non-modified thermodynamic database, predicts intensive reactions between calcite and H_2 , resulting in extensive calcite dissolution and methane formation. Our conclusion, therefore, is that the thermodynamic databases of geochemical modeling must be reviewed for UHS and modified for such projects to provide reliable results. This study gives practical insight into the potential path forward to correct this problem.

1. Introduction

The shift from fossil fuel-based systems of energy production and consumption to renewable energy sources has made hydrogen (H_2) an attractive energy carrier as it is capable of balancing weather dependent energy production. This requires the development of various H_2 flexible storage technologies that could offer advantages for the required applications (e.g., industry, transport, and power generation). One of the potential storage solutions is Underground Hydrogen Storage (UHS), which provides a promising method to store large amount (TWh range) of energy in various geological formations such as salt caverns, deep aquifers and depleted oil and gas reservoirs [1–3]. Compared to surface

gas storage possibilities, it is better protected by the overlying geological strata and provides greater storage pressure (so higher energy density), a smaller surface footprint, and lower specific investment costs than surface storage [2,4].

The most cost-effective UHS option is to store H_2 in depleted natural gas reservoirs since detailed geological data of the sites are available, as well as having the surface and underground infrastructure already built [3,5,6]. Additionally, repurposing depleted gas/oil reservoirs for the UHS produced from wind and solar farms has the potential to be a sustainable energy source [7] decoupled from the daily weather variations. Nevertheless, most of these reservoirs, have varied mineral, gas and fluid compositions and their interaction with H_2 may result in alteration of reservoir and caprock permeability or integrity over time

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Abbreviations

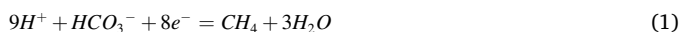
Cc	calcite
ELTE	Eötvös Loránd University
Eq.	equation
H ₂	hydrogen (in gaseous form)
ICP-OES	inductively coupled plasma – optical emission spectroscopy
ID	identification number
LRG	Lithosphere Fluid Research Lab
N ₂	nitrogen (in gaseous form)
RPM	revolution per minute
SEM-EDX	scanning electron microscopy equipped with energy dispersive X-ray spectroscopy
UHS	underground hydrogen storage

[7]. Consequently, before H₂ can be injected into the subsurface the study of key geochemical processes is fundamental, especially those which may lead to H₂ loss [8,9]. Geochemical modeling [10–12], experimental [13–17], and wettability studies [18–21] on various rock types has been published in the last decade, however the knowledge about rock–porewater–H₂ interactions is still poorly developed [6].

In the Pannonian Basin of Central Europe, sandstone reservoirs often contain significant calcite (CaCO₃). It is found in this sedimentary rock both as grains and as cement. The Szolnok Sandstone Formation is proposed as a UHS reservoir with the highest storage capacity as it is a common natural gas reservoir in the region [22], however the effect of H₂ on the reservoir rock and its caprock is virtually not investigated.

Calcite is one of the main sources of the carbonate anion (CO₃^{2−}) in aqueous environments, which due to its buffering effect, usually governs the groundwater geochemistry [23]. The reactivity of calcite in H₂ underground storage will be a critical issue because, in addition to the potential loss of H₂, mobilization of its ions and their subsequent precipitation could potentially cause pore clogging, thus reducing reservoir injectivity and productivity.

However, comprehensive knowledge about the effect of H₂ injection and storage on carbonate minerals contained in reservoir rocks, more specifically calcite, has still not been acquired. Several geochemical modeling studies connected to UHS were published [10–12,15,24,25], some of them consider the calcite as a reactive mineral in H₂ environments [10,11]. In these models, the pH of the pore water decreases as the dissociation of H₂ occurs, followed by the CO₃^{2−} ions (either already dissolved in water or originating from the dissolution of calcite) reacting with these H⁺ ions in the solution and forming methane (CH₄) and carbon dioxide (CO₂). The CH₄ formation was proposed according to Eq. (1) and its combination with Eq. (2) [10,11].



These or similar reactions are common parts of the thermodynamic databases used in geochemical modeling [26,27]. These databases contain thermodynamic properties at standard state conditions (e.g. infinite dilution) and at reference temperature and pressure in a code-specific format [28].

