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# HyUSPRe

## Hydrogen **U**nderground **S**torage in **P**orous **R**eservoirs

### Database of mineral reaction rates with hydrogen and their dependence on temperature and pressure.

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## Executive summary

Geological storage of hydrogen is believed to be a promising solution for balancing fluctuations in renewable energy supply and consumer energy demand. When assessing geological formations for their potential to store hydrogen, it is important to ensure that this can be done safely and economically. The key to uncovering the full potential and successfully implementing large-scale hydrogen storage is a deep understanding of hydrogen-induced geochemical reactions.

Published studies and the commercial storage of town gas (containing ~50% H<sub>2</sub>, with CH<sub>4</sub>, CO<sub>2</sub>, CO, and N<sub>2</sub>), in porous saline aquifers in the 1970's and 1980's indicate that geological hydrogen storage is technically feasible. However, several reviews have identified challenges which must be addressed to prove the safe containment and necessary recovery efficiencies of hydrogen in porous reservoirs. Of particular concern are the promotion of abiotic geochemical reactions between the reservoir rocks, formation fluids, and stored hydrogen. It is particularly important to identify the geochemical interactions between the rock and hydrogen and whether these may jeopardise storage integrity. Hydrogen induced mineralogical changes can potentially modify the porous structure of the rock, affect its storage capacity and consume or contaminate the stored hydrogen. In addition, the presence of hydrogen as an electron donor can promote redox processes that can alter the mechanical properties of the rock.

This deliverable summarises all the currently published work on the geochemical reactivity of hydrogen during geological storage in porous rocks. It draws on work published across many disciplines including that of the nuclear waste industry to present a database of mineral reaction rates with hydrogen and their dependence on temperature and pressure.

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## About HyUSPRe

### Hydrogen **U**nderground **S**torage in **P**orous **R**eservoirs

The HyUSPRe project researches the feasibility and potential of implementing large-scale underground geological storage for renewable hydrogen in Europe. This includes the identification of suitable porous reservoirs for hydrogen storage, and technical and economic assessments of the feasibility of implementing large-scale storage in these reservoirs to support the European energy transition to net zero emissions by 2050. The project will address specific technical issues and risks regarding storage in porous reservoirs and conduct an economic analysis to facilitate the decision-making process regarding the development of a portfolio of potential field pilots. A techno-economic assessment, accompanied by environmental, social, and regulatory perspectives on implementation will allow for the development of a roadmap for widespread hydrogen storage by 2050, indicating the role of large-scale hydrogen storage in achieving a zero-emissions energy system in the EU by 2050.

This project has two specific objectives. Objective 1 concerns the assessment of the technical feasibility, associated risks, and the potential of large-scale underground hydrogen storage in porous reservoirs for Europe. HyUSPRe will establish the important geochemical, microbiological, flow, and transport processes in porous reservoirs in the presence of hydrogen via a combination of laboratory-scale experiments and integrated modelling; and establish more accurate cost estimates to identify the potential business case for hydrogen storage in porous reservoirs. Suitable storage sites will be identified, and their hydrogen storage potential will be assessed. Objective 2 concerns the development of a roadmap for the deployment of geological hydrogen storage up to 2050. The proximity of storage sites to large renewable energy infrastructure and the amount of renewable energy that can be buffered versus time varying demands will be evaluated. This will form a basis for developing future scenario roadmaps and preparing for demonstrations.

## Document information, revision history, approval status

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## 1 Introduction

Changing reservoir pressure and temperature during hydrogen injection and production, coupled with dissolution of hydrogen into formation fluids, may induce mineral reactions, altering the reservoir, caprock and well cement integrity over time. In the presence of hydrogen, abiotic (nonmicrobially mediated) reactions can occur in rocks (Hassanpouryouzband et al., 2022). It is particularly important to identify the geochemical interactions between the storage rocks (reservoir and caprock) and hydrogen and whether these may compromise storage integrity and/or impact performance.

Experience with porous geological hydrogen storage was developed during the storage of town gas, containing ~50% H<sub>2</sub>, with CH<sub>4</sub>, CO<sub>2</sub>, CO, and N<sub>2</sub> (Amigan et al., 1990; Buzek et al. 1994). Town gas storage sites in Germany, France, and the Czech Republic were successfully operated for decades before they were converted to natural gas storage in the 1980's. Recognizing though that CO, CO<sub>2</sub> and traces of sulfur present in town gases make them chemically more reactive than pure hydrogen, the experience with town gas storage cannot be directly applied to storage of pure hydrogen.

