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► **To cite this version:**

Murad S. Abuaisha, Ahmed Rouabhi, Joel Billiotte, Faouzi Hadj-Hassen. Non–isothermal two–phase hydrogen transport in rock salt during cycling in underground caverns. *International Journal of Hydrogen Energy*, 2020, 10.1016/j.ijhydene.2020.11.152 . hal-03084358

HAL Id: hal-03084358

<https://hal.science/hal-03084358>

Submitted on 13 Feb 2023

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Non-isothermal two-phase hydrogen transport in rock salt during cycling in underground caverns

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Abstract

For a good management and precise tracks of hydrogen quantities stored in salt caverns, this paper presents a study on hydrogen transport in rock salt during cycling. It provides a novel mathematical-numerical model that couples the cavern thermodynamics with the transport mechanisms of hydrogen in the saturated rock salt in a fully coupled thermo-hydraulic framework. Both the two-phase Darcian percolation and the Fickian diffusion are used to account for hydrogen migration in the interstitial brine of the rock salt. Due to the absence of experimental data, a parametric study is furnished. The effect of cycling within the cavern on the migration mechanisms is discussed in detail. Simulations have confirmed the dependency of the Darcian percolation on the model parameters. However, for similar applications, this dependency might be limited. The value of the Fickian diffusion coefficient affects indirectly the Darcian percolation. The two-phase percolation becomes more of a piston-like for very small values of the diffusion coefficient. On a real-scale typical cavern, and over a period of 40 years, simulations have proven that the quantity of hydrogen lost into the surrounding rock salt is unimportant. Besides, cycling renders this quantity more insignificant.

Keywords: Underground salt caverns; hydrogen transport; cavern thermodynamic state; hydrogen percolation and diffusion; two-phase flow, Fickian diffusion; thermo-hydraulic coupling

1. Introduction

Driven by concerns related to climate change, energy transition has led to the use of new clean energy resources [1]. Hydrogen has been regarded as an important energy vector in this transition [2–4]. However, the increasing energy demands and the intermittency problems [5–7] require large-scale storage techniques [8, 9]. Underground salt caverns offer the most promising option owing to their low investment cost and low cushion gas requirement [9]. Rock salt/halite occurs within sedimentary rocks where it has formed from the evaporation of seawater or salty lakes. Rock salt is consequently deposited in cycles

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8 which affects its directional properties like the elastic modulus and the permeability. Depending on the
9 location, the rock salt properties, mechanical and hydraulic, differ as well.

10 During cavern operation, hydrogen undergoes changes in its temperature and pressure. Such changes
11 are expected to affect its migration into the surrounding rock domain. Hydrogen invasion into this
12 embracing rock takes place either through the rock salt itself, or through the more permeable and porous
13 interlayers (if they happen to exist). Since underground storage caverns are constructed in networks, the
14 lost hydrogen into the surrounding rock can weaken the neighboring caverns structure. Moreover, the
15 cost of hydrogen production as well as a good management of storage require to keep precise tracks of
16 the injected and withdrawn hydrogen quantities. Studies addressing hydrogen or gas transport through
17 rock salt are scarce. For instance, *Liu et al.* [10] provided a cavern scale study to estimate the hydrogen
18 tightness. Their approach assumed that hydrogen filtrates through the rock salt following a Darcian flow
19 type. Besides, they assigned a relatively small permeability value to the rock salt while assuming a zone
20 of dilatancy. They eventually concluded that the salt caverns are hydrogen-tight except for the regions
21 of interlayers which can also be considered as hydrogen-tight for permeabilities less than 10^{-18} m². *Liu*
22 *et al.* [11] presented a general study about gas tightness of abandoned salt caverns. Though their study
23 did not include hydrogen, they have concluded that the permeability of the interlayers was a key factor
24 in influencing gas seepage in the vicinity of the caverns and that interlayers formed primary channels for
25 gas migration. They used as well a generalized Darcian flow type model to evaluate the fluid seepage
26 around the cavern. They found that the upper threshold permeability of the interlayers must be no more
27 than 10^{-16} to 10^{-17} m² to guarantee tightness when storing natural gas, and no more than 10^{-16} m²
28 when storing oil. There are, however, considerable research papers that treat hydrogen percolation and
29 diffusion in the clay sedimentary basins in the context of radioactive waste storage [12, 13].