In contrast, other geochemical models were constructed with decoupled CH₄–HCO₃[−] redox pairs, inhibiting methane formation. This approaches realistic conditions, however no background or detailed explanation has been presented [12,24]. Additionally, the “inert” behavior of H₂ was previously reported in experimental studies, concluding that H₂ would not enhance any chemical reaction at storage pressure (100 bar) and temperature (up to 200 °C) [14,15]. However, Flesch et al. (2018) raised concerns about the reactivity of H₂ with

Permian sandstone as dissolution with an alteration of carbonate cement was observed [16].

Herein, we report a detailed, comprehensive experimental and modeling study of calcite with the goal to determine if its presence in the rock can cause the model-predicted H₂ loss at typical UHS conditions. The calcite reactivity in an H₂ atmosphere under UHS pressure and temperature was studied. Geochemical models and experiments are shown and compared in this study (Fig. 1). The experiments introduced in this paper demonstrated a weakness of the current geochemical modeling related to the carbonate–H₂ reactions. With currently accepted geochemical modeling, the calcite dissolution induced by H₂ injection can be overestimated. The results of this combined study could provide geochemical level information for further, more complex, and more representative modeling studies.

2. Materials and methods

2.1. Materials and sample preparation

The calcite–water–gas (H₂ and N₂) experiments were carried out using natural pure calcite (Iceland spar) as a model substrate. The homogenous calcite was provided by the Mineralogical Collection of Natural History Museum, Eötvös Loránd University (ID: BE24569) because of its chemical (proved by chemical analysis) and structural purity (proved by the lack of fluid and solid inclusions). The calcite was crushed by hammer and powdered in agate mortar and the calcite grains for the experiments were selected with a particle size between 100 and 200 μm by the use of wet sieving. Gas of H₂ (purity ≥ 99.95 %) and N₂ (purity ≥ 99.996 %) were provided by Linde®.

Thin sections of the original and treated calcite grains were prepared for physical (optical) and chemical analyses. Both the thin section and the handpicked grains, placed on carbon tape, were coated with carbon for scanning electron microscopy analyses.

The liquid samples of experiments were filtered through a 0.2 μm syringe filter and mixed with ca. 5 mL of 1 wt% HNO₃ solution. The sealed samples were stored in scintillation vials for later analysis.

2.2. Experimental setup

The calcite–H₂O–H₂ batch experiments were performed in a 160 mL Hastelloy Steel High-pressure Parr® reactor at the Department of Chemical and Environmental Process Engineering, University of Technology and Economics, Budapest. In a typical experiment 2 g calcite and 70 mL of distilled water with a ratio of 1:35 were placed into the reactor followed by its pressurization up to 80 bar for both the N₂ and H₂ containing experiments (Fig. 2). The reaction mixture was then heated up to 105 °C and the total system pressure was set up to 100 bar at an RPM of 345 min^{−1}. At given reaction times (3, 24, 78 h), ca. 2 mL of liquid samples were taken via a deep-leg into the sample holders for off-line analysis to detect the changes of Ca²⁺ concentration in the solutions. The liquid sample amount was small, so as not to affect the original mineral–water ratio, but sufficient for concentration measurements.

2.3. Analytical techniques

2.3.1. Optical microscopy

Optical microscopy was applied on the prepared thin sections to observe differences between H₂-treated and untreated calcite grains. For this purpose, stereo (Nikon® SMZ 800) and polarized microscopes (Nikon® Eclipse E600POL) were used in the Lithosphere Fluid Research Lab (LRG), Eötvös Loránd University (ELTE), Budapest.

2.3.2. SEM-EDX

To obtain the major element composition of the calcite and to observe the shape of grains before and after experiments, a Hitachi TM4000Plus with Oxford AZtec One 30 mm² SDD EDS was used at the