More recently, the Underground Sun Storage (RAG, Austria) and HyChico (Argentina) projects successfully demonstrated that hydrogen can be safely injected into, stored and withdrawn from a depleted natural gas reservoir in mixtures with natural gas at percentages up to 20%. This pre-commercial experience supported by recent published studies consider geological hydrogen storage to be technically feasible. However, several reviews have identified challenges which must be addressed to prove the safe containment and necessary recovery efficiencies of hydrogen in porous reservoirs, (Hassanpouryouzband et al, 2021, Heinemann et al, 2021, Tarkowski et al, 2022 & 2017, Reitenbach et al, 2015 and Foh et al, 1979). These studies identified that the promotion of abiotic geochemical reactions between the reservoir rocks, formation fluids, and stored hydrogen could present a risk for the storage of hydrogen in porous reservoirs. This is because hydrogen consists of small molecules, with a high mobility in porous media and can be reactive with the minerals that make up the rock (Yekta et al., 2018). These reactions may be detrimental to geological hydrogen storage by altering the composition of the stored hydrogen and causing mineral precipitation and dissolution which may impact reservoir integrity and recovery efficiencies.

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## 2 Review of the literature on geochemical reactivity during geological hydrogen storage

Experience of town gas storage in Ketzin (Germany) and Beynes (France) provides context to the potential significance of geochemical interactions in underground hydrogen storage. In both cases, alterations to the composition of stored gas were observed. Bourgeois et al. (1979) suggest that the increased concentration of hydrogen sulfide observed at Beynes can be accounted for by the abiotic reduction of pyrite as opposed to the action of sulfate-reducing bacteria. Reitenbach et al. (2015) suggests that the hydrogen partial pressure (5–10 MPa), temperature (25 °C), and alkalinity that characterize the Beynes storage site support this argument. At Ketzin, gas losses in the order of  $2 \times 10^8$  m<sup>3</sup> were observed between 1964 and 1985; the processes causing the gas loss and evolution of gas composition have not been identified but are not considered to be sufficiently explained by microbial degradation alone, Reitenbach et al. (2015).

One of the first studies on the geotechnical feasibility of subsurface hydrogen storage was conducted by Foh et al. (1979). The authors studied the chemical mono-mineral reactions between hydrogen and 15 minerals typical of subsurface reservoirs under conditions they considered representative of a subsurface reservoir (temperature of about 40°C and pressure of 2000 psi). They concluded that underground storage of hydrogen could be conducted safely and economically. However, the authors ignored the effect of formation fluid composition and microbial interactions on hydrogen-induced geochemical reactions.

Similarly, Carden and Paterson (1979) found no major physical or chemical problems associated with underground storage of hydrogen. They did, however, recognise the possibility of hydrogen reacting with sulphur in sulphur-bearing minerals, which, being exothermic, would result in severe overheating and release of poisonous hydrogen sulphide (H<sub>2</sub>S).

Yekta et al. (2018) assessed the geochemical reactivity of hydrogen with a lower Triassic Vosges sandstone. The aim of their work was to “evaluate the mineralogical impact of hydrogen exposure on a sandstone lithology under conditions of natural hydrogen storage.” Most experiments were performed at 100°C as static batch reactor experiments using both core and powder rock samples. The study found that hydrogen had little to no effect on the Vosges sandstone lithology. It should be noted, however, that the samples in their study do not show significant mineralogical variation, with only some minor phase proportion variations (Yekta et al., 2018).