30 Since rock salt contains interstitial brine and characterized by extremely low permeabilities and porosi-
31 ties, the application of one-phase generalized Darcian flow to describe hydrogen transport is questioned.
32 Moreover, none of the available literature is addressing the effect of cavern cycling on the migration mech-
33 anisms. Indeed, the cavern thermodynamic state is a function of cycling. Consequently, in the cavern
34 vicinity, both the interstitial rock salt brine pressure and temperature evolutions are functions of cycling
35 as well. These changes in the interstitial brine pressure and temperature must influence the migration
36 of hydrogen into the rock domain. The novelty of this research stems from providing a mathematical-
37 numerical model that couples the cavern thermodynamics with the non-isothermal transport mechanisms
38 of hydrogen into the rock salt. Both the Darcian two-phase percolation and the Fickian diffusion are
39 considered as well as the interaction between them. This model addresses as much as possible of the
40 problem complex physics for good estimation of the exchanged hydrogen mass. Besides, it precisely
41 presents effect of cycling. Due to the absence of any literature or experimental data treating hydrogen
42 migration in saturated rock salt, we offered a parametric study that investigated the effect of the two-

43 phase van Genuchten model parameters as well as the Fickian diffusion coefficient on the total mass of
44 exchanged hydrogen. The van Genuchten model allows to describe the two-phase percolation of hydrogen
45 (characterized by very low viscosity) in rock salt (characterized by very small pore size)¹. Eventually,
46 an overestimating scenario of model parameters, of diffusion coefficient, and of boundary conditions, was
47 considered to estimate the amount of hydrogen migrated during a 40-year period of hydrogen cycling in
48 a typical spherical cavern.

49 This paper proceeds as follows: the problem of hydrogen migration in the context of underground
50 storage is first presented; the expected transport mechanisms between the cavern phases are discussed;
51 the mathematical and numerical models are then shown for cycling in a typical spherical cavern; after the
52 parametric study is implemented, an overestimating scenario is simulated for a 40-year time period of
53 cycling. The simulations have shown that even for a pessimistic scenario of overestimating model param-
54 eters and boundary conditions, the amount of lost hydrogen into the rock domain rests very negligible
55 compared to the cycled mass of hydrogen.

56 **2. Hydrogen migration in rock salt**

57 This section aims at addressing the problem of hydrogen exchange/transport mechanisms in the con-
58 text of underground storage. Each mechanism is described briefly and an overall conclusion is eventually
59 drawn about the mechanism that will be considered in the simulations.

60 *2.1. Hydrogen storage in salt caverns*

61 Solution mining is commonly used to create large caverns in rock salt formations. In this process, a
62 single well, drilled from the ground surface to the targeted depth (Fig. 1(a)), is generally used to inject
63 fresh water and withdraw brine through a concentric tubing system (the leaching process) [16, 17]. Once
64 leaching is completed, brine within the cavern is reduced to minimal quantities by a debrining/filling
65 phase where it is moved out by hydrogen injection [18, 19].

66 Figure 1(a) shows an underground cavern filled with hydrogen at a certain pressure and temperature.
67 The figure also depicts the amount of brine left in the cavern at the end of the debrining process. Hydrogen
68 within the cavern is expected to experience cycles of pressure and temperature changes according to the
69 intended usage. During its life time, the cavern mainly contains, simultaneously or sequentially, two
70 different immiscible phases: the stored hydrogen and the brine. The third important phase of this
71 storage outline is the surrounding rock salt domain. This domain is constituted of the salt mass which
72 itself is a mixture of grains or crystals of halite and the brine occupying the inter-grain spaces. Each of the

¹This type of percolation is defined using the capillary and mobility numbers, for details see *Yortsos et al.* [14], *Lenormand* [15]

