

Kinetic modelling of chemical interactions of hydrogen with reservoir and caprock minerals over the operational lifetime including real subsurface site data

Dissemination level: PU - Public Hystories deliverable D2.4-0 Date: 20 July 2022





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Revision History

Revision	Revision date	Summary of changes
0	12 July 2022	Initial version

Checked by:

Name	Institute	Date	
Rasmus JAKOBSEN	CO2Geonet -GEUS	12 July 2022	

Approved by:

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Yann LE GALLO WP2 Leader	Geostock	20 July 2022
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1.Introduction

In underground hydrogen storage, chemical reactions and their consequences can potentially affect the performance or safety of the storage. Therefore, it seems important to anticipate and assess the possible reactions of hydrogen before storing it in a reservoir. The identification of the potential effects of H_2 reacting in underground storage listed below is derived from various review articles (Reitenbach et al., 2015; Beckingham and Winningham, 2020; Dopffel et al., 2021; Heinemann et al., 2021).

The hydrogen injected in a reservoir will change the chemical equilibrium between the formation water, the dissolved gases and rock minerals. The resulting geochemical reactions can lead to:

- i) loss of H₂;
- ii) pollution of the H₂ stored by other gases produced and in particular H₂S;
- iii) precipitation and dissolution of minerals resulting in an improvement or a deterioration of injectivity in the reservoir;
- iv) a change in the integrity of wells and installations (corrosion) due to the production of H₂S;
- v) dissolution of minerals altering the mechanical properties of the reservoir or the caprock;
- vi) dissolution of minerals resulting in the formation of gas leakage pathways through the caprock.

Although geochemical processes can have a significant impact on technical and economic aspects of H_2 storage, the magnitude and rates of reactions are subject to high uncertainties. Indeed, there is currently no consensus on the effect or absence of effects of geochemical reactions in storage operations. This uncertainty lies in the complex kinetics of redox reactions involving H_2 and in its strong coupling with the bacterial dynamics. The uncertainty in the importance of H_2 reactivity is explained by the low number of experimental studies in the laboratory and by the limited in number and often poorly documented feedback from the storage of H_2 , pure or mixed, in reservoirs. As a result, modelling approaches still need to be improved to account for the kinetics of H_2 reactivity at the reservoir scale.

The goal of the work presented in this deliverable is to progress in establishing a model able to evaluate the gas/water/rock interactions during underground H_2 storage. Although the processes involved in H_2 reactions are complex, the modelling approach focusses on finding a simple way to simulate H_2 reactions. In particular, the growth and biochemistry of redox reactions involving H_2 are not simulated being out of scope for this report. The models are applied for a mineralogy and in a range of pressure and temperature corresponding to the conditions of underground hydrogen storage in porous reservoirs.



2.Conceptual model of H₂ reactivity during its storage in aquifers

2.1.Feedback on H₂ reactivity observed in storage sites

Feedback from underground gas storage operations of gas containing H₂ is a priori a valuable source of information on the reactivity of H_2 in reservoirs. Worldwide and in recent decades, several dozen gas storage sites have stored gas mixtures containing H₂ in different proportions (MARCOGAZ, 2017), especially in town gas or coal gas storage. Monitoring the composition of the gas over time makes it possible to estimate the losses of H₂, related to flows, its diffusion, its capillary trapping and its reactivity. The concentration of H₂S in the stored gas is the main indicator of H₂ consumption. However, the information available is often limited and has restricted access. Compilations of gas storage sites containing H₂ have emerged in recent years (Tarkowski, 2019; Dopffel et al., 2021), but use or refer to indirect studies. Confusions also exist, for example, for the gas storage site of Beynes (Yvelines, France), the article of Bourgeois et al. (1979) is cited several times in the literature while this article deals with the gas storage site of Chémery (Loir-et-Cher, France) in which H₂ was not stored. The article of Bourgeois et al. (1979) investigated hydrogen sulfide formation in natural gas storages without sulfatereducing bacterial activity. The pyrite contained in the reservoir rock makes up a source of sulfides capable of supplying the natural gas with H₂S mainly linked to CO₂ partial pressure. Thus, the technical note of MARCOGAZ, a European technical association of gas manufacturers, seems to be the most reliable source because it is written by people from the industry. However, the information remains fragmentary (MARCOGAZ, 2017).

These compilations show that there is no H_2 reactivity in storage sites in saline cavities (Dopffel et al., 2021). Several sites are referenced such as Teeside (UK), Clemens (USA), Moss Bluff (USA), Spindletop (USA), Yakshunovskoe (Russia), Kiel (Germany) in which gases containing up to 95% H_2 have been stored since the 1970's, for some, and where no loss of H_2 due to its reactivity or associated production of H_2S has been observed.

Conversely, in storage sites in sandstone reservoirs, a reactivity of H₂ could be observed with, sometimes, very high consumption of stored H₂. The most emblematic case is that of the town gas storage of Lobodice (Czech Republic), which is documented by two scientific articles (Smigan et al., 1990; Buzek et al., 1994). In Lobodice, gas composed of 54% H₂, 22% CH₄, 12% CO₂, 9% CO and 2.5% N₂ was stored in a sandstone reservoir at a depth of 500 m (pressure of 4 MPa and temperature of 25 to 45°C). After 7 months of storage, 10 to 20% of the gas volume was lost and the composition of the gas changed, with the formation of CH₄ and decreases in H₂, CO₂ and CO (gas composition after 7 months: 40% CH₄, 37% H₂, 9% CO₂, 9% N₂ and 3% CO). Buzek et al. (1994) showed that some hydrogen losses are linked to cap-rock heterogeneities with respect to its tightness to hydrogen. The formation of CH₄ observed at Lobodice was accompanied by a growth of methanogenic bacteria and a development in the isotopic signature of CH₄ typical for microbially generated CH₄.

At the sandstone reservoir storage site of Ketzin (Germany), 61% of the volume of H_2 was lost, corresponding to 8 million m³/year, and significant changes in the composition of the stored



city gas were observed, with the generation of H_2S , pressure losses and temperature changes (MARCOGAZ, 2017). In the Beynes saline aquifer (France), Storengy describe a proven but still limited reactivity of H_2 (MARCOGAZ, 2017).

The bibliography on storage sites of H_2 in sandstone reservoirs also includes the Underground Sun Storage pilot¹ storage site of H_2 (Austria) operated by RAG Austria AG (RAG, 2017). In 2016, 115000 m³ of gas containing 10% H_2 was injected into a sandstone formation at a depth of 1200 m for 3 months. Following this injection, about 18% of H_2 was lost, through diffusion, dissolution and conversion. Methanogenic and sulphate-reducing bacteria have been identified, but their effect seems limited with only 3% of H_2 appearing to have been converted into CH₄. The Hychico project (Argentina) of methanation in a sandstone reservoir at a depth of 815 m also reports a consumption of H_2 (Pérez, 2016).

2.2.Dissolution of H₂ in water

Hydrogen is a gas with a high energy density per mass ($\approx 120 \text{ MJ/kg}$) but with a low density (0.081272 kg/m³ at 25°C and 1 bar). Compared to hydrocarbons, a higher storage volume is required for H₂ to store the same amount of energy. Its storage efficiency increases with depth thanks to an increase in the density of H₂ with pressure that is higher than the decrease in density of H₂ with temperature, within the range of pressure and temperature of common reservoirs.

Hydrogen will be stored mainly as a gas phase because its solubility in water is low. Like other gases, the solubility of H₂ increases with increasing pressure and temperature but decreases with increasing salinity. The solubility of H₂ is lower than the solubility of CO₂ and is in the same range as the solubility of CH₄. At 1 bar and 25°C, the solubility of H₂ is about half the solubility of CH₄ and 5 times lower than the solubility of CO₂. At higher pressure, the solubility of H₂ becomes higher than the solubility of CH₄. To illustrate the evolution of the solubility of H₂ compared to other gases, Figure *1* shows the evolution of the solubility of H₂, CH₄ and CO₂ in pure water calculated using PHREEQC (Parkhurst and Appelo, 2013) for increasing pressure and at temperatures of 25, 50 and 75°C. The evolution of these solubilities for increasing temperature at a temperature of 30 bar is also shown. The Peng-Robinson equation-of-state is used by PHREEQC when using the phreeqc.dat thermodynamic database, allowing an accurate description of the fugacity of gases at high pressure and temperature and, thereby their solubilities (Appelo, 2014).

The solubility of H_2 determines the potential reactivity of H_2 since the reactivity occurs in solution between water and rock. The reactivity of gases at dry state with rocks is negligible.

¹ <u>https://www.underground-sun-storage.at/en/</u>





Figure 1: Solubility of H₂ in water compared to CO₂ and CH₄ as a function of pressure and temperature.