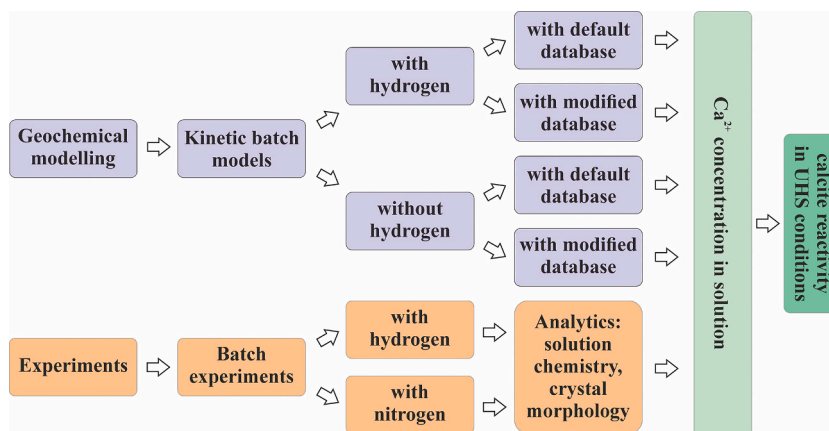


Fig. 1. Flowchart of the geochemical modeling and experimental work. The steps of geochemical modeling and experiments are shown with purple and orange colors, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

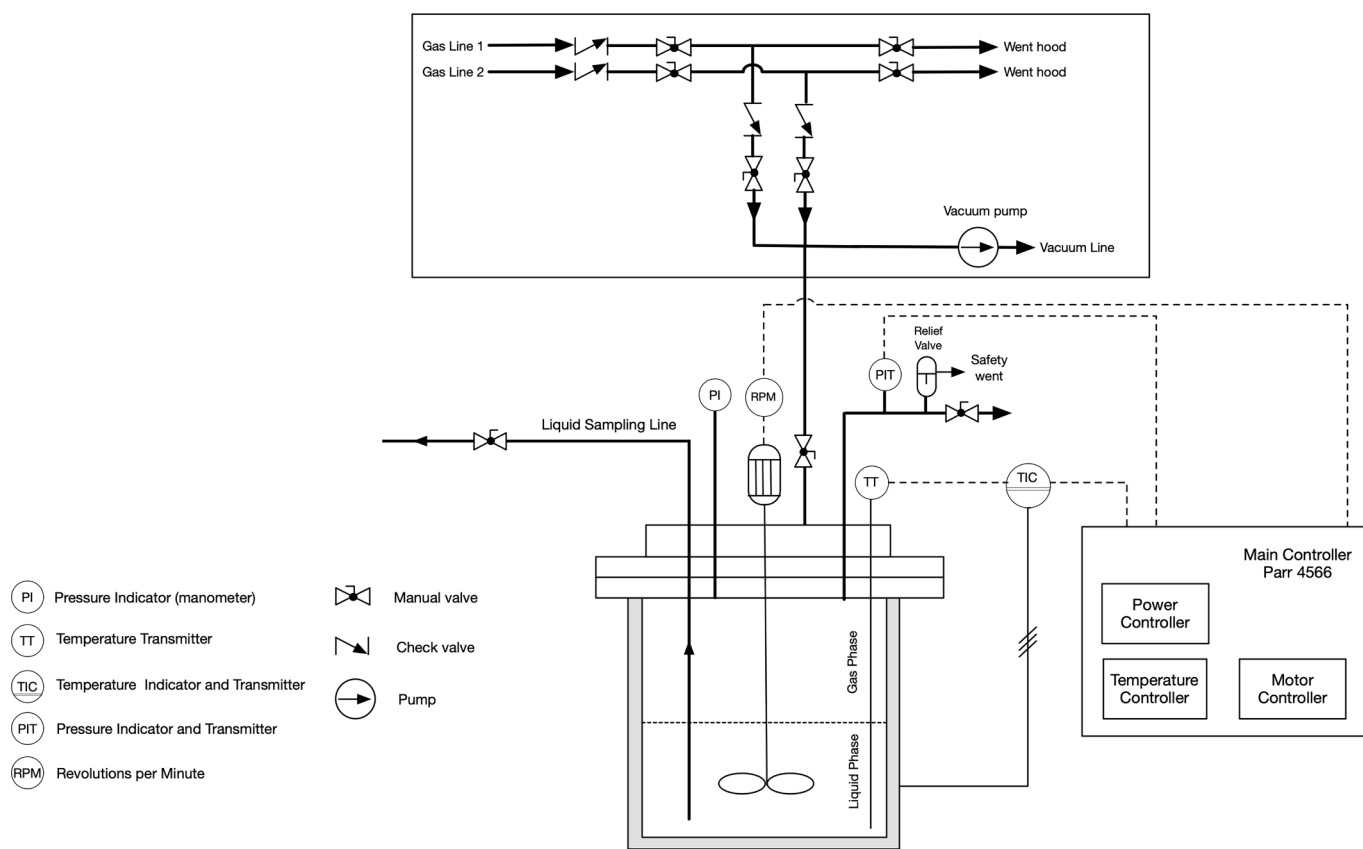


Fig. 2. Schematic of the mineral-water-gas experimental setup.