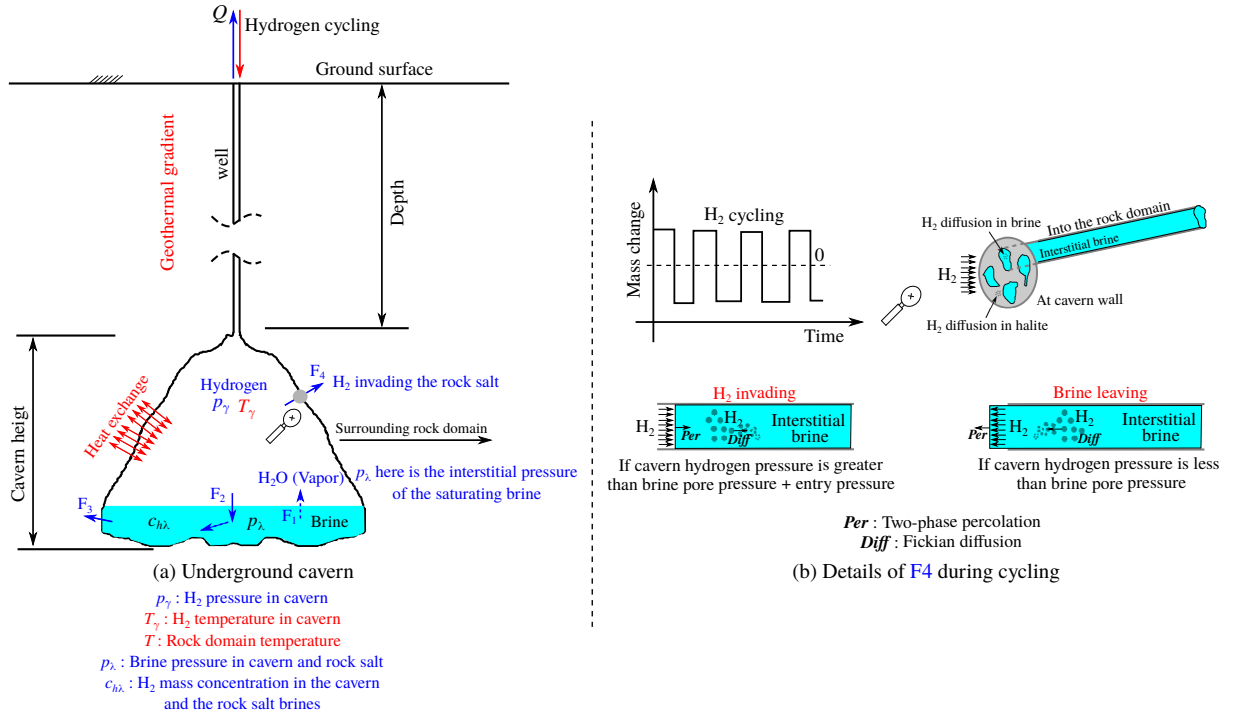


Figure 1: (a) Schematic representation of hydrogen storage in salt caverns and its transport mechanisms between phases. (b) Transport of hydrogen into the rock salt domain (flux F_4).

73 three phases is characterized by state variables which are for hydrogen: the pressure and the temperature,
 74 for brine: the pressure, the temperature, the salt concentration, and the hydrogen concentration, for the
 75 rock salt: the stress and the temperature. Since hydrogen may be present in the non-gaseous phase in
 76 the other phases (brine and solid), its presence will be characterized by a mass concentration.

77 While the cavern is operated, the three phases are interacting as follows (Fig. 1(a)): brine is evap-
 78 orating into the stored hydrogen (F_1); hydrogen is dissolving in the brine (F_2) and is percolating and
 79 diffusing into the porous rock salt (F_4); brine at the cavern bottom is flowing into the rock salt with its
 80 dissolved hydrogen (F_3).

81 2.2. Transport mechanisms

82 Transport mechanisms between phases include three components: the cavern hydrogen-brine inter-
 83 action; the brine-rock salt interaction; and the hydrogen-rock salt interaction. The first component
 84 happens at the hydrogen-brine interface within the cavern where hydrogen dissolves in brine (flow F_2 in
 85 Fig. 1(a)) according to Henry's law [20]. The dissolution induces a flow of hydrogen in the brine which
 86 enriches the hydrogen concentration by diffusion [21, 22] and convection [24, 25].

87 In the second component the brine-rock salt interface moves depending on the degree of salinity of
 88 the cavern brine. Salt can precipitate from brine onto the interface or the interface can be worn away

89 by the brine to achieve saturation continuity at the cavern working temperature and pressure [26–28].
90 As the cavern brine pressure is equal to the cavern hydrogen pressure, cavern brine can flow into the
91 saturated rock salt, or the interstitial rock salt brine can move out into the cavern (flow F_3 in Fig. 1(a)).
92 Due to the ambiguity with regard to knowing the inter–grain connectivity of rock salt, the pressure of
93 the interstitial brine is poorly defined. However, its value can be limited to two extreme values [29]:

- 94 1. the so–called halmostatic pressure, which considers that the brine occupies a totally connected
95 space in the rock mass. Consequently, this pressure is the equivalent to the hydrostatic pressure
96 calculated using the brine density;
- 97 2. a lithostatic pressure, which considers that the brine occupies an isolated space in the rock salt
98 phase. Therefore, the brine pressure is assumed in equilibrium with the geologic stresses of the rock
99 salt mass. This pressure extremity is calculated using the rock salt density [30].

100 At the hydrogen–rock salt interface (see also Fig. 1(b)), the penetration of hydrogen into the saturated
101 rock salt (flow F_4 in Fig. 1(a)) can take place either [31]:

- 102 1. in the solid phase itself, i.e. the halite crystals;
- 103 2. in the interstitial brine.