A detailed study of the hydrogen-induced geochemical reactivity of sandstones was carried out by Hassanpouryouzband et al. (2022). Using a range of sandstone samples, the authors conducted batch reaction experiments at 80 °C up to 20 MPa for 2-8 weeks, reflecting geological hydrogen storage. In their experiments, Hassanpouryouzband et al. (2022) used solutions of different salinities and samples disaggregated to particle sizes of 0.335-4 mm to enhance the kinetics of potential reactions. Hydrogen-induced geochemical reactions were assessed by comparing element concentrations in solutions after exposure to hydrogen with control experiments. In their analysis, the authors targeted 6 elements involved in potential geochemical reactions associated with hydrogen: Fe, S, Ca, Mg, K, Ba, Mn and Ni. No changes in the concentrations of these ions were detected, hence no geochemical reactions were observed. However, within the grinded rock samples, the concentrations of reactive minerals could have been too small to observe any changes in the formation water. In addition, the minerals could have interacted with each other. In addition, the steel of the reactors and lines could have scavenged any potential H<sub>2</sub>S or sulfide in the solution if it was created in the experiment. Furthermore, reservoirs at temperatures higher than 80 °C could be more conducive

for geochemical reactions. Therefore, the authors recognize the need for further investigation of potential geochemical reactions under site specific storage, rock/fluid chemistry, temperatures and pressures.

## 2.1 Hydrogen-induced pyrite reduction

Pyrite is a mineral that is particularly susceptible to hydrogen-induced alteration (Truche et al., 2010 & 2013). While it is stable in the reducing conditions of sediments (under temperature and pressure conditions of subsurface), pyrite becomes unstable in the presence of hydrogen, as the redox potential drops.

Truche et al. (2010) studied abiotic hydrogen-induced redox reactions and found that when pyrite is exposed to hydrogen, it reduces to pyrrhotite, releasing sulphide anions into the solution. Their work consisted of batch reaction experiments performed under slightly alkaline conditions with pyrite, hydrogen, and calcite-buffered solutions. At elevated hydrogen partial pressures, ranging from 3 to 30 bar (~44-435 psi) and elevated temperatures, ranging from 90 to 180°C, they observed a partial transformation of pyrite to pyrrhotite via a coupled dissolution-precipitation. Truche et al. (2013) reported the reduction of pyrite and subsequent pyrrhotite precipitation at temperatures at 90°C and higher as the dominant hydrogen-induced geochemical disturbance in clay-rich rocks, and suggest that temperature is one of the main driving forces in hydrogen-induced pyrite reduction.

It should be noted, however, that Truche et al. (2010) used fine-sized pyrite particles in their experiments, which offered a greater surface for reactions with hydrogen. This allows for higher reactivity and better assessment of the reaction rate under laboratory conditions and time scales. Under geological hydrogen storage conditions, reactive surfaces will be restricted to the mineral surface areas available in the pore network through which the hydrogen could flow. To extrapolate these results to subsurface conditions and expected H<sub>2</sub>S concentrations, a realistic surface area and concentrations of pyrite should be taken into account, as well as longer time scales (tens of years). The temperature of several hydrogen storage reservoirs is anticipated to be cooler than the 90 °C used in these experiments. Therefore, further investigation is required to confirm these results, especially at lower temperatures. Finally, the experiments of Truche were performed with 10% H<sub>2</sub> in 90% Ar at pressures of 80-180 bar, e.g. 8 and 18 bar H<sub>2</sub> (partial) pressure. The effect of higher H<sub>2</sub> partial pressures (80-200 bar) on the kinetic reaction rate has yet to be established.

## 2.2 Hydrogen induced redox reactions

Increased hydrogen concentrations in porous reservoirs will reduce the redox potential and will bring oxidized species such as electron acceptors nitrate, Fe<sup>3+</sup>, sulfate, and carbonate out of thermodynamic equilibrium. In reality, these reactions will not take place abiotically at reservoir conditions as they are either kinetically extremely slow (e.g. for sulfate reduction; see Truche, 2009) or require a very high activation energy (e.g. carbonate reduction by Fischer-Tropsch process, see e.g. Santos-Carballal et al 2021). Hydrogen-induced redox reactions with iron-bearing minerals such as hematite, and micas and clays containing Fe<sup>3+</sup> may be observed (Berta et al, 2018; Yekta et al 2018; Alpermann and Ostertag-Henning; Thuns), although it is currently not clear how fast these reactions are, which should be part of future research.

Redox reactions induced by hydrogen are mainly catalysed microbially, for example for hydrogen reactions with NO<sub>2</sub><sup>-</sup>, Fe<sup>3+</sup>, SO<sub>4</sub><sup>2-</sup>, and HCO<sub>3</sub><sup>-</sup> (Truche, 2013; Berta et al, 2018). With the right terminal electron acceptors present, hydrogen becomes a universal electron donor for bacteria and archaea and may be consumed (metabolically converted; Reitenbach et al., 2015) to produce NH<sub>3</sub>, Fe<sup>2+</sup>, H<sub>2</sub>S and CH<sub>4</sub> respectively. This phenomenon was observed by

Smigán et al. (1990) in a town gas storage in Lobodice, Czech Republic, where a change in the composition of the stored gas was noted. According to the authors, the recorded decrease in hydrogen content and an increase in CH<sub>4</sub> concentration was due to the activity of hydrogen-consuming microbes.