2.3.Reductive effect of H₂ in water

Hydrogen is an electron donor for oxidized species present in the pore water, that will possibly lead to a depletion of H₂. In the subsurface, H₂ can be oxidized by various electron acceptors such as carbonates and bicarbonates, sulfates and other sulfur species, nitrate and other oxidized forms of nitrogen, ferric iron or oxygen. In aquifers and reservoirs that could host an underground hydrogen storage, H₂ is mainly expected to induce the redox reactions ferrireduction, sulfate reduction, methanogenesis and acetogenesis, from the energetically more favorable to the less favorable, respectively. The reaction of sulfate reduction may lead to the formation of H₂S depending upon the pH conditions, a toxic and corrosive gas that requires gas treatment. Methane is formed during methanogenesis and changes the gas mixture composition. An overview of the main redox reactions consuming H₂ in the subsurface is shown in Table 3. These reactions are sorted depending on their expected importance in an underground hydrogen storage (Dopffel et al., 2021). The negative of the free energy of formation ΔG_f^0 listed for each reaction is the energy released using 1 mole of H₂ at standard conditions where all substances have activities or fugacities of 1.

Process consuming H ₂	Reaction	Free energy ΔG_f^0 (kJ/mol H2)
Methanogenesis	${}^{1}\!\!/_{4} HCO_{3}^{-} + H_{2} + {}^{1}\!\!/_{4} H^{+} \rightarrow {}^{1}\!\!/_{4} CH_{4} + {}^{3}\!\!/_{4} H_{2}O$	-33.9
Acetogenesis	$\frac{1}{2}HCO_{3}^{-} + H_{2} + \frac{1}{4}H^{+} \rightarrow \frac{1}{4}CH_{3}COO^{-} + 2H_{2}O$	-26.1
Sulfate reduction	$\frac{1}{2}SO_4^{2-} + H_2 + \frac{1}{2}H^+ \rightarrow \frac{1}{2}HS^- + H_2O$	-38.0
Iron-reduction	$2 FeOOH + H_2 + 4 H^+ \rightarrow 2 Fe^{2+} + 4 H_2O$	-228.3
Denitrification	$2/5 \text{ N}O_3^- + H_2 + 2/5 H^+ \rightarrow 1/5 N_2 + 11/5 H_2O$	-240.1
Sulfur reduction	$S + H_2 \rightarrow H_2 S$	-33.1
Aerobic H ₂ oxidation	$\frac{1}{2} O_2 + H_2 \rightarrow H_2 O$	-237.0

Table 1: Reactions involving H₂ in underground hydrogen storage.



However, these redox reactions involving H_2 are known to be restricted, because of the high energetic barrier necessary to break the strong H-H bounds before the electron transfer can take place. In the absence of catalyst such as bacteria or possibly metal and mineral surfaces, these reactions induced by H_2 are minor under the temperature conditions expected in an underground hydrogen storage. Indeed, the experiments conducted by Truche et al. (2009) showed that sulfate reduction in absence of bacteria exhibited a sulfate half-life of 210 000 years at 90°C. Similarly, the same range of half-life (160 000 years) was measured under sterile conditions for carbonate during methanogenesis at 100°C (Seewald et al., 2006).

Without going into the details of the description of bacterial dynamics, their growth and their kinetic effects on H_2 consumption, we will mention the study by Berta et al. (2018). This study reports kinetics of consumption of H_2 by the reactions of acetogenesis and sulphate-reduction measured in the laboratory under conditions corresponding to those of an underground storage of H_2 . Methanogenesis was not observed in this study. Under conditions where the H_2 pressure is high (2 to 15 bar) and much higher than the natural H_2 content in a reservoir, the kinetics of H_2 consumption are similar, regardless of the H_2 or salinity of the solution. Although probably catalyzed by bacterial activity, the kinetics of consumption of H_2 is independent on bacterial dynamics in these experiments and the results can be simulated using a 0-order kinetic law, where only the reaction rate is considered, without dependence on environmental parameters.

2.4. Minerals reactive to H₂

The chemical equilibrium between the formation pore water, the dissolved gases and the rock minerals is expected to be changed by the injection of large amounts of H_2 . The dissolution of hydrogen induces redox reactions in solution that form species such as HS^- or uses inorganic carbon that will impact the pH. Mineral dissolution and precipitation reactions that can occur because of H_2 injection are driven both by redox and acid-base reactions.

In the literature, only few studies report interaction experiments between H₂ and rocks in the context of underground hydrogen storage in porous reservoirs. The review of these experiments, their conditions and the main results is reported in Table 2. The observed changes in mineralogy are minor and consist in the dissolution of minerals of high solubility, located in the cement rather than in the rock matrix. A recent experimental study by Hassanpouryouzband et al. (2022) confirms that very little mineralogical changes are occurring because of H₂ injection in sandstones under abiotic conditions. These authors perform 250 batch experiments of exposure to H₂ using different reservoir sandstones for different pressure, water/rock ratio, rock particle size, temperature and salinity conditions. By monitoring the water composition changes, they conclude that there is a lack of abiotic reactivity of H₂ with sandstone mineral assemblages. These different experimental evidences on the reactivity of H₂ can be supplemented by studies made on the reactivity of H₂ with clay rocks in the context of nuclear waste storage, where H₂ is formed by steel corrosion.



Reference	Rock material	Temperature	Gas composition	H2 partial pressure	Total pressure	Water-rock ratio	Experiment duration	Mineralogical changes	Changes in solution	Changes in gas composition
Yekta et al. (2018)	Triassic sandstones (Buntsandstein Fm, Vosges, France) as core or powder	100°C and 200°C	• pure H2 (dry) • 1 experiment with wet H2 (H2O)	• 100 bar • 10 to 50 bar (wet H2)	100 bar	• 0 (no water) • 0.1 (with wet H2)	1.5, 3 or 6 months	Minor dissolution of muscovite and hematite	only gas	not reported
Shi et al. (2020) Henkel et al. (2014)	Core plugs from California Ulility NG storage site • reservoir • caprock • cement • wellhead polymeric material siliciclastic reservoirs and caprocks from 25 well sites in Germany	80°C sample specific T	13 % H2 + 87 % natural gas (96.4% CH4, 3.39% C2H6 and 0.21% C3H8) H2 + water	340 bar H2	26.2 Mpa sample specific P	0 (no water) sample specific solution salinity	3 months	 Complete dissolution of gypsum (1 to 2%) in reservoir and caprock samples (no changes in pyrite) Dissolution of portlandite and precipitation of calcite in cement sample No changes in porosity Increase of permeability pore structure changed) Preliminary results: reactivity with H2 expected 	only gas	Increase of %H2 and decrease of %CH4, due to lower absorption behaviour of H2 compared to hydrocarbons
	and Austria									
Flesch et al. (2018)	Core plugs • Tertiary siltstones (Austria) • Triassic sandstones rich in lithics (Emsland, NW Germany) • Permian sandstones rich in quartz (Altmark, Germany)	 40°C (Tertiary) 100°C (Triassic) 130°C (Permian) 	H2 + water		 10 MPa (Tertiary) 10 MPa (Triassic) 20 MPa (Permian) 	core plugs immerged in solutions of salinities: • 35 g/L (Tertiary) • 288 g/L (Triassic) • 350 g/L (Permian)	6 weeks	 Changes observed in sandstone samples, not in siltstone Complete dissolution of pore-filling cement (Carbonate and anhydrite) Porosity increase 	not reported	not reported

Table 2: Review of studies on the reactivity of H2 with rocks in conditions relevant for underground hydrogen storage.



The minerals potentially affected by redox reactions contain oxidized species that are destabilized by the on-going reduction due to H_2 . This is the case of the Fe(III)-bearing minerals, such as Fe(III) oxides and oxi-hydroxides or clay minerals and mica containing Fe(III). A dissolution of hematite is suggested by Yekta et al. (2018) in the modelling of their experiments of interaction of H_2 with a lithic-rich sandstone at 100 bar and 100°C or 200°C. This dissolution of hematite was reported in the modelling when Fe(II) phases were considered as secondary phases but was not clearly observed during the laboratory experiments. The reduction of Fe(III) contained in smectite, illite and mica is reported by several authors as a potential mineral alteration induced by H_2 (Liebert et al., 2011; Hernsdorf et al., 2017; Heinemann et al., 2021; Thaysen et al., 2021). The evidence is provided by Esnault et al. (2010) that showed that, whether H_2 was consumed or not in Fe(III)-smectite suspensions in laboratory experiments at 40°C and a partial pressure of H_2 of 0.6 bar, depended on the presence or absence of iron-reducing bacteria.