104 These are two different mechanisms, the first is equivalent to hydrogen diffusion in the solids [32, 33]. The
105 second includes hydrogen Fickian diffusion in the interstitial brine and the two–phase Darcian percolation
106 [13, 34, 35].

107 During cycling, the fluxes F_2 , F_3 , and F_4 need to be considered in order to calculate the total mass
108 of exchanged hydrogen. Only flow F_4 will be considered in this research paper. Flows F_2 and F_3 will be
109 addressed in a future research.

110 **3. Mathematical and numerical models**

111 This section presents the mathematical and numerical models needed to evaluate the quantity of
112 hydrogen transported to the rock salt domain surrounding a typical underground cavern. Simulations are
113 done for a seasonal cycling in a spherical cavern created at 910 m depth and for a 40–year time period.

114 *3.1. The mathematical model*

115 The mathematical model couples the hydrogen thermodynamics in the cavern with the non–isothermal
116 hydrogen transport in the saturated rock salt domain. To simplify the problem, the following assumptions
117 are made. Some assumptions are adopted for an overestimating study:

- 118 1. the underground cavern is assumed to be filled with a mono–component single–phase hydrogen;

- 119 2. hydrogen cycling is seasonal/slow, consequently, a uniform thermodynamic state is assumed within
120 the cavern [36];
- 121 3. rock salt domain is assumed saturated with brine;
- 122 4. for an overestimating study, brine pressure within the rock salt domain is assumed halmostatic;
- 123 5. for an overestimating study, rock salt creep due to cavern operation is neglected;
- 124 6. hydrogen diffusion in the halite structure is neglected;
- 125 7. hydrogen concentration is initially disregarded in the rock salt domain;
- 126 8. rock salt, interstitial brine, and the invading hydrogen are assumed in thermal equilibrium;
- 127 9. hydrogen invasion into the rock salt domain is assumed to follow the van Genuchten percolation
128 model [14, 15];
- 129 10. for an overestimating study, hydrogen entry pressure into the saturated rock salt is neglected.

130 Hydrogen thermodynamics in underground caverns is presented in the work of *Rouabhi et al.* [37]
131 and *AbuAisha and Rouabhi* [36]. As an example to modeling a uniform thermodynamic state within the
132 cavern, the following system of equations is used:

$$\begin{aligned}
\text{mass balance: } \quad \mathcal{M}(-\chi_{p\gamma}\dot{T}_\gamma + \chi_{T\gamma}\dot{p}_\gamma) &= Q_e - \mathfrak{S}; \\
\text{energy balance: } \quad \mathcal{M}C_{p\gamma}\dot{T}_\gamma - \mathcal{V}\chi_{p\gamma}T_\gamma\dot{p}_\gamma &= Q_e^+ C_{p\gamma}(T_\gamma^{\text{inj}} - T_\gamma) - \Psi,
\end{aligned}
\tag{1}$$

133 where \mathcal{M} (kg) is the cavern hydrogen mass, T_γ (K) is the cavern uniform hydrogen temperature, $\chi_{p\gamma}$
134 (1/K) is the hydrogen isobaric thermal expansivity, p_γ (Pa) is the cavern uniform hydrogen pressure,
135 $\chi_{T\gamma}$ (1/Pa) is the hydrogen isochoric compressibility, Q_e (kg/s) is the well/external flow rate, Q_e^+ is
136 the positive/injection part of Q_e , \mathfrak{S} (kg/s) is the internal/exchanged mass rate between the cavern and
137 the rock domain, $C_{p\gamma}$ (J/kg/K) is the hydrogen heat capacity at a given pressure, \mathcal{V} (m³) is the cavern
138 volume, T_γ^{inj} (K) is the injection temperature, and Ψ (W) is the power exchanged between the cavern
139 hydrogen and the surrounding rock. Both the exchanged power Ψ and mass rate \mathfrak{S} are positive when
140 given to the rock domain.

141 Once the cavern thermodynamic state (p_γ and T_γ) is known, it can be used to calculate the hydrogen
142 invasion into the surrounding rock salt domain. Figure 1(b) shows the mechanisms related to hydrogen
143 transport in the saturated rock salt while assuming a van Genuchten two-phase percolation. When
144 hydrogen pressure within the cavern exceeds the rock salt pore pressure plus the entry pressure, hydrogen
145 invades the rock salt in a two phase percolation type flow. However, when hydrogen pressure becomes
146 less than the interstitial brine pressure, brine moves towards the cavern and tends to pour down the
147 cavern wall. Fickian diffusion of hydrogen in the rock salt interstitial brine is function of hydrogen
148 cycling. This diffusion is related to the hydrogen mass concentration gradient between the cavern and

149 the rock salt domain. The temperature changes within the cavern lead to temperature changes in the
 150 rock salt domain. In this study, rock salt, interstitial brine, and the invading hydrogen are assumed to
 151 be in local thermal equilibrium. Besides, a temperature continuity is assumed at the cavern wall. The
 152 thermo-hydraulic coupling in the rock domain is accounted for through the pressure and temperature
 153 effects on the hydrogen and the brine densities.