## 2.3 Hydrogen adsorption on clays

Many studies on hydrogen in the subsurface have been undertaken as part of nuclear waste disposal assessments. The nuclear industry investigations looked at the hydrogen migration in the subsurface and clay tightness to hydrogen (Galle and Tanai, 1998; Ortiz et al., 2002). High-level and medium-level nuclear waste are frequently disposed of in special waste canisters and then in clay rich geological formations, like the Boom Clay (Ortiz et al., 2002) or the Callovo-Oxfordian Clay (Lassin et al., 2011). The heat produced by the radioactive decay aids the anaerobic corrosion of metallic components of the waste canisters and produces significant amounts of hydrogen (Lassin et al., 2011). The hydrogen can then interact geochemically with the clay rock in which the waste container is placed (Didier et al., 2012), thus compromising its safe containment. Didier et al. (2012) studied the effects of hydrogen adsorption on Callovo-Oxfordian Clay. The Callovo-Oxfordian Clay is mainly composed of smectite/illite and calcite minerals, although there are a few components in the clay fraction known to react with hydrogen, such as pyrite and clay structural Fe<sup>(III)</sup> (Truche, 2009; Didier et al., 2012). Didier et al. (2012) found that the Callovo-Oxfordian Clay rock reacting with hydrogen at 90°C was geochemically stable. No reduction of Fe<sup>(III)</sup> was found under these temperature conditions – hydrogen slightly reduced clay structural Fe<sup>(III)</sup>, but for temperatures lower than 350 °C this is almost impossible (Didier et al., 2012). Hydrogen may be adsorbed by clay minerals, which could potentially cause a loss of hydrogen (Truche, 2018).

## 2.4 Anhydrite and calcite dissolution under hydrogen storage

Another study on the feasibility of geological hydrogen storage was conducted by Flesch et al. (2018). The authors conducted a series of static batch experiments using cores of Tertiary, Triassic and Permian silt- and sandstone samples, exposing them to hydrogen under reservoir-specific conditions (i.e. temperature, pressure, salinity) for up to 6 weeks. All core samples were examined petrologically and measured for porosity and permeability before and after the experiments, and then data was compared to determine whether any hydrogen-induced changes had occurred. Flesch et al. (2018) found that some samples showed extensive change in porosity and permeability after being exposed to hydrogen. The affected samples had pore-filling anhydrite and carbonate cements which, after the long exposure to hydrogen, extensively or totally dissolved. Hydrogen-induced dissolution of carbonates and anhydrites is not in line with fundamental geochemical understanding (e.g. Truche 2009, 2013; Santos-Carballal et al, 2021), hence it remains a puzzle whether the changes are induced by hydrogen, or are the result of any pre-treatment and/or undersaturation of the minerals in the water or reactivity with any chemicals (resin) used.

The observed prevalent dissolution of calcite and anhydrite cements resulted in newly formed pore networks responsible for the increase in porosity and permeability values. These results may be significant in the context of the present study, as the pressure and temperature range is anticipated to be similar to that of geological hydrogen storage reservoirs. If proven to occur in a subsurface hydrogen storage setting, the reactions described above hold the potential to alter reservoir and caprock porosity and permeability and thus threaten storage integrity. Therefore, further research is required to investigate the potential impacts of these reactions.

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## 2.5 Geochemical modelling of geological hydrogen storage

Hemme & van Berk (2018) created a hydrogeochemical model to identify potential risks associated with hydrogen storage in depleted gas fields. In their model, the authors assumed conditions specific to a North Sea reservoir and modelled storage periods of 30 and 300 years. The authors found that after 30 years of hydrogen storage, changes in the mineralogy of the reservoir were minimal, with dissolution and precipitation accounting for a combined porosity loss of 0.05-0.21%. In addition, the authors found that, over 30 years, hydrogen loss through microbial conversion (to CH<sub>4</sub> and hydrogen), gas-water-rock interaction and water diffusion would be approximately 76%. The results clearly show that longer storage periods lead to increased hydrogen loss.