The reduction of pyrite to pyrrhotite is a reaction involving H_2 that may be significant at low temperature. Indeed, several authors have shown that the formation of pyrrhotite from pyrite can occur at low or mid-hydrothermal temperatures and does not need to be catalysed by bacterial activity (Bourgeois et al., 1979; Truche et al., 2010, 2013). Hence, this reaction can eventually occur when predicted by thermodynamics. This reduction of pyrite to pyrrhotite corresponds to a coupled dissolution-precipitation reaction at the pyrite surface and writes:

 $FeS_2 + (1 - x)H_2 \rightarrow FeS_{(1+x)} + (1 - x)H_2S$, where 0 < x < 0.125The H₂S formed during the pyrite to pyrrhotite reaction can modify the redox potential and the pH of the formation water and, then, destabilize other minerals. Truche et al. (2010) observed that under pH conditions buffered by calcite the kinetics of the pyrite to pyrrhotite reduction increased with the temperature (from 90 to 180°C), the partial pressure of H₂ (8 to 18 bar), the mineral surface area and the water/solid ratio but decreased with the increase of H₂S concentration. These authors established a kinetic rate law dependent on time, H₂ partial pressure and temperature.

Carbonate and sulfate minerals can be dissolved as a result of the removal of sulfate and the formation of an acid such as HS⁻ resulting in the displacement of chemical equilibria. Calcite will thus dissolve when the equilibrium of the carbonate system is changed, due to variations in partial pressure in CO₂, the formation of CH₄, acetate or variations in pH, temperature or Ca concentrations. In potential H₂ storage reservoirs, calcite, anhydrite and gypsum are the minerals that can be dissolved (Flesch et al., 2018; Shi et al., 2020).

Well cements may also be subject to mineralogical changes due to the injection of H_2 into a reservoir. In the presence of H_2S , a more marked reactivity, related to acidic conditions, was observed with degradation of cement minerals (portlandite, CSH...) and calcite precipitation (Jacquemet et al., 2012; Kiran et al., 2017; Shi et al., 2020). However, such cement degradation is not expected from storage of a mixture of hydrogen and natural gas (Jacquemet et al., 2022). Le Gallo et al., 2022).



3.Establishment of a geochemical model to evaluate H₂ reactivity

3.1.Calculation code, thermodynamic database and kinetic rates

The modelling tool used is the widely used PHREEQC 3.0 (Parkhurst and Appelo, 2013). This makes it possible to include the relevant processes and their kinetics. The database used is a modified version of phreeqc.dat database included in the installation, the phreeqc.dat database includes data so that the Peng-Robinson equation of state for calculating the solubility of gases at high pressure can be used. Also, specific volumes of aqueous species are calculated as a function of the dielectric properties of water and the ionic strength of the solution, which allows calculation of pressure effects on chemical reactions and the density of a solution, potentially significant at the high pressures relevant for hydrogen storage. The kinetic rate expressions for mineral dissolution and precipitation are taken from the database of kinetic rates established by Marty et al. (2014).

3.2.Simulation scenario: reservoir conditions, water composition and mineralogical assemblage

To evaluate the reactivity of H_2 for a generic case of underground hydrogen storage, the temperature and pressure conditions used in the simulations are set to correspond to potential depths of geological reservoirs (Figure 2). The temperature evolution with depth is considered to follow a linear geothermal gradient of 3°C/100 m, starting from a surface temperature of 15°C. The fluid pressure is considered as hydrostatic, with an increase of 0.1 bar/m. Calculations are made for temperature and pressure conditions corresponding to the surface and reservoir depths of 500, 1000 and 1500 m, with most of the calculations done for a depth of 1000 m (45°C and 100 bar).





Figure 2: Selection of temperature and pressure conditions of the calculations corresponding to reservoirs at different depths.

For the simulation, a generic sandstone is defined, with a porosity of 30 % and composed of 75 % quartz, 5 % calcite, 2 % pyrite and 1 % hematite as reactive minerals. Pore water has a salinity of about 10 g/L and its pH is buffered by calcite. Composition is given in Table 3. A volume of 0.2 L of gas is considered per L of water and the gas species are H_2 , H_2O , CO_2 , CH_4 and H_2S .

Table 3: Initial pore water composition considered in the generic sandstone case.

Component or parameter	Concentration or value	Units	
рН	7		
ре	-4		
Т	45	°C	
Na	7.2 10 ⁻²	mol/L	
Са	1.5 10 ⁻²	mol/L	
Cl	10-1	mol/L	
SO ₄	10-3	mol/L	
HCO ₃	10-3	mol/L	

3.3.Modelling approaches to simulate H₂ induced redox reactions in solution

Redox reactions at equilibrium

In the simplest form, water/rock interaction models usually consider the aqueous speciation reactions occurs following thermodynamic equilibrium, including the oxidation and reduction reactions. As a first approach in the simulations evaluating H₂ reactivity, no constrain is



considered on redox reactions that may occur at thermodynamic equilibrium. A first set of calculations considers mineral dissolution and precipitation reactions are also occurring at thermodynamic equilibrium. A second set of calculations includes a kinetic control of the mineral reactions.

Abiotic reactions, without reactivity of H₂

As highlighted by the literature review, if the redox reactions involved by H₂ are not catalysed by bacterial activity, these reactions are almost negligible at the time scale of gas storage operations. Therefore, assuming abiotic conditions, it is reasonable to consider H₂ as being non-reactive. Using PHREEQC, it is possible to have two uncoupled versions of hydrogen. The first one is the classical hydrogen system, involved in the water dissociation, pH and many chemical reactions. The second type of hydrogen is an inert hydrogen that only participates in gas dissolution reactions. In the phreeqc.dat thermodynamic database, the uncoupled unreactive type of hydrogen is called "Hdg".

Kinetic control on aqueous redox reactions: global consumption rate of H₂

The catalysis by bacterial activity of reduction reactions involving H_2 leads to a situation where the redox reactions are controlled by thermodynamics but with a kinetic delay due to bacterial dynamics such as growth, decay, etc. The reactions with H_2 then occur somewhere between complete thermodynamic control and abiotic, uncatalyzed conditions. The first way of considering a kinetic control on aqueous redox reactions is to introduce a rate on the consumption of H_2 . Using two uncoupled types of hydrogen, it corresponds to a progressive conversion of the inert "Hdg" hydrogen to the reactive "H" hydrogen. Following this conversion, the sulfate-reduction and methanogenesis reactions are free to occur. The rate of conversion of H_2 taken in the calculations corresponds to the rate of H_2 induced reduction reactions determined by Berta et al. (2018), respecting the stoichiometry of H_2 consumption (2 10⁻⁸ mol/s).

 Kinetic control on aqueous redox reactions: simulation of sulfate-reduction and acetogenesis

As described above, given the temperatures relevant for hydrogen storage, redox reactions involving hydrogen as a reductant are not expected to take place without microbial (or other catalysts). However, contrary to salt caverns, sandstone aquifers have been found to normally host microbial life, and since anaerobic reduction processes can use H₂ as the electron donor, if not there initially, it can be expected that a microbial community capable of using the injected hydrogen will be established over time. Under natural conditions, hydrogen concentrations are limited by the production of hydrogen from fermenting processes and the reduction processes, except for Fe(III) reduction, occur separated due to the differences in energy yields. The differences are reflected in the hydrogen concentrations that are normally below 20 nmol/l in the water corresponding to ~30 ppm in a gas phase. The reason Fe(III) reduction is different is that the source of the Fe(III) is Fe-oxides with a very large range in stabilities. In a reservoir with high concentrations of hydrogen, all of the microbial processes may, from a thermodynamic point of view, occur concomitantly. Berta et al. (2018) have carried out tests with high levels of hydrogen (up to 15 bar P_{H2}) and found that acetogenesis, and sulfate reduction occurred concomitantly. They could not quantify Fe(III) and Mn(IV)



reduction, but suggest that these also occurred. Interestingly, they found that the rates, for the processes were not very different and showed little effect of the hydrogen level. Based on this, we have chosen to set a constant rate of 5E-9 mol/l/s as the highest rate of the microbial reactions that could be expected. This is close to the range of rates observed by Berta et al. (2018) where conditions are more optimal due to fully saturated conditions. In addition, simulations are performed using rates that are 10% and 1% of the Berta et al. (2018) rates to take into account the expectation, that the rates at in situ conditions (unsaturated, high pressures, high temperatures, high salinity etc.) will be lower. Also models without the redox reactions are modelled. For all reactions, the rates are defined so that at a pH > 12, the microbial redox reactions stop.