154 As the mechanical deformation of the rock salt is neglected, the subsequent percolation–diffusion
 155 equations are established in the initial configuration of the solid matrix. The rock salt porosity is denoted
 156 by n , and T denotes the temperature for all the phases in the rock salt domain. For each fluid phase
 157 $\alpha \in \{\lambda \text{ (liquid)}, \gamma \text{ (gas)}\}$, p_α stands for the pressure, n_α the partial porosity, $S_\alpha = n_\alpha/n$ the saturation
 158 degree, and ρ_α (kg/m³) the density. In the liquid phase λ , $c_{h\lambda}$ denotes the mass concentration of hydrogen
 159 and $\rho_{h\lambda} = c_{h\lambda} \rho_\lambda$ denotes its density. For a given quantity X , the apparent value (per unit volume of the
 160 entire porous medium) is denoted X^α with $X^\alpha = n_\alpha X_\alpha$, where X_α is per unit volume occupied by the
 161 α -phase.

162 The rock salt interstitial brine density is characterized by four state variables which are the brine
 163 pressure p_λ , its temperature T , the hydrogen concentration $c_{h\lambda}$, and the salt concentration. In this
 164 study, the interstitial brine is assumed saturated with salt at any time. Besides the mass of the dissolved
 165 hydrogen is assumed very minor to affect the brine density. Therefore, the mass balance equations of the
 166 components b (brine) and h (hydrogen) of the liquid phase can be written in the following form [38–40],

$$\begin{aligned}
 \dot{m}_b^\lambda + \nabla \cdot [\rho_\lambda(1 - c_{h\lambda})\mathbf{v}_\lambda - \rho_\lambda \mathcal{J}_{h\lambda}] &= \pi_b, \\
 \dot{m}_h^\lambda + \dot{m}^\gamma + \nabla \cdot [\rho_\lambda(c_{h\lambda}\mathbf{v}_\lambda + \mathcal{J}_{h\lambda}) + \rho_\gamma\mathbf{v}_\gamma] &= \pi_h, \\
 \text{with } m^\alpha &= nS_\alpha\rho_\alpha \text{ for } \alpha \in \{\lambda, \gamma\}, \\
 m_b^\lambda &= (1 - c_{h\lambda})m^\lambda, \quad \text{and} \quad m_h^\lambda = c_{h\lambda}m^\lambda,
 \end{aligned} \tag{2}$$

where ρ_α is the density of the α -phase, \mathbf{v}_α (m/s) is the filtration velocity of the α -phase, $\mathcal{J}_{h\lambda}$ (m/s) is the Fickian diffusion of hydrogen in the liquid phase λ , π_b and π_h (kg/m³/s) are the total mass creation terms of the two components in the fluid phase. If heat convection in the rock salt domain is neglected, the following energy equation can be used to describe heat transfer within the rock salt domain due to cycling in the cavern,

$$\begin{aligned}
 m C_p \dot{T} + \nabla \cdot \boldsymbol{\psi} &= 0, \\
 \text{with, } m C_p &= \sum_\alpha m^\alpha C_{p\alpha}, \quad \text{and, } \boldsymbol{\psi} = -\underline{\underline{\mathbf{A}}}\cdot\nabla T,
 \end{aligned} \tag{3}$$

with $\alpha \in \{\lambda, \gamma, \sigma \text{ (solid)}\}$, and $\underline{\underline{\mathbf{A}}}$ (W/m/K) is the saturated rock salt domain thermal conductivity tensor. If the thermal conductivities of the three phases are assumed isotropic, the domain thermal

conductivity Λ is expressed by the geometric mean of the phases thermal conductivities [41],

$$\Lambda = \Lambda_{\sigma}^{n_{\sigma}} \Lambda_{\lambda}^{n_{\lambda}} \Lambda_{\gamma}^{n_{\gamma}}. \quad (4)$$