Hassannayebi et al. (2019) conducted a study to evaluate the behaviour of the geochemical system in a depleted gas reservoir, Molasse Basin, Upper Austria, in the presence of hydrogen. To assess gas-brine-mineral interactions, they created equilibrium and primary kinetic batch models, incorporating geochemical data for brine and formation rock. They discovered that the injection of hydrogen increased the pH value of the geochemical system. Furthermore, the equilibrium geochemical model implied dissolution of primary minerals (muscovite, dolomite, pyrite, ankerite) and precipitation of secondary minerals (anorthite, pyrrhotite, clinocllore and daphnite). The equilibrium model results suggest that hydrogen can significantly affect the integrity of the Molasse Basin reservoir. However, after considering the kinetic parameters, the authors noted that the dissolution and precipitation that occurred in the equilibrium batch models are unlikely to occur on seasonal timescales, as most would require a time beyond the typical hydrogen storage cycle. The authors concluded that the possibility of hydrogen loss and disruption of reservoir integrity owing to hydrogen-induced abiotic reactions is not entirely ruled out given the range of uncertainties, primarily resulting from the absence of reliable kinetic data.

## 2.6 Kinetic limitations of geochemical reactions

It is possible that under the pressure and temperature ranges and time scales associated with seasonal hydrogen storage, mineral transformations would be kinetically limited. (Hassannayebi, 2019). However, a scarcity of experimental data has resulted in a lack of agreement in recent literature as to the significance of geochemical reactions in porous underground hydrogen storage. An insufficient account of abiotic geochemistry in geological hydrogen storage in the published literature increases uncertainty and means that this remains a technical barrier to the development of geological hydrogen storage. To facilitate the geological storage of hydrogen, the uncertainty associated with hydrogen loss and reduction in reservoir integrity because of abiotic geochemical reactions between the reservoir rocks, formation fluids, and hydrogen must be understood.

The above review highlights that investigations of abiotic hydrogen reactions in porous media are rather limited and do not sufficiently describe the extent to which geochemical reactions might be expected during geological hydrogen storage. Many studies into hydrogen geochemical reactivity are restricted to nuclear waste disposal rather than geological hydrogen storage, where storage temperatures, pressures, and fluid saturation conditions are very different. This data can be extrapolated to subsurface storage conditions, however, there is also the need to validate the reactivity with hydrogen with especially pyrite, at conditions relevant to subsurface hydrogen storage, hence experimental research should be undertaken to obtain kinetic rate laws for relevant reactions at those conditions (pH<sub>2</sub> = 50-150 bar, T = 60-120 °C).

### 3 Database of published articles assessing the geochemical reactivity of hydrogen

Data from all the experimental articles is collated into the excel file associated with this deliverable. The numbering of the sheets in the excel file follows the same order as the following list:

#### 3.1 Experimental (or Experimental and modelling) Studies

1. Hassanpouryouzband, A., Adie, K., Cowen, T., Thaysen, E.M., Heinemann, N., Butler, I.B., Wilkinson, M. and Edlmann, K., 2022. Geological Hydrogen Storage: Geochemical Reactivity of Hydrogen with Sandstone Reservoirs. *ACS Energy Letters*, 7, pp.2203-2210. <https://pubs.acs.org/doi/full/10.1021/acscenergylett.2c01024>
2. Bensing, J.P., Misch, D., Skerbisch, L. and Sachsenhofer, R.F., 2022. Hydrogen-induced calcite dissolution in Amaltheenton Formation claystones: Implications for underground hydrogen storage caprock integrity. *International Journal of Hydrogen Energy*. <https://doi.org/10.1016/j.ijhydene.2022.07.023> (no quantitative data presented only visual observations)
3. Loder, A., Siebenhofer, M., Böhm, A. and Lux, S., 2021. Clean iron production through direct reduction of mineral iron carbonate with low-grade hydrogen sources; the effect of reduction feed gas composition on product and exit gas composition. *Cleaner Engineering and Technology*, 5, p.100345. <https://doi.org/10.1016/j.clet.2021.100345>
4. Thüns, N., Krooss, B.M., Zhang, Q. and Stanjek, H., 2019. The effect of H<sub>2</sub> pressure on the reduction kinetics of hematite at low temperatures. *International Journal of Hydrogen Energy*, 44(50), pp.27615-27625. <https://doi.org/10.1016/j.ijhydene.2019.08.178>
5. Flesch, S., Pudlo, D., Albrecht, D., Jacob, A. and 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(45), pp.20822-20835. <https://doi.org/10.1016/j.ijhydene.2018.09.112>
6. Berta, M.; Dethlefsen, F.; Ebert, M.; Schäfer, D.; Dahmke, A. Geochemical effects of millimolar hydrogen concentrations in groundwater: an experimental study in the context of subsurface hydrogen storage. *Environ. Sci. Technol.* 2018, 52, 4937– 4949, DOI: 10.1021/acs.est.7b05467
7. Yekta, A. E.; Pichavant, M.; Audigane, P. Evaluation of geochemical reactivity of hydrogen in sandstone: Application to geological storage. *Appl. Geochem.* 2018, 95, 182– 194, DOI: 10.1016/j.apgeochem.2018.05.021
8. Yekta, A.E. 2017. Characterization of geochemical interactions and migration of hydrogen in sandstone sedimentary formations: application to geological storage (Doctoral dissertation, Université d'Orléans). <https://tel.archives-ouvertes.fr/tel-01713106/>
9. Henkel, S., Pudlo, D., Werner, L., Enzmann, F., Reitenbach, V., Albrecht, D., Würdemann, H., Heister, K., Ganzer, L. and Gaupp, R., 2014. Mineral reactions in the geological underground induced by H<sub>2</sub> and CO<sub>2</sub> injections. *Energy Procedia*, 63, pp.8026-8035. [doi.org/10.1016/j.egypro.2014.11.839](https://doi.org/10.1016/j.egypro.2014.11.839) (no quantitative data presented mainly visual observations)
10. Truche, L., Jodin-Caumon, M.C., Lerouge, C., Berger, G., Mosser-Ruck, R., Giffaut, E. and 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 30 bar. *Chemical Geology*, 351, pp.217-228. <https://doi.org/10.1016/j.chemgeo.2013.05.025>
11. Truche, L., Berger, G., Destrigneville, C., Guillaume, D. and 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(10), pp.2894-2914. <https://doi.org/10.1016/j.gca.2010.02.027>
12. Truche, L., Berger, G., Destrigneville, C., 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(16). p.4824- 4835. <https://doi.org/10.1016/j.gca.2009.05.043>
  13. Heinrich, E.W., Salotti, C.A. and Giardini, A.A., 1978. Hydrogen-mineral reactions and their application to the removal of iron from spodumene. In *Lithium Needs and Resources* (pp. 273-279). Pergamon. <https://doi.org/10.1016/B978-0-08-022733-7.50011-3>
  14. Giardini, A.A., Salotti, C.A. and Lakner, J.F., 1968. Synthesis of graphite and hydrocarbons by reaction between calcite and hydrogen. *Science*, 159(3812), pp.317-319. <https://www.science.org/doi/10.1126/science.159.3812.317>
  15. Giardini, A.A. and Salotti, C.A., 1969. Kinetics and relations in the calcite-hydrogen reaction and relations in the dolomite-hydrogen and siderite-hydrogen systems. *American Mineralogist: Journal of Earth and Planetary Materials*, 54(7-8), pp.1151-1172. [https://pubs.geoscienceworld.org/msa/ammin/article/54/7-8/1151/540534/Kinetics-and-relations-in-the-calcite-hydrogen?casa\\_token=e1zL2gvh0jcAAAAA:kGunRoplwgmZ0F-ZXAVzbDOHuda2FViofhKWt5gROzRjvFfQRMI26aHfA93pzoQi-wD2ew](https://pubs.geoscienceworld.org/msa/ammin/article/54/7-8/1151/540534/Kinetics-and-relations-in-the-calcite-hydrogen?casa_token=e1zL2gvh0jcAAAAA:kGunRoplwgmZ0F-ZXAVzbDOHuda2FViofhKWt5gROzRjvFfQRMI26aHfA93pzoQi-wD2ew)