4.Modelling results of H₂ reactivity in underground Hydrogen storage in a porous media reservoir: generic case and Advisory Board sites

4.1.Calculations with mineral dissolution and precipitation at thermodynamic equilibrium

The simplest way to calculate gas/water/rock interactions is to perform a calculation at thermodynamic equilibrium. This approach is tested here, as a first step, and therefore does not consider a kinetic delay on precipitation and dissolution reactions of minerals or on redox reactions in solution. However, the reader is hereby reminded that the reactions are not expected to occur at thermodynamic equilibrium and that the thermodynamic approach is not suitable to model the reactivity in hydrogen storage and should be seen as a hypothetical endpoint. The reactions are controlled by the amount of H₂, expressed as the partial pressure of H₂. The results at thermodynamic equilibrium (Figure 3) show that the mineral assemblage is stable for partial pressure of H₂ lower than 0.001 bar. For a partial pressure of H₂ between 0.001 and 0.01 bar, calcite become unstable and totally dissolves. The formation of CH₄ that accumulates in the gas phase and uses CO₂ increases the dissolution of calcite, by displacing the carbonate system equilibrium. At a partial pressure of H₂ between 0.1 and 1 bar, pyrite and hematite are unstable and their dissolution is total. Dissolution of pyrite occurs for partial pressure of H₂ a little lower than for the dissolution of hematite, mainly at increasing temperature. In these calculations, hematite and pyrite are replaced by pyrrhotite.

The calculations made for pressure and temperature conditions corresponding to different reservoir depths are similar, with only small differences in H_2 partial pressure needed for the initiation of the dissolution reactions.

When the amount of H_2 is expressed as litre of injected H_2 (at 1 atm) per volume of reservoir rock (Figure 4), the total dissolution of the reactive minerals is observed for about 1000 to 1200 L H_2/m^3 rock, depending on the reservoir depth and the temperature considered.





Figure 3: Evolution of generic case sandstone mineralogical assemblage as a function of partial pressures of H_2 for different depth related pressure and temperature conditions, when mineral dissolution/precipitation reactions and H_2 induced redox reactions are considered at thermodynamic equilibrium.





Figure 4: Evolution of generic case sandstone mineralogical assemblage as a function of injected amount of H_2 for different depth related pressure and temperature conditions, when mineral dissolution/precipitation reactions and H_2 induced redox reactions are assumed to occur at thermodynamic equilibrium.

4.2. Calculations in 1D assuming mineral dissolution and precipitation at thermodynamic equilibrium

Batch calculations can simulate the reaction pathway, including the mineral dissolutions and precipitations. However, the non-renewal of the reacting H_2 rich fluid could imply changes in the reactions compared to an injection over time in a reservoir where the H_2 is replenished. To assess this issue, simulations in a system where H_2 is replenished were performed to check that the simulated reactive pathway is not modified compared to the batch reaction simulation. Note that the objective is not to simulate an injection and the behaviour of H_2 in the near-well zone, but to evaluate the reactions of H_2 with the rock when H_2 is replenished and reacts over time when reactions occur during transport.

A 1D column of 100 cells of 1 m has been considered using PHREEQC. In the first cell of the column, 0.5 moles of H_2 dissolved in formation water is injected at each time step. As for the simulations in Sect. 4.1, the 1D calculations are performed at 45°C and 100 bar, at thermodynamic equilibrium, both for redox aqueous reactions and mineral dissolutions and precipitations.



Results shown in Figure 5 are obtained after the simulation of 10, 25 and 50 timesteps of H_2 injection in the column. Rock alteration is simulated in the first cells close to the injection of H_2 . Calcite is simulated to dissolve, followed by pyrite and hematite. Precipitation of pyrrhotite is also simulated. The precipitation of pyrrhotite starts when the partial pressure of H_2 exceeds 1 bar in the column cell. The reactive pathway simulated in batch conditions, assuming infinite reaction rates is the same as the one simulated in batch conditions and the mineral dissolutions and precipitations occur under the same H_2 partial pressure conditions. It is assumed that the reaction pathways will then also be similar when kinetics, implying slower rates are used. Hence, the reaction pathways of H_2 with the rock can be evaluated and discussed based on batch simulations without considering the effects of flow and transport as done in the following.



Figure 5: Evolution of generic case sandstone mineralogical assemblage in a 1D column where H2 is injected at distance 0 at different time of simulation. Calculations at 45°C and 100 bar, when mineral dissolution/precipitation reactions and H2 induced redox reactions are considered at thermodynamic equilibrium.



4.3.Calculations with kinetic control of mineral dissolution and precipitation

At in situ conditions at low water saturation and lack of flow to remove reaction products, it is expected that most mineral reactions will not take place controlled by thermodynamic equilibrium, but under kinetic control. There are kinetic expressions available for many minerals based on experimental data. However, compared to the in-situ conditions, the conditions used for producing the experimental data used for deriving kinetic parameters are generally very different from the in-situ conditions assumed present in a H_2 storage. Nevertheless, without experiments at in-situ conditions, there is no alternative to using rate descriptions from the literature. A major difference is the low water saturation, which probably means that most rates will be overestimated compared to in-situ conditions. In Figure 5, the evolution over time of the mineralogical assemblage is shown at different partial pressure of H₂, in conditions corresponding to a reservoir depth of 1000 m. In these calculations, dissolution and precipitation of minerals are controlled by kinetics. However, the associated redox reactions between H_2 and mineral dissolution products are still considered to occur at thermodynamic equilibrium. For example, the reaction between CO_2 and H_2 forming CH₄ will cause the activity of CO_3^{2-} to be very low resulting in the solution being highly undersaturated for calcite, and since the saturation state of calcite enters into the kinetic expression used, the resulting rate of dissolution becomes very high. This is further discussed in the next section. When the partial pressure of H₂ is higher than 0.1 bar, a total dissolution of calcite and pyrite is simulated in a few days. The dissolution is too fast to be seen on Figure 5, where the time scale is 100 years. Hematite also dissolves but only partially, with only 3 % of the initial hematite simulated to dissolve after 100 years under 10 bar of H₂. When the redox reactions occur at thermodynamic equilibrium, a large dissolution of minerals is simulated even at low partial pressures of H₂. However, such a large effect is not expected and the simulation of redox reactions involving H₂ as occurring at thermodynamic equilibrium seems unrealistic.



Figure 5: Evolution of generic case sandstone mineralogical assemblage as a function of time for different partial pressures of injected H_2 (10⁻³, 10⁻¹ and 10 bar) at 45°C and 100 bar, when H_2 induced redox reactions are considered to occur using kinetic expressions from the literature.



4.4.Kinetic control of redox aqueous reactions

As described in section3.3, there is a high probability that microbial redox reactions will occur due to the high availability of hydrogen. The simulations presented here include these reactions, which, depending on the actual rates may have a pronounced effect on the water chemistry, thereby affecting the rates of the inorganic mineral reactions. Different ways of considering a control on the redox reactions in solution have been tested in these simulations: i) an abiotic case where the hypothesis is that the redox reactions cannot occur in absence of bacteria; ii) a case where a global rate on H₂ consumption is considered; and iii) a case where specific rates for sulfate-reduction and acetogenesis reactions are considered.

In the abiotic case i) (Figure 6), the minerals remain stable over time and no dissolution is simulated. The formation of pyrrhotite is also not simulated. These calculations are made considering an uncoupled species for the injected hydrogen that does not cause the reduction usually induced by H_2 . This abiotic case calculations confirm that reduction reactions induced by H_2 in solution are driving the rapid reactions of the rock in presence of H_2 as described in section 4.2.



Figure 6: Evolution of generic case sandstone mineralogical assemblage as a function of time for different partial pressures of injected H_2 (10⁻² and 10 bar) at 45°C and 100 bar, in an abiotic situation, where H_2 induced redox reactions are not allowed.

In the case of a kinetic control of the redox reactions by a global rate of H₂ consumption, the uncoupled species for injected H₂ considered in the abiotic case is progressively converted to reactive H₂. The rate of H₂ consumption used in these calculations corresponds to the rate determined by Berta et al. (2018) for acetogenesis and sulfate-reduction, expressed as a consumption of H₂. The calculated evolution of the mineralogical assemblage considering a progressive consumption of H₂ is shown in Figure 7 for different injected partial pressure of H₂. Substantial amounts of reactions of the minerals with H₂ are simulated for partial pressures of H₂ higher than 0.1 bar. Calcite dissolves progressively during the first 15 to 30 years of the simulation and, then, the dissolution and reactivity stop because the energy available become too small as the pH increases to very high values. Small amounts of pyrite are dissolving, accompanied by a little precipitation of pyrrhotite.





Figure 7: Evolution of generic case sandstone mineralogical assemblage as a function of time for different partial pressures of injected H_2 (10⁻³, 10⁻¹ and 10 bar) at 45°C and 100 bar, where H_2 induced redox reactions are controlled by a global kinetic rate on H_2 consumption.