167 In a two-phase percolation flow, the liquid saturation degree S_{λ} can be calculated using the *van*
168 *Genuchten* [42] expression,

$$\tilde{S}_{\lambda} = \frac{S_{\lambda} - S_{\lambda r}}{S_{\lambda s} - S_{\lambda r}} = \left(1 + \left(\frac{p_c}{P_r} \right)^{1/(1-\ell)} \right)^{-\ell}, \quad (5)$$

169 where $p_c = p_{\gamma} - p_{\lambda}$ is the capillary pressure, \tilde{S}_{λ} is the effective degree of saturation, the parameters $S_{\lambda r}$
170 and $S_{\lambda s}$ represent the liquid residual and maximum saturation values respectively ($S_{\lambda} \in [S_{\lambda r} - S_{\lambda s}]$), ℓ
171 and P_r (Pa) are model parameters. The equation does not introduce the notion of an entry pressure as
172 it will be neglected in this research.

173 The hydraulic problem (Eq. 2) needs to be completed with constitutive and state laws. The filtration
174 velocity vectors are assumed to follow a Darcian flow nature,

$$\mathbf{v}_{\alpha} = -\frac{k_{r\alpha}}{\mu_{\alpha}} \underline{\underline{\mathbf{k}}} \cdot (\nabla p_{\alpha} - \rho_{\alpha} \mathbf{g}), \quad \text{for } \alpha \in \{\lambda, \gamma\}, \quad (6)$$

where $\underline{\underline{\mathbf{k}}}$ (m^2) is the intrinsic permeability tensor, μ_{α} (Pa s) is the dynamic viscosity of the α -phase,
 \mathbf{g} (m/s^2) is the gravitational acceleration vector, and $k_{r\alpha}$ is the relative permeability of the α -phase.
Relative permeabilities can be calculated using the Mualem-van Genuchten model [43],

$$k_{r\lambda} = \sqrt{\tilde{S}_{\lambda}} \left[1 - \left(1 - \tilde{S}_{\lambda}^{1/\ell} \right)^{\ell} \right]^2, \quad \text{and} \quad k_{r\gamma} = \sqrt{1 - \tilde{S}_{\lambda}} \left(1 - \tilde{S}_{\lambda}^{1/\ell} \right)^{2\ell}. \quad (7)$$

The diffusion vector of hydrogen in the liquid phase is related to the concentration gradient through
the Fick's law,

$$\mathcal{J}_{h\lambda} = -\underline{\underline{\mathbf{D}}}_{h\lambda} \cdot \nabla c_{h\lambda} = c_{h\lambda} (\mathbf{v}_{h\lambda} - \mathbf{v}_{\lambda}), \quad (8)$$

where $\underline{\underline{\mathbf{D}}}_{h\lambda}$ (m^2/s) and $\mathbf{v}_{h\lambda}$ (m/s) are the diffusivity coefficient tensor and the diffusive velocity of hydro-
gen in the λ -phase respectively. This coefficient can be determined experimentally for a given component,
a phase, and a porous medium [44], or empirically from the plain diffusivity in the liquid phase ($\bar{D}_{h\lambda}$)
modified by the characteristics of the porous network (porosity, tortuosity, and constrictivity). A com-
monly used expression is $D_{h\lambda} = \bar{D}_{h\lambda} n^q$, where q is an empirical parameter that generally lies between
1.8 and 2.4 [21]. The exchanged hydrogen mass rate between the cavern and the surrounding rock salt
can, therefore, be calculated as,

$$\mathcal{G} = \underbrace{\int_{\mathcal{S}} \rho_{\gamma} \mathbf{v}_{\gamma} \cdot \mathbf{n} dA}_{\text{Percolated mass rate}} + \underbrace{\int_{\mathcal{S}} \rho_{\lambda} (\mathcal{J}_{h\lambda} + c_{h\lambda} \mathbf{v}_{\lambda}) \cdot \mathbf{n} dA}_{\text{Diffused mass rate}}, \quad (9)$$

with \mathbf{n} being the outward unit vector normal to the cavern surface.

The hydrogen phase is assumed to behave as a real gas (see Appendix A). The state equation is described using the two state functions; the density $\rho_\gamma(p_\gamma, T_\gamma)$, and the heat capacity $C_{p\gamma}(T_\gamma)$ at a given pressure. The thermodynamic variables are related to each other through the formula $p_\gamma = \rho_\gamma T_\gamma Z$, with Z (J/kg/K) being the gas compressibility factor. The chemical potential equality between the λ - and γ -phases leads to the definition of the Henry's law $p_\gamma = (K_H/M_h)\rho_{h\lambda} = Hc_{h\lambda}$, with K_H (L Pa/mol) being the Henry's constant, M_h (kg/mol) the hydrogen molecular weight, and $H = K_H \rho_\lambda/M_h$ (Pa). The brine phase is assumed to be slightly compressible, i.e. $\dot{\rho}_\lambda/\rho_\lambda = \chi_{T\lambda}\dot{T} - \chi_{p\lambda}\dot{p}_\lambda$ with $\chi_{T\lambda}$ (1/Pa) and $\chi_{p\lambda}$ (1/K) being the isochoric compressibility and the isobaric thermal expansion coefficient respectively.