### 3.2 Modelling only studies

1. Zeng, L., Keshavarz, A., Xie, Q. and Iglauer, S., 2022. Hydrogen storage in Majiagou carbonate reservoir in China: Geochemical modelling on carbonate dissolution and hydrogen loss. *International Journal of Hydrogen Energy*. <https://doi.org/10.1016/j.ijhydene.2022.05.247>
2. Labus, K. and Tarkowski, R., 2022. Modeling hydrogen–rock–brine interactions for the Jurassic reservoir and cap rocks from Polish Lowlands. *International Journal of Hydrogen Energy*, 47(20), pp.10947-10962. <https://doi.org/10.1016/j.ijhydene.2022.01.134>
3. Hemme, C. and Van Berk, W., 2018. Hydrogeochemical modeling to identify potential risks of underground hydrogen storage in depleted gas fields. *Applied Sciences*, 8(11), p.2282. <https://doi.org/10.3390/app8112282>
4. Yekta, A.E., Pichavant, M. and Audigane, P., 2018. Evaluation of geochemical reactivity of hydrogen in sandstone: Application to geological storage. *Applied Geochemistry*, 95, pp.182-194. <https://doi.org/10.1016/j.apgeochem.2018.05.021>
5. Hassannayebi, N., Azizmohammadi, S., De Lucia, M. and Ott, H., 2019. Underground hydrogen storage: application of geochemical modelling in a case study in the Molasse Basin, Upper Austria. *Environmental Earth Sciences*, 78(5), pp.1-14. <https://doi.org/10.1007/s12665-019-8184-5>
6. Bo, Z., Zeng, L., Chen, Y. and Xie, Q., 2021. Geochemical reactions-induced hydrogen loss during underground hydrogen storage in sandstone reservoirs. *International Journal of Hydrogen Energy*, 46(38), pp.19998-20009. <https://doi.org/10.1016/j.ijhydene.2021.03.116>
7. Groenenberg, R., Juez-Larré, J., Goncalvez, C., Wasch, L., Dijkstra, H., Wassing, B., Orlic, B., Brunner, L., van der Valk, K., Hajonides van der Meulen, T., and Kranenburg-Bruinsma, K., 2020. *Techno-Economic Modelling of Large-Scale Energy Storage Systems*. TNO report 2020 R12004. <https://publications.tno.nl/publication/34637698/2VA30k/TNO-2020-R12004.pdf>

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### 3.3 Conference Abstracts

1. Hassanpouryouzband, A., Thaysen, E.M., Wilkinson, M. and Edlmann, K., 2022. The Geochemistry of Pure Minerals with Pure Hydrogen in Aqueous Solutions (No. EGU22-6162). Copernicus Meetings. <https://doi.org/10.5194/egusphere-egu22-6162>
2. Hassanpouryouzband, A., Edlmann, K. and Wilkinson, M., 2021, April. Geochemistry of Geological Hydrogen Storage in Sandstone Reservoirs. In EGU General Assembly Conference Abstracts (pp. EGU21-9894). <https://doi.org/10.5194/egusphere-egu21-9894>
3. Audigane, P., Ebrahimiyehta, A. and Pichavant, M., 2015, February. Evaluation of Hydrogen migration and geochemical reactivity into underground. In 6th International Conference on Fundamentals & Development of Fuel Cells. HAL, Toulouse, France. <https://core.ac.uk/download/pdf/52718559.pdf>
4. T. Alpermann, C. Ostertag-Henning. Abiotic Redox Reactions of H<sub>2</sub> with Iron-containing Minerals under Geologic Storage Conditions. EAGE/DGMK Joint Workshop on Underground Storage of Hydrogen 24 April 2019, Celle, Germany

## 4 Summary table of the temperatures and pressures used in the geochemical reaction experiments from the available published data

Table 1 presents a summary of the temperature and pressure condition of all published data into the experimental investigation of the mineral reaction rates with hydrogen.