Considering a separate kinetic control on acetogenesis and sulfate-reduction has the advantage compared to the approach using a global rate of H₂ consumption that it simulates the processes that are effectively described by Berta et al. (2018). Since methanogenesis was not reported by Berta et al. (2018) this reaction is not considered in the calculations. Only negligible amounts of calcite and pyrite dissolve for H₂ partial pressures lower than 10 bar (Figure 8). At 10 bar of H₂, calcite is calculated to slightly dissolve, in smaller amounts than in the calculations using a global rate for H₂ consumption. Because of the absence of methanogenesis in the model, the carbonate system is only affected by the use of CO₂ by acetogenesis and not also by the use of CO₂ from forming CH₄ as in the previous calculation of pyrrhotite. The mineral assemblage evolves during the first years of the simulation and, then, the reactions cease. Dissolution and precipitation reactions are no longer active at pH higher than 12 (Figure 9).



Figure 8: Evolution of generic case sandstone mineralogical assemblage as a function of time for different partial pressures of injected H_2 (10⁻², 10⁻¹ and 10 bar) at 45°C and 100 bar, where redox reactions of sulfate-reduction and acetogenesis are controlled by kinetics.



4.5.Comparison of modelling approaches on the pH and gas composition evolutions

The dissolution of redox reactive H₂ in the pore water strongly modifies its pH (Figure 9), also for low partial pressures of H₂ that do not lead to mineral changes. This increase of the pH is due to the consumption of protons or the production of hydroxides during redox reactions such as sulfate-reduction ($SO_4^{-2} + 4 H_2 = HS^- + 3 H_2O + OH^-$) or methanogenesis ($CO_3^{-2} + 4 H_2 =$ $CH_4 + H_2O + 2 OH^-$). Higher amounts of H₂ reacting results in the large pH jump.

In the abiotic case, H_2 remains inert and the pH stays at its initial value of 7.1, whatever the H_2 partial pressure and over time. When redox reactions are considered to occur at equilibrium, the pH increases to 12.4 for a partial pressure of H_2 increasing to 0.01 bar and then remains at this value also for higher partial pressure of H_2 . Seen over time, for a partial pressure of H_2 of 10 bar, the pH increases up to 13.5 during the first days of the simulation and is then buffered to 12.4 by the dissolution of calcite, which is delayed by kinetics. When a global rate on H_2 consumption is considered, the pH follows a similar trend as when redox reactions are considered at equilibrium, with the exception that the initial pH increase is not simulated in this case. When a separate rate for the sulphate-reduction and acetogenesis reactions is considered, the pH increase is restricted to a value of 12. Simply because, the model stops microbial sulphate-reduction and acetogenesis for pH values higher than 12.



Figure 9: Evolution of pH as a function of partial pressures of injected H_2 and of time (10 first years of the simulation) for different ways of considering H_2 induced redox reactions.

Besides the mineral evolution and the changes in solution reflected by the pH evolution, the gas composition is an important result in the evaluation of the H_2 reactions. The evolution of the gas composition is shown for the different calculation cases for increasing partial pressure of H_2 after a given simulation time in Figure 10 and as a function of time when a H_2 partial pressure of 10 bar is considered in Figure 11.

Before injecting H_2 , at low H_2 partial pressure (Figure 10), the gas phase is mainly composed of water vapour. The reductive conditions are reflected by the prevalence of CH_4 compared to CO_2 . When H_2 is considered as an inert gas, namely the abiotic case, H_2 progressively becomes the major gas component as the partial pressure of H_2 increases. Consequently, the content in other gas species decreases, because of dilution. At 10 bar of H_2 , the composition



of the gas phase is acquired immediately. When H_2 is reactive and in absence of a kinetic control on the redox reactions, a noticeable production of CH₄ is induced by increasing the H₂ partial pressure and CH₄ becomes the main phase component. Because of methanogenesis, CO_2 disappears for H₂ partial pressure higher than 0.001 bar. This high production of CH₄ is made possible by the dissolution of calcite and the H_2 content in the gas phase only increases when calcite dissolution stops. In the calculation case with redox reactions at equilibrium, pyrite also dissolves but the released sulphur is used to form pyrrhotite and the content of H₂S in the gas phase remains low. The evolution of the gas composition over time indicates that the kinetics on dissolution and precipitation reactions only induce a little delay in the gas composition evolution. The gas phase composition simulated when kinetics of the H₂ consumption is considered is similar to the case with redox reactions at equilibrium. When a separate kinetic rate of acetogenesis and sulfate-reduction is considered, the gas composition evolution is different, mainly because CH₄ is not considered. In these conditions, water vapour is replaced by H_2 as the main gas component when H_2 partial pressure increases. H_2S is also simulated to increase but due to the dominance of the S²⁻ species at high pH, its concentration remains below 0.0001 % for a partial pressure of H₂ of 100 bar. The kinetics on redox reactions do not induce a delay in the gas phase composition evolution.



Figure 10: Evolution of the gas composition as a function of partial pressures of injected H_2 for different ways of considering H_2 induced redox reactions.





Figure 11: Evolution of the gas composition as a function of time when 10 bar of H_2 are injected at 45°C and 100 bar for different ways of considering H_2 induced redox reactions.

$\begin{array}{l} \text{4.6.Sensitivity on the kinetic rate of H_2} \\ \text{induced redox reactions} \end{array}$

Considering a kinetic rate of the H₂ induced redox reactions in solution is a promising approach as it aims at simulating the catalysing effect of bacteria on the redox reactions, without considering the complex dynamics of bacterial behaviour. However, this approach and its application to the simulation of the reactivity of H₂ in a reservoir remain uncertain because the rates we applied are issued from only one experimental study and kinetic rates obtained in laboratory experiments can be non-representative of conditions in a geological media. This uncertainty is highlighted by a sensitivity analysis on the rate of acetogenesis and sulfatereduction used in the model, where the rate is divided by 10 and 100 in two simulations. The mineral evolutions calculated using the rate by Berta et al. (2018) and the rates divided by 10 and 100 are shown in Figure 12. When the rate of acetogenesis and sulfatereduction is divided by 10, the same amounts of calcite and pyrite dissolve and the same amount of



pyrrhotite precipitates at the end of the simulation compared to the calculation with the original rate. However, the minerals dissolve more slowly when the rate is divided by 10 with the mineral changes occurring only during the first 30 years of the simulation, compared to the first 4 years with the rate measured in the experiments by Berta et al. (2018). When the rate of acetogenesis and sulfate-reduction is divided by 100, the mineral changes are still ongoing at the end of the 100 years of the simulation. In this case and at a partial pressure of H₂ of 10 bar, 0.5% of calcite and 0.3 % of pyrite dissolve and about 0.2 % of pyrrhotite precipitate after 100 years of simulation. The pH is also influenced by the rate of sulfate-reduction and acetogenesis (Figure 13). The pH increases strongly in both cases after the injection of H₂ but the pH of 12 is reached after 2 years with the rate obtained in experiments by Berta et al. (2018) and after 30 years when the rate is divided by 10. The pH does not reach a value of 12 after 100 years when the rate is divided by 100.



Figure 12: Sensitivity analysis of the rate of reduction by H_2 considered in the calculations on the mineralogical assemblage evolution following the injection of 10 bar of H_2 at 45 °C, 100 bar.



Figure 13: Sensitivity analysis of the rate of reduction by H_2 considered in the calculations on the pH evolution following the injection of 10 bar of H_2 at 45°C, 100 bar.



4.7. Synthesis of the results of the H₂ reactivity simulation applied to Advisory Board members storage sites

The reactivity of H_2 has been evaluated in reservoirs used or studied as H_2 gas storage sites by different members of the advisory board of the HyStories project. The main reactivity trends are summarized in this section.

The simulation of the reactivity of H_2 in the different reservoirs is made considering a kinetic rate on the aqueous reduction reactions induced by H_2 . The approach considering kinetics of sulfate-reduction and acetogenesis presented for the calculations on the generic sandstone has been retained and extended to methanogenesis with the constant kinetic rate issued from Berta et al. (2018). The importance of the effect of bacterial activity is shown by a calculation of the reactivity of H_2 under abiotic conditions, using a rate for sulfate-reduction, acetogenesis and methanogenesis 6 order of magnitude lower than the reference rate used to simulate the effect of bacteria.

In the absence of bacterial catalysis of the reduction reactions induced by H_2 , almost no reactivity is simulated in the different considered reservoirs. The gas phase composition is not changed, without conversion of H_2 to CH_4 . The pH of the formation water remains at its initial value, at neutral pH values. No mineral dissolution is simulated under abiotic conditions, even after decades of interaction with H_2 .