Center for Research and Industrial Relations ELTE, Budapest. The instrument was set to 15 kV accelerating voltage and 200 pA beam current.

2.3.3. ICP-OES

For chemical composition analysis of the solution samples an inductively coupled plasma - optical emission spectrometry instrument (ICP-OES), a HORIBA Jobin Yvon® ULTIMA 2C was used at the Supervisory Authority for Regulatory Affairs. The measured concentration values are given as mg/L with a relative error of 10 %.

2.4. Geochemical modeling

2.4.1. Modeling concept

Geochemical modeling was carried out using the PHREEQC ver. 3 geochemical software [26]. The following geochemical simulations were performed as representatives for batch experiments:

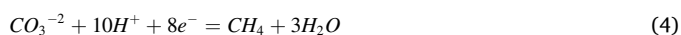
- Model #1: As a first step, a thermodynamic batch model was run to simulate the equilibrium between water, calcite, and air at atmospheric conditions. The results of this model represent the initial state of the experiments before heating and pressurization.
- Model #2: Using the output from Model #1 as initial solution composition, a kinetic batch model was run to follow the calcite

dissolution in water at 105 °C and 100 bar H₂ pressure. Time steps were selected to follow the experimental solution sampling times.

- Model #3: Since, geochemical reactions are taking place under aqueous conditions even without the presence of any injected gas, a reference model was built with the same input data as Model #2, but including the addition of H₂. This model is comparable with the N₂ experiments and helps to differentiate between natural and H₂ injection induced geochemical effects.

2.4.2. Thermodynamic and kinetic input data

Calculations were performed using both the original *phreeqc.dat* thermodynamic database, which is a plain-text ASCII file containing thermodynamic data in a code-specific format. Subsequently, a modified *phreeqc.dat* thermodynamic database was created. In the modified version, the equations connected to the potentially non-realistic reactions forming CH₄ were blocked. To avoid CH₄ creation in the model, it was necessary to block both Eqs. (3) and (4). The specific lines in the database, referred as equations are as follows:



Kinetic rate data of calcite were defined similar to earlier works of the authors [29] and following the report of Palandri and Kharaka [30].

3. Results

3.1. Experimental results

The results of the Ca²⁺ content measurements in solution, which represents the dissolution of calcite in distilled water with injected H₂ and N₂ under 100 bar at 105 °C, are shown in Figs. 3 and 4. The concentration changes are very similar in each run showing a slight but consistent increase in Ca²⁺ throughout the experimental period. It is important to highlight that no significant differences between the results were obtained neither under H₂ nor under N₂ as a reference inert gas.