**Table 1 Temperature and pressure condition of the published experimental investigation into the geochemical reactivity of hydrogen during underground geological storage in porous rocks (the numbers in brackets match the paper numbers listed in section 3.1 above).**

Reference	Batch / flow experiment	Temp (°C)	Pressure (MPa)	Additional comments	Findings –
Hassanpouryouzband et al, 2022 (1)	Batch reaction vessel	50 – 80	1 – 20	Run time between 1 and 8 weeks. 2 red aeolian Permian, 1 Carboniferous, and 6 aeolian Leman (Rough gas field) sandstones	No significant reactions
Bensing et al, 2022 (2)	Batch reaction vessel - Dry hydrogen treatment	25	15	Amaltheenton Formation claystone	Calcite fossil fragment dissolution
Loder et al 2021 (3)	Batch reaction vessel	600	0.1	Reduction of mineral iron carbonate with low-grade hydrogen	Temp beyond that of geological storage
Thuns et al, 2019 (4)	Batch reaction vessel	200, 270	3,6 and 8	Effect of hydrogen pressure on the reduction kinetics of haematite at low temperatures	Temp beyond that of geological storage but showed hematite can be reduced to iron by hydrogen consumption at high temps. Pressure increased the reaction rate.
Flesch et al, 2018 (5)	Batch reaction vessel	40, 100, 130	10, 20	Range of sandstone samples, 6 week run time	No significant reactions, but Evidence of anhydrite and carbonate cement reactions – may be a result of pressure rather than hydrogen
Berta et al, 2018 (6)	Percolation columns	20	0.2 – 1.5	Investigation into shallow aquifer leakage of hydrogen	Mostly microbial related study-No significant geochemical reactions – any hydrogen consumption was through biotic sulphate reduction.
Yekta et al, 2018 (7)	Batch reaction vessel	100 - 200	1 - 10	Three sandstone types (Adamswiller, Cleebourg and Rotbach), up to 6 months	Minimal reactions with hydrogen

Reference	Batch / flow experiment	Temp (°C)	Pressure (MPa)	Additional comments	Findings –
Yekta, 2017 (8)	Batch reaction vessel	100 – 200	1-10	Buntsandstein formation, Paris basin, up to 6 months	Limited reaction between sandstone minerals and hydrogen
Henkel et al, 2014 (9)	Batch reaction vessel	Not stated	Not stated	Permian form Saxony-Anhalt, Triassic Brandenburg and Bavarian and Austrian tertiary sandstones.	CO <sub>2</sub> and hydrogen experiments.
Truche et al 2013 (10)	Batch reaction vessel	90 – 250	0.3 - 3	Sulphide mineral reactions with hydrogen in clay rich rocks. Powdered pyrite	At temps above 90°C saw a partial transformation of pyrite.
Truche et al 2010 (11)	Batch reaction vessel	90 – 180	0.8 – 1.8	Kinetic of Pyrite to Pyrrhotite by hydrogen in calcite buffered solution.	carbonates act as a buffer to keep the pyrite stable
Truche et al 2009 (12)	Batch reaction vessel	250 – 300	0.4 – 1.6	Reaction of hydrogen gas with a sulphate solution	Temperature is one of the main driving forces in hydrogen-induced pyrite reduction.
Heinrich et al 1978 (13)	Batch reaction vessel	605	13.7	Hydrogen induced reactions in pegmatitic deposits.	
Giardini et al 1968 (14)	Batch reaction vessel	480 – 835	60 – 80	Synthesis of graphite and hydrocarbons by reaction between calcite and hydrogen	
Giardini et al 1969 (15)	Batch reaction vessel	535 – 870		calcite-hydrogen reaction and relations in the dolomite-H <sub>2</sub> and siderite-hydrogen systems	

The following highlights some of the limitations and considerations from the assessment of the database of mineral reaction rates with hydrogen and their dependence on temperature and pressure:

- There are only four studies (No. 1, 11, 5, 9) at temperatures and pressures representative of geological storage, of which No. 5 is mainly a petrophysical study and No. 2 and 9 are only visual observation studies.
- Temperature in studies No. 10, 11, and 8 are in the range of geological hydrogen storage but the pressure is lower than expected during geological storage.
- All studies follow different methodologies for analysing the geochemical reactivity, highlighting the lack of a standardised methodology.
- Study No.1 confirmed there is no risk of hydrogen reactions at temperatures below 353 K (80 °C).
- Study No.10, 11 and 12 highlighted the risk of pyrite to pyrrhotite reduction by hydrogen in calcite buffered solutions at temperatures over 363 K (90 °C).

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- Despite being conducted at higher temperatures than the expected storage conditions, the temperature range of study No. 4 is close to the realistic storage conditions. This study shows that at temperatures over 473 K (200 °C), hematite can be reduced to iron by hydrogen consumption.

## 5 References

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