When the effect of bacteria is considered through kinetic rates of sulfate-reduction, acetogenesis and methanogenesis, H_2 is simulated to react during its underground storage. Regarding the gas composition evolution, about half of H_2 is simulated to be converted to CH_4 during the first year of the injection scenario considering the effect of bacteria. CH_4 is produced using the injected H_2 and the inorganic carbon species initially present in solution and, then, the carbonates liberated by the dissolution of carbonate minerals. Note that acetogenesis also uses a fraction of the inorganic carbon in solution and from calcite. The small amount of CO_2 initially present in the gas phase is consumed by the acetogenesis and methanogenesis reactions. Despite being considered in the calculations, sulfate-reduction is less pronounced than methanogenesis and no substantial H_2S production is to report. The low amount of sulfate-reduction is due to the small stock of sulfate in the system, limited to the initially dissolved sulfate. This would change dramatically if the reservoir contained sulfate minerals.

Some mineral dissolution is also simulated when the effect of bacteria is considered. Carbonate minerals (dolomite and calcite) and pyrite are the phases expected to be partially dissolved because of H₂. The considered sandstone or siliciclastic reservoirs contain between 1 and 20% of carbonate minerals and 0.3 to 1% are simulated to dissolve. When dolomite and calcite are present, dolomite is preferentially dissolved. In siliciclastic reservoirs, no pyrite to 0.7% of pyrite are initially present. In presence of pyrite, 0.2% of pyrite are reduced to pyrrhotite. The considered carbonate reservoirs contain 55% and 71% of carbonate minerals and 0.3% and 3.3% of dolomite are simulated to dissolve. When present in the carbonate reservoir mineralogical assemblage, about 1% of pyrite is reduced to pyrrhotite.



Fluid chemistry is also changed according to the model that considers the effect of bacteria activity, with an increase of the pH up to a value of 12 (defined in the model as a limit for the microbially mediated H_2 reactions. Without bacteria, the pH remains at its initial near neutral value.

The calculations of the reactivity of H_2 in different reservoirs show that the presence or the absence of bacteria able to catalyse the reduction reaction induced by H_2 is crucial. Without bacteria, H_2 acts as an inert gas and does not induce reactivity. When bacteria are present, the progress of the reactions of sulfate-reduction, acetogenesis and methanogenesis is kinetically controlled and some amount of reactions are expected. According to the simulations, the main expected effects are a partial conversion of H_2 to CH_4 and a pronounced increase of the pH. However, the reactivity model needs to be calibrated on further experimental data and observations on gas storage operations, because the model parameters are derived from only one study.



5.Model of H₂ reactivity at Lobodice town gas storage

The literature review and the previous simulations of H₂ reactivity on the generic sandstone have highlighted the importance of the kinetics of aqueous redox reactions involving H₂. The application of these kinetics rates of sulfate-reduction and methanogenesis reactions to real reservoir conditions is uncertain because these rates were obtained from few experiments and the upscaling of these rates is perhaps not direct. In this section, a model of H₂ reactivity is applied to the case of Lobodice town gas storage, where conversion of H₂ and CO₂ to CH₄ have been documented (Smigan et al., 1990; Buzek et al., 1994). The goal is to evaluate if the kinetic rates used in the generic model can simulate the H₂ reactions at Lobodice gas storage or if it is necessary to adjust the kinetic rates.

The Lobodice reservoir is hosted in sediments of lower Badenian age in the Carpathian Foredeep (Eastern part of The Czech Republic). The reservoir consists of water saturated strata in an anticline structure and is made of gravels and sandstones. It has a thickness of about 18 m and is overlain by about 300 m of a caprock formed by impermeable clay rocks and clay sands. The reservoir was used as a town gas storage from 1965 to 1991 and has been used for natural gas storage since 1991. The temperature varies between 25°C and 45°C and the exploitation pressure was between 4.5 and 5.9 MPa. Before its conversion into a natural gas storage, the evolution of the town gas composition has been monitored in the Lobodice reservoir (Smigan et al., 1990; Buzek et al., 1994). During 7 months of storage, 10 to 20% of the gas volume was lost and the composition of the gas changed, with an increase in CH₄ and decreases in H₂, CO₂ and CO. The stored gas initially composed of 54% H₂, 22% CH₄, 12% CO₂, 9% CO and 2.5% N₂ evolved after being stored during 7 months to 40% CH₄, 37% H₂, 9% CO₂, 9% N₂ and 3% CO. The formation of CH₄ observed at Lobodice was accompanied by growth of methanogenic bacteria and a development in the isotopic signature of CH₄ typical for microbially generated CH₄.

The composition of the mineralogical assemblage and the pore water used in the model were taken from Labus et al. (2016). These mineral and water composition data correspond to another reservoir of Badenian age in the Carpathian foredeep, deeper than Lobodice reservoir, but are used in absence of site-specific data. A temperature of 25°C and a pressure of 50 bar are considered in the model. Mineral dissolutions and precipitations are controlled by kinetics.

In the models tested using a generic sandstone assemblage, only the model considering a global rate of H_2 consumption simulates a progressive conversion of H_2 to CH_4 . Therefore, this model is used, as a first approach.

The calculated gas composition evolution is shown in Figure 14 and compared to the measured gas composition at Lobodice at the time of injection and after 7 months of storage. For this simulation a global rate of H₂ consumption of $2 \cdot 10^{-8}$ mol/s is used, corresponding to the rate used for this model in the generic case calculations. Although not exactly fitting the evolution of the gas composition, the range of variation of the observed CH₄ formation and



the H_2 and CO_2 consumption is satisfactorily reproduced using the *a priori* rate of H_2 consumption. The simulated evolution in the mineralogical assemblage during town gas storage at Lobodice is shown in Figure 15. No changes in mineral composition are simulated during town gas storage. Carbonate minerals are not dissolved because of the presence of CO_2 in the gas phase, which is preferentially consumed during methanogenesis. In the calculations of the reactivity of H_2 in a generic sandstone, carbonate in calcite was consumed to form CH₄. The presence of a surplus of CO_2 works as an acidic pH buffer together with the carbonate minerals, implying a relatively stable pH (pH between 5.8 and 6.3 in the simulations).

A kinetic rate of H_2 consumption in the range of the kinetic rate used in the generic simulations and obtained from the experiments of Berta et al. (2018) seems able to simulate H_2 reactivity at the reservoir scale. This is contrary to expectations since you would expect the only partially saturated conditions in the gas storage to have a negative effect on the microbial rates. However, it should be recalled that methanogenesis was not observed in the experiments of H_2 induced redox reactions made by Berta et al. (2018), but only sulfate-reduction and acetogenesis. Therefore, some caution is needed in the interpretation of the model.



Figure 14: Monitored gas composition evolution in Lobodice town gas storage and modelled evolution using a global rate of H_2 consumption of 2 10⁻⁸ mol/s.



Figure 15: Simulated mineral evolution of Lobodice during H_2 injection, using a global rate of H_2 consumption of 2 10⁸ mol/s.



6.Extension of H₂ reactivity model to 3D

As described previously, the batch simulations of H_2 reactivity under abiotic conditions have shown that the reactions are quite limited for most of the cases . When bacteria are not catalysing the redox reactions induced by H_2 , no mineral dissolution are simulated. Under abiotic conditions, the gas phase remains mainly composed of H_2 , without conversion of H_2 to CH₄.

Very little impact is foreseen in these 0-D kinetic simulations without microbial activity. The simulations do not consider any renewal of gas or brine overtime. The mineral composition does not vary significantly, and hydrogen does not react under these conditions. In most cases, no H₂S and no CH₄ is generated, and pH remains constant. In one of the cases, there is some reactivity due to bicarbonate present in solution.

To verify the non-reactive abiotic behaviour in a transport situation, two different mineralogy are modelled for one of the synthetic cases elaborated in Task 2.1 (Hystories D2.2, 2022). The same storage model will be assigned different mineral compositions corresponding to a carbonate and sandstone formation. The model considers the same operational conditions as in Task 2.1 i.e., an initial injection of hydrogen for one year, followed by several seasonal cycles (injection/withdrawal) of hydrogen through a set of four horizontal wells. The initial conditions of the models assume a storage in a deep saline formation, the pressure and temperature conditions are related to the abiotic 0-D cases. For each composition, the brine is assumed to initially be in equilibrium with the minerals. The simulation runs were performed with the 2021.10 commercial version of GEM[™].

The petrophysical (porosity, permeability) parameters are distributed within the storage as shown in Figure 16



Figure 16: Distribution of the key petrophysical parameters of the storage and well locations



6.1.Hydrogen reactivity simulation in an abiotic carbonate storage

For the carbonate case, the mineral composition and kinetic parameters considered are summarized in Table 4 below and are consistent with the 0-D model. The initial conditions of the storage are shown in Table 5.