3.2. Saturated/unsaturated state transition

The set of differential equations and primary variables (Eq. 2) needs to be controlled to assure the transition from fully saturated state to unsaturated state, or vice versa. In this paper, we only consider the problem of hydrogen appearance in rock salt where the brine phase is always present. The modeling approach of *Mahjoub et al.* [39] is proposed. It consists of using the dissolution and diffusion phenomena to derive a set of differential equations applicable for both saturated and unsaturated states.

The choice of the primary variables is crucial. The pressure p_λ can be chosen as the first primary variable because the brine phase is assumed present at any time. With regard to the second unknown, due to dissolution and diffusion phenomena, the mass concentration $c_{h\lambda}$ is a permanent unknown, whether the medium is saturated or unsaturated. Thus, it is chosen as the second primary variable. However, to assure the homogeneity in the primary variables, a pseudo-hydrogen pressure is defined as $\tilde{p}_\gamma = Hc_{h\lambda}$. It represents the real hydrogen pressure only when the hydrogen phase is present ($\tilde{p}_\gamma = p_\gamma$ if $S_\lambda < 1$), and it is just a definition in the saturated case. To use the same equations in the saturated case, a new pseudo-capillary pressure is introduced $\tilde{p}_c = \tilde{p}_\gamma - p_\lambda$. The saturation degree is expressed as a function of this pseudo-capillary pressure such that $S_\lambda(\tilde{p}_c) = S_\lambda(p_c)$ when $\tilde{p}_c \geq 0$ (because $\tilde{p}_c = p_c$), and $S_\lambda(\tilde{p}_c) = 1$ when $\tilde{p}_c < 0$.

Taking these definitions into consideration, the γ -Darcy and Fick laws have to be reformulated and integrated into the conservation equations. The same equation for γ -Darcy law (Eq. 6) can be used after replacing p_γ by \tilde{p}_γ , with $\rho_\gamma(\tilde{p}_\gamma, T_\gamma)$. In Fick's law (Eq. 8), $c_{h\lambda}$ is replaced by \tilde{p}_γ/H , and the variation of H is assumed negligible compared to the variation of \tilde{p}_γ . The reformulated mass conservation equations

204 can be cast into the following system of coupled partial differential equations,

$$\begin{aligned}
\dot{m}_b^\lambda - \nabla \cdot (\underline{\mathcal{B}}_{b\lambda} \cdot (\nabla p_\lambda - \rho_\lambda \mathbf{g}) + \underline{\mathcal{B}}_{b\gamma} \cdot \nabla \tilde{p}_\gamma) &= \pi_b, \\
\dot{m}_h^\lambda + \dot{m}_\gamma - \nabla \cdot (\underline{\mathcal{B}}_{h\lambda} \cdot (\nabla p_\lambda - \rho_\lambda \mathbf{g}) + \underline{\mathcal{B}}_{h\gamma}^f \cdot \nabla \tilde{p}_\gamma + \underline{\mathcal{B}}_{h\gamma}^p \cdot (\nabla \tilde{p}_\gamma - \rho_\gamma \mathbf{g})) &= \pi_h, \\
\text{with } \underline{\mathcal{B}}_{b\lambda} &= [(1 - c_{h\lambda}) \rho_\lambda k_{r\lambda} / \mu_\lambda] \underline{\mathbf{k}}, \quad \underline{\mathcal{B}}_{b\gamma} = (-\rho_\lambda / H) \underline{\mathbf{D}}_{h\lambda}, \\
\underline{\mathcal{B}}_{h\lambda} &= (c_{h\lambda} \rho_\lambda k_{r\lambda} / \mu_\lambda) \underline{\mathbf{k}}, \quad \underline{\mathcal{B}}_{h\gamma}^f = (\rho_\lambda / H) \underline{\mathbf{D}}_{h\lambda}, \quad \text{and,} \quad \underline{\mathcal{B}}_{h\gamma}^p = (\rho_\gamma k_{r\gamma} / \mu_\gamma) \underline{\mathbf{k}}.
\end{aligned} \tag{10}$$