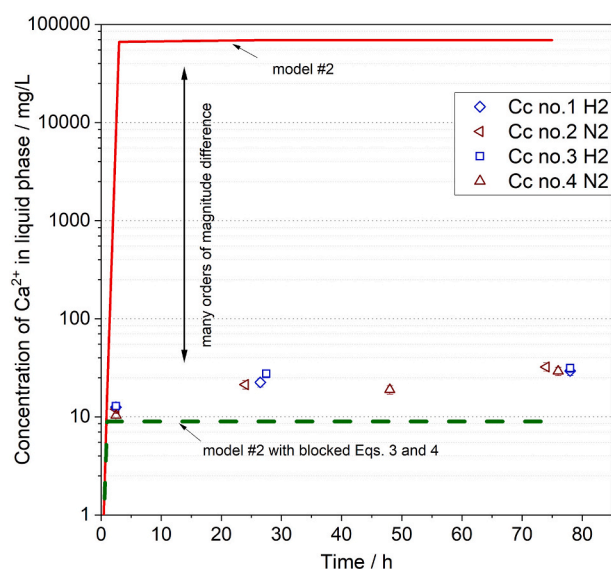


Fig. 3. Comparison of experimental and modeling data (Model #2) of Ca²⁺ concentration (mg/L) in solution as a function of time (h). The symbols (◊, □) and (◁, △) represent the concentrations of calcite (Cc) experiments with H₂ and N₂, respectively. Red line indicates the Model #2 results with default database (*phreeqc.dat*). Green dashed line shows the Model #2 results with modified database (with blocked reactions in Eqs. (3) and (4)). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The solution samples collected after 3 h show an average concentration of 12.7 ± 1.27 mg/L in H₂ experiments and 11.17 ± 1.12 mg/L Ca²⁺ in N₂ environment, respectively. The solutions collected right before the depressurization (after ~78 h), have Ca²⁺ concentration of 30.3 ± 3.03 mg/L in H₂, and 30.7 ± 3.07 mg/L in N₂ experiments (Fig. 3).

As for the morphological observation, the H₂-treated calcite grains are translucent, have intact edges and flat cleavage planes and show no differences compared to the untreated grains (Fig. 4). Noteworthy, that both morphological observations and chemical data established that no dissolution of calcite occurs, indicating that reaction Eq. (4), which could lead to CH₄ formation, is invalid in this environment.

3.2. Geochemical modeling results

Model #2, run with the original *phreeqc.dat* database predicts that significant calcite dissolution takes place under H₂ pressure. After 27 h, the modeled Ca²⁺ concentration in solution reaches a plateau at around 69,000 mg/L (Fig. 3, Table 1). Model #2, run with the modified database with blocked reaction given by Eqs. (3) and (4), resulted in a 9 mg/L Ca²⁺ concentration (Fig. 3, Table 1), indicating rapid calcite saturation in the reaction mixture. In Model #3, in the absence of H₂, the Ca²⁺ concentration is again predicted to be 9 mg/L, regardless of time and the database used (Table 1).

4. Discussion

4.1. Evaluation of experimental results

The dissolution of carbonate minerals in water, including calcite, has received considerable attention in the scientific literature. Although much experimental data are available about the dissolution kinetics of calcite, a significant uncertainty in the absolute value of the dissolution rate under different pressures could be observed [31]. Additionally, literature data are scarce in the situation of temperature (>100 °C) and pressure (~100 bar), at which our study was performed. Therefore, relative dissolution rates were considered and results of H₂ experiments were compared to N₂ experiments.

The ICP-OES results indicate a close to non-significant, or at most a very small increase in calcite dissolution induced by H₂, compared to the outcomes of N₂ experiments (Fig. 3). Despite the contradictions in the literature referred previously, the SEM observation of H₂-treated calcite grains of our study also confirms that no obvious dissolution process occurred. Since there were no precipitates detected on the samples, neither is a recrystallization process expected (Fig. 4). These results are consistent with those of solution analysis (Fig. 3) and indicate that H₂ has no apparent effect on calcite dissolution compared to the reference (N₂) experiments at the tested pressures and temperatures.

4.2. Integration of experiments and models

The calcite dissolution in Model #2 with the non-modified, original *phreeqc.dat* thermodynamic database is significantly higher than that observed in the experiments (Table 1). In the geochemical modeling work of Bo et al. (2021) and Zeng et al. (2022) considerable H₂ loss is triggered in water–calcite–H₂ simulations due to H₂ induced carbonate dissolution [10,11]. Their results, as well as Model #2 of this study, are based on calculations including CH₄ producing reactions. On the contrary, Model #2 with a database modification (blocking Eqs. (3) and (4)), resulted in predicted Ca²⁺ concentrations in the solutions at the same order of magnitude as in the experiments (Fig. 4). This modification is in line with the kinetic models of the Underground Sun Storage report and work of Hassanayebi et al. (2019) since the methane/bicarbonate redox pair was blocked in their models [12,24], however no experimental evidence was presented. According to our best knowledge, this present study is the first providing experimental evidence to decide which modeling practice provides more realistic data.