Table 4: Kinetic parameters for the carbonate case					
Mineral	Volume Fraction	Reactive surface (m ² mol ⁻¹)	log k* (mol m ⁻² s ⁻¹)	Activation Energy* (kJ mol ⁻¹)	
Calcite	0.70	0.7	-5.81	23.5	
Pyrite	0.02	0.05	-4.55	56.9	
Quartz	0.13	0.05	-13.99	87.6	
Pyrrhotite	0.00	0.05	-8.04	50.8	
Dolomite	0.03	0.09	-7.53	52.2	
Chlorite	0.03	0.0027	-12.52	88	
Illite	0.10	30	-14.41	48	

* from Palandri and Kharaka (2004)

Table 5: Initial conditions for the carbonate case

	Initial Condition	Unit
Pressure	100	bar
Temperature	67	°C
рН	6.2	
Water Saturation	1	
Salinity	~2	g/L

The results of the 3-D model (Figure 16 to Figure 22) are consistent with the 0-D result with no mineral changes and no release of hydrogen sulfide and no significant pH change. In this modelling, hydrogen either in the gas phase or dissolved in the water phase remains in the vicinity of the wells. When extending the simulation period (Figure 23), the same behavior is observed: no impact on hydrogen injection on the storage rock. Similarly, when increasing the reactivity of the different minerals, no change was predicted.





Figure 17: Distribution at initial conditions for pH, gas saturation and minerals changes (pyrite, calcite, dolomite) and mole fractions of hydrogen sulfide and hydrogen for carbonate case



Figure 18: Distribution at the end of initial fill up for pH, gas saturation and minerals changes (pyrite, calcite, dolomite) and mole fractions of hydrogen sulfide and hydrogen for carbonate case





Figure 19: Distribution at the end of second injection period for pH, gas saturation and minerals changes (pyrite, calcite, dolomite) and mole fractions of hydrogen sulfide and hydrogen for carbonate case



Figure 20: Distribution at the end of third production period for pH, gas saturation and minerals changes (pyrite, calcite, dolomite) and mole fractions of hydrogen sulfide and hydrogen for carbonate case





Figure 21: Distribution at the end of last production period for pH, gas saturation and minerals changes (pyrite, calcite, dolomite) and mole fractions of hydrogen sulfide and hydrogen for carbonate case



Figure 22: Distribution at the end of last injection period for pH, gas saturation and minerals changes (pyrite, calcite, dolomite) and mole fractions of hydrogen sulfide and hydrogen for carbonate case





Figure 23: Distribution at the end of the seasonal cycles for pH, gas saturation and minerals changes (pyrite, calcite, dolomite) and mole fractions of hydrogen sulfide and hydrogen for carbonate case

6.2.Hydrogen reactivity simulation in an abiotic sandstone storage

For the sandstone case, the mineral composition and kinetic parameters considered are summarized in Table 4 below and are consistent with the 0-D model. The initial conditions of the storage are shown in Table 5.

Mineral	Volume Fraction	Reactive surface (m ² mol ⁻¹)	log k* (mol m ⁻² s ⁻¹)	Activation Energy* (kJ mol ⁻¹)
Calcite	0.11	0.7	-5.81	23.5
Pyrite	0.00	0.05	-4.55	56.9
Quartz	0.63	0.05	-13.99	87.6
Pyrrhotite	0.00	0.05	-8.04	50.8
Dolomite	0.11	0.09	-7.53	52.2
Chlorite	0.01	0.0027	-12.52	88
Plagioclase	0.07	0.08	-12.56	69.8
K-feldspar	0.05	0.11	-12.41	38
Illite	0.02	30	-14.41	48

Table 6: Kinetic parameters for the sandstone case

* from Palandri and Kharaka (2004)



Table 7: Initial conditions for the sandstone case			
	Initial Condition	Unit	
Pressure	78	bar	
Temperature	40	°C	
рН	6.2		
Water Saturation	1		
Salinity	~6	g/L	

The results of the 3-D model (Figure 24 to Figure 29) are consistent with the 0-D result with no mineral changes and no release of hydrogen sulfide and no significant pH change. In this modelling, hydrogen either in the gas phase or dissolved in the water phase remains in the vicinity of the wells.



Figure 24: Distribution at initial conditions for pH, gas saturation and minerals changes (pyrite, calcite, dolomite) and mole fractions of hydrogen sulfide and hydrogen for sandstone case



Figure 25: Distribution at the end of initial fill up for pH, gas saturation and minerals changes (pyrite, calcite, dolomite) and mole fractions of hydrogen sulfide and hydrogen for sandstone case





Figure 26: Distribution at the end of second injection period for pH, gas saturation and minerals changes (pyrite, calcite, dolomite) and mole fractions of hydrogen sulfide and hydrogen for sandstone case



Figure 27: Distribution at the end of third production period for pH, gas saturation and minerals changes (pyrite, calcite, dolomite) and mole fractions of hydrogen sulfide and hydrogen for sandstone case





Figure 28: Distribution at the end of last production period for pH, gas saturation and minerals changes (pyrite, calcite, dolomite) and mole fractions of hydrogen sulfide and hydrogen for sandstone case



Figure 29: Distribution at the end of last injection period for pH, gas saturation and minerals changes (pyrite, calcite, dolomite) and mole fractions of hydrogen sulfide and hydrogen for sandstone case



7. Discussion and conclusions

The reactivity of H₂ in underground hydrogen storage and its impact remain difficult to evaluate, in particular for a storage in porous reservoirs or aquifers. The appropriate models able to predict with confidence the reactivity of H_2 are still under construction. This uncertainty in the evaluation of the reactivity of H₂ is the consequence of the complex coupling with bacterial activity that catalyse the reactivity of H₂ with dissolved and chemical species and with the rock minerals. To date, there are very few experimental studies describing the reactivity of H_2 in the gas, water and with the minerals under conditions corresponding to an underground hydrogen storage. For an extrapolation of the experimental results in models, the reactivity of H₂ identified in these experiments also needs to be quantified and related to chemical, mineralogical or biological processes. Building a model from laboratory observations and measurements is a first still on-going step, but it will not be sufficient to achieve robust predictions of the H_2 reactivity at the reservoir scale. Indeed, the reaction rates determined in laboratory conditions, for example the mineral dissolution and precipitation rates, are rarely of direct use in geological media because of the pore water and minerals accessibility compared to dispersed powders frequently used in experiments, because the reactions rates are often determined far from the thermodynamic equilibrium or because of the different duration of the interaction. One interesting option to calibrate a model of H₂ reactivity at the reservoir scale could be to reproduce the reactivity observed in past H_2 storage operations. However, the information on these H_2 storages in reservoirs is scarce, restricted to the gas composition evolution and rarely available, at the exception of the town gas storage of Lobodice, which is documented by two publications.

In the present study, different modelling approaches have been implemented and tested to simulate the H_2 reactivity in a generic sandstone reservoir. These models assess the way to consider the aqueous redox reactions induced by H_2 and go from considering a thermodynamic equilibrium to introducing kinetic control on these reactions.

Our calculations show that the reactivity due to H_2 seems exaggerated when the aqueous redox reaction induced by H_2 , such as sulfate-reduction and methanogenesis, are considered at thermodynamic equilibrium. Indeed, when compared to H_2 storages in reservoirs, a total dissolution of the reactive minerals of the rock, including at relatively low partial pressure of H_2 , is not expected. Similarly, a massive, sometimes total, conversion of H_2 to CH_4 is simulated but unexpected. The conversion of 20 % H_2 to CH_4 monitored at Lobodice storage reservoir is already an indication of a substantial reactivity.

Therefore, the approaches to simulate H_2 reactivity needs to consider the catalytic role of bacteria on the aqueous redox reactions involving H_2 . Under abiotic conditions, there is no reaction catalysis by bacteria and this situation can be modelled by considering an inert species of H_2 . With this modelling assumption, there is no reactivity and, then, this model can be used for different problems where H_2 is inert (evolution of water and gas during the storage of gas mixture in saline formations or at high pressure, for example) but not for evaluating the H_2 reactivity. Two models were established to consider progressive redox reactions induced by H_2 , but without explicitly considering bacterial activity such as in Monod type growth models. Considering bacterial dynamics is beyond the scope of this Hystories work package and, for the sake of simplicity, it is interesting to evaluate if a model without specifically modelled biological processes can simulate H_2 reactions. Using models including a kinetic



control on redox reactions, it is possible to simulate progressive minerals changes. However, the models still suggest large changes in pH and the gas phase composition. Compared to the model considering a global reaction rate on H₂ consumption, the model including kinetics on individual redox processes is promising. This model was established based on the study of Berta et al. (2018) that stipulates that the rates of acetogenesis and sulfate-reduction reactions obtained in experiments can be modelled without considering microbial dynamics. However, methanogenesis was not observed in the Berta et al. (2018) experiments and, then, CH₄ is not considered in the model and is currently a limitation in the application of the model. The sensitivity analysis made on the rates of acetogenesis and sulfate-reduction shows that the kinetic rates determined at the laboratory can probably not be used as directly in a geological reservoir but it seems that these rates will only need small adjustments (about one order of magnitude) for this application.



8.References

- Beckingham, L.E., Winningham, L., 2020. Critical Knowledge Gaps for Understanding Water-Rock-Working Phase Interactions for Compressed Energy Storage in Porous Formations. ACS Sustainable Chem. Eng. 8, 2–11.
- Berta, M., Dethlefsen, F., Ebert, M., Schäfer, D., Dahmke, A., 2018. Geochemical Effects of Millimolar Hydrogen Concentrations in Groundwater: An Experimental Study in the Context of Subsurface Hydrogen Storage. Environ. Sci. Technol. 52, 4937–4949.
- Bourgeois, J.P. Aupaix N. Bloise R. Millet J.L., 1979. Proposition d'explication de la formation d'hydrogène sulfuré dans les stockages souterrains de gas naturel par reduction des sulfures minéraux de la roche magasin. Revue de l'Institut Français du Pétrole 34, 371–386.
- Buzek, F., Onderka, V., Vančura, P., Wolf, I., 1994. Carbon isotope study of methane production in a town gas storage reservoir. Fuel 73, 747–752.
- Computer Modeling Group, GEM™ release 2021.10 https://www.cmgl.ca/software/general-release-2021.
- Dopffel, N., Jansen, S., Gerritse, J., 2021. Microbial side effects of underground hydrogen storage Knowledge gaps, risks and opportunities for successful implementation. International Journal of Hydrogen Energy 46, 8594–8606.
- Esnault, L., Libert, M., Bildstein, O., Jullien, M., Mustin, C., 2010. Clay-iron reducing bacteria interaction in deep geological environment: experimental and modeling approach. Water-Rock Interaction 13, 939–942.
- Flesch, S., Pudlo, D., Albrecht, D., Jacob, A., Enzmann, F., 2018. Hydrogen underground storage—Petrographic and petrophysical variations in reservoir sandstones from laboratory experiments under simulated reservoir conditions. International Journal of Hydrogen Energy 43, 20822–20835.
- Hassanpouryouzband, A., Adie, K., Cowen, T., Thaysen, E.M., Heinemann, N., Butler, I.B., Wilkinson, M., Edlmann, K., 2022.
- Geological Hydrogen Storage: Geochemical Reactivity of Hydrogen with Sandstone Reservoirs. ACS Energy Letters, 7, 2203-2210.
- Heinemann, N., Alcalde, J., Miocic, J.M., Hangx, S.J.T., Kallmeyer, J., Ostertag-Henning, C., Hassanpouryouzband, A., Thaysen,
 E.M., Strobel, G.J., Schmidt-Hattenberger, C., Edlmann, K., Wilkinson, M., Bentham, M., Stuart Haszeldine, R.,
 Carbonell, R., Rudloff, A., 2021. Enabling large-scale hydrogen storage in porous media the scientific challenges.
 Energy Environ. Sci. 14, 853–864.
- Henkel, S., Pudlo, D., Werner, L., Enzmann, F., Reitenbach, V., Albrecht, D., Würdemann, H., Heister, K., Ganzer, L., Gaupp, R., 2014. Mineral Reactions in the Geological Underground Induced by H2 and CO2 Injections. Energy Procedia 63, 8026–8035.
- Hernsdorf, A.W., Amano, Y., Miyakawa, K., Ise, K., Suzuki, Y., Anantharaman, K., Probst, A., Burstein, D., Thomas, B.C., Banfield, J.F., 2017. Potential for microbial H2 and metal transformations associated with novel bacteria and archaea in deep terrestrial subsurface sediments. The ISME Journal 11, 1915–1929.
- HYSTORIES D2.2. 2022. 3D multi-realization simulations for fluid flow and mixing issues at European scale.
- Jacquemet, N., Pironon, J., Lagneau, V., Saint-Marc, J., 2012. Armouring of well cement in H2S–CO2 saturated brine by calcite coating Experiments and numerical modelling. Applied Geochemistry 27, 782–795.
- Kiran, R., Teodoriu, C., Dadmohammadi, Y., Nygaard, R., Wood, D., Mokhtari, M., Salehi, S., 2017. Identification and evaluation of well integrity and causes of failure of well integrity barriers (A review). Journal of Natural Gas Science and Engineering 45, 511–526.
- Labus, K., Bujok, P., Klempa, M., Porzer, M., Matýsek, D., 2016. Preliminary geochemical modeling of water-rock-gas interactions controlling CO2 storage in the Badenian Aquifer within Czech Part of Vienna Basin. Environmental Earth Sciences 14, 1086.
- Libert, M., Bildstein, O., Esnault, L., Jullien, M., Sellier, R., 2011. Molecular hydrogen: An abundant energy source for bacterial activity in nuclear waste repositories. Physics and Chemistry of the Earth, Parts A/B/C 36, 1616–1623.
- MARCOGAZ, 2017. Guidance: injection of Hydrogen/natural gas admixtures in Underground Gas Storage (UGS). Technical Association of the European Natural Gas Industry.
- Palandri, J. L., and Kharaka, Y. K. 2004.A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling. US Geological Survey Report 2004-1068.
- Pérez, J. A. Pérez E. Dupraz S. Bolcich, 2016. Patagonia Wind-Hydrogen project: underground storage and methanation, in: 21stWorldHydrogenEnergyConference2016.Zaragoza,Spain.
- RAG, 2017. Underground Sun Storage. RAG Austria AG.
- Reitenbach, V., Ganzer, L., Albrecht, D., Hagemann, B., 2015. Influence of added hydrogen on underground gas storage: a review of key issues. Environmental Earth Sciences 73, 6927–6937.
- Seewald, J.S., Zolotov, M.Y., McCollom, T., 2006. Experimental investigation of single carbon compounds under hydrothermal conditions. Geochimica et Cosmochimica Acta 70, 446–460.
- Shi, Z., Jessen, K., Tsotsis, T.T., 2020. Impacts of the subsurface storage of natural gas and hydrogen mixtures. International Journal of Hydrogen Energy 45, 8757–8773.
- Smigan, F. P. Greksak M. Kozankova J. Buzek, Onderka, V., Wolf, I., 1990. Methanogenic bacteria as a key factor involved in changes of town gas stored in an underground reservoir. FEMS Microbiology Letters 73, 221–224.



- Tarkowski, R., 2019. Underground hydrogen storage: Characteristics and prospects. Renewable and Sustainable Energy Reviews 105, 86–94.
- Thaysen, E.M., McMahon, S., Strobel, G.J., Butler, I.B., Ngwenya, B.T., Heinemann, N., Wilkinson, M., Hassanpouryouzband, A., McDermott, C.I., Edlmann, K., 2021. Estimating microbial growth and hydrogen consumption in hydrogen storage in porous media. Renewable and Sustainable Energy Reviews 151, 111481.
- Truche, L., Berger, G., Destrigneville, C., Guillaume, D., Giffaut, E., 2010. Kinetics of pyrite to pyrrhotite reduction by hydrogen in calcite buffered solutions between 90 and 180°C: Implications for nuclear waste disposal. Geochimica et Cosmochimica Acta 74, 2894–2914.
- Truche, L., Berger, G., Destrigneville, C., Pages, A., Guillaume, D., Giffaut, E., Jacquot, E., 2009. Experimental reduction of aqueous sulphate by hydrogen under hydrothermal conditions: Implication for the nuclear waste storage. Geochimica et Cosmochimica Acta 73, 4824–4835.
- Truche, L., Jodin-Caumon, M.-C., Lerouge, C., Berger, G., Mosser-Ruck, R., Giffaut, E., Michau, N., 2013. Sulphide mineral reactions in clay-rich rock induced by high hydrogen pressure. Application to disturbed or natural settings up to 250°C and 30bar. Chemical Geology 351, 217–228.
- Yekta, A.E., Pichavant, M., Audigane, P., 2018. Evaluation of geochemical reactivity of hydrogen in sandstone: Application to geological storage. Applied Geochemistry 95, 182–194.





Hystories project consortium





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Mineral and Energy Economy Research Institute Polish Academy of Sciences

MicroPro GmbH

Microbiological Laboratories

Acknowledgment

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under grant agreement No 101007176.

This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme and Hydrogen Europe and Hydrogen Europe Research