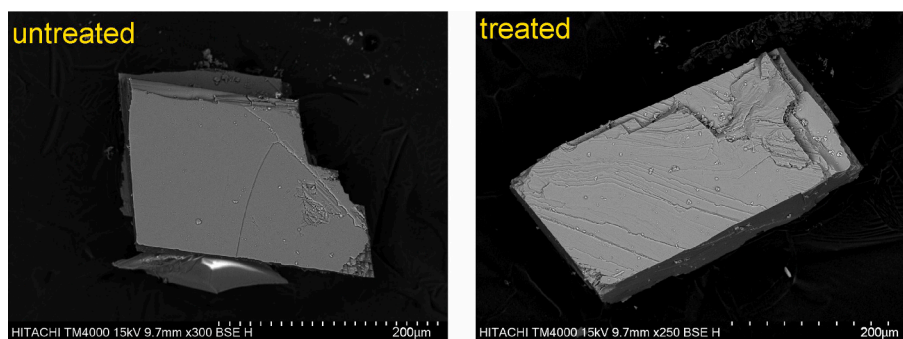


Fig. 4. Scanning electron microscopic images of calcite grains. Selected untreated calcite grain is on the left and treated grain after H₂ exposure is shown on the right. Both grains are translucent, with intact edges and flat cleavage planes.

Table 1

Variation in Ca²⁺ concentration (mg/L) in the solutions of Models #2 and #3 in time (sec). Results are shown for both original and modified databases, where Eqs. (3) and (4) are blocked. In models where H₂ was not used, the same Ca²⁺ concentration is predicted.

Time (sec)	Database			
	Model #2 (with H ₂)		Model #3 (without H ₂)	
	Default database	Modified database	Default database	Modified database
0	8.69	8.69	8.69	8.69
1	15.60	8.95	9.01	9.01
10,801	66,604.84	8.96	9.01	9.01
97,201	69,126.16	8.96	9.01	9.01
270,001	69,126.16	8.96	9.01	9.01
543,601	69,126.16	8.96	9.01	9.01

Eqs. (3) and (4) are responsible for the severe carbonate mineral dissolution in the original unrealistic model. These or similar reactions can be found in many recently used databases (e.g., *lnl.dat*, *Thermo-Chimie.dat*, *PHREEQC_ThermodemV1.10_06Jun2017.txt*, *thd-dem_aug09t4.dat*), not only the *phreeqc.dat* used in our study. This reaction is known to proceed in the presence of a catalyst (e.g., Pd), which could not be expected in the UHS rocks and under the conditions studied [32]. Therefore, to obtain acceptable simulations, Eqs. (3) and (4) should be manually blocked in the used model database avoiding unrealistic results that could lead to incorrect conclusions for UHS.

Consequently, the numerical values (e.g., equilibrium constants of the reactions, change in enthalpy of the reactions and activity coefficients) are herein proposed to be adjusted in the model databases to provide a better match with the abiotic geologic environments if manual modifications are aimed to be avoided.

5. Summary and conclusions

- Several underground hydrogen storage studies rely solely on modeling data and do not review reactions included in the used database, therefore, they might reach false conclusions. Calcite reactions are an important example. As a common constituent of porous geologic media, it is a matter of interest in the geochemical studies of underground hydrogen storage.
- In this study, comparison between laboratory experiments and geochemical modeling is used to understand the calcite–H₂ interactions at reservoir pressure (100 bar) and temperature (105 °C).
- The experimental work confirmed that the extent of calcite dissolution calculated by models using many of the default thermodynamic databases is unrealistic under usual H₂ storage conditions.
- Therefore, modifications of the geochemical model databases are recommended to better constrain the abiotic CO₃²⁻–H₂ reactions in

the models since underground hydrogen storage should generally not assume significant interactions with carbonates.

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CRediT authorship contribution statement

O. Gelencsér: Conceptualization, Data curation, Investigation, Software, Formal analysis, Visualization, Methodology, Writing – original draft, Writing – review & editing. **Cs. Árvai:** Investigation. **L.T. Mika:** Visualization, Writing – original draft, Writing – review & editing, Resources. **D. Breitter:** Funding acquisition, Visualization. **D. LeClair:** Writing – review & editing. **Cs. Szabó:** Resources, Validation, Writing – review & editing. **Gy. Falus:** Validation, Writing – review & editing. **Zs Szabó-Krausz:** Methodology, Validation, Software, Visualization, Writing – original draft, Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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