205 *3.3. The numerical model*

206 The numerical model represents a spherical cavern of volume $\mathcal{V} = 300,000 \text{ m}^3$ in a surrounding rock
207 domain. The well extends from the surface at $z = 0 \text{ m}$ to the cavern top at $z = z_w = -910 \text{ m}$ (Fig. 2(a)).
208 The cavern has been leached (full of brine) and is initially in thermal equilibrium with the surrounding
209 rock domain at $T = 40 \text{ }^\circ\text{C}$. The brine pressure within the cavern is also in equilibrium with the surrounding
210 salt pore pressure at the halmostatic value of $p_\lambda = -\rho_\lambda \mathbf{g} z = 11.2 \text{ MPa}$. The cavern brine is then
211 replaced by hydrogen during a debrining/filling phase of 90 days where hydrogen pressure of 22 MPa is
212 attained within the cavern. The cavern is later left unsolicited for a similar period of time. Consequently,
213 after 90 days of standstill, the cavern volume averaged temperature and pressure are $46 \text{ }^\circ\text{C}$ and 22 MPa
214 respectively. Cavern then undergoes seasonal cycling following the program shown in Fig. 2(b) for a
215 40–year time period, where hydrogen is injected at $T_\gamma^{\text{inj}} = 40 \text{ }^\circ\text{C}$

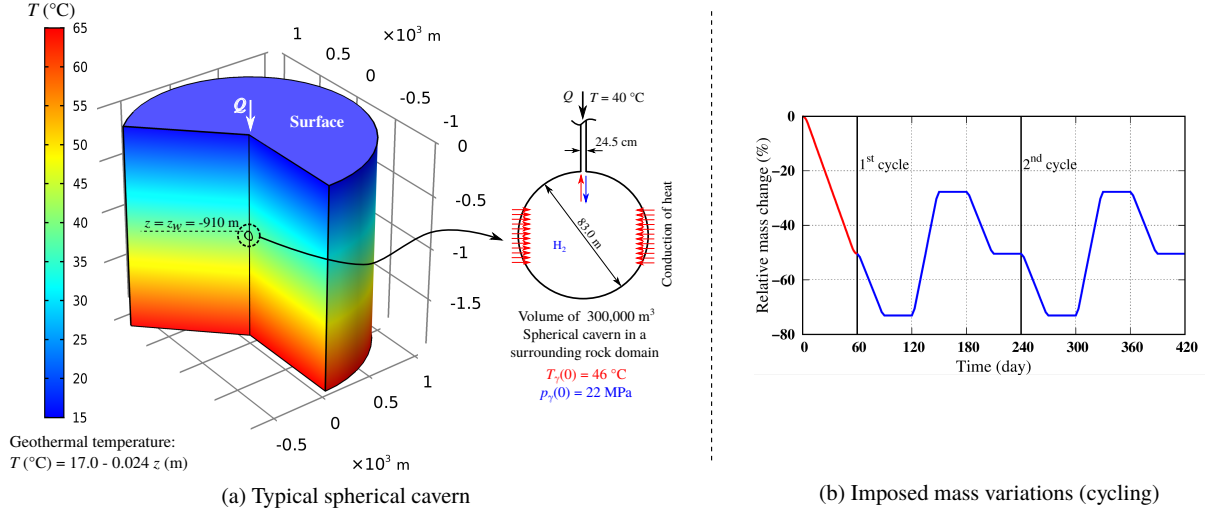


Figure 2: (a) Schematic diagram of the boundary value problem: it represents a spherical cavern created at 910 m depth in a surrounding rock salt domain. The cavern has been filled with hydrogen during a 90–day time period, and then left unsolicited for an equivalent period of time. This has led to a cavern volume averaged temperature and pressure of $46 \text{ }^\circ\text{C}$ and 22 MPa respectively. (b) Imposed cavern relative mass variations; only the first two cycles are shown.

216 Figure 2(b) shows the cycling scheme that will be considered in our simulations in terms of relative
 217 mass change $\tilde{\mathcal{M}} = (\mathcal{M}/\mathcal{M}(0) - 1) \times 100\%$. The program starts with a withdrawal phase of 60 days,
 218 cycling then begins where each cycle extends over a 6-month period. Only the first two cycles are shown,
 219 however, simulations are conducted for a 40-year time period, i.e. 80 cycles.

220 Since there are no available COMSOL modules that couples computational fluid dynamics with the
 221 two-phase percolation and diffusion in porous media, the available general forms of the coefficient Partial
 222 Differential Equations (cPDE), of the domain Ordinary Differential Equations (dODE), and of the
 223 boundary Ordinary Differential Equations (bODE), are used to solve our systems of equations in a coupled
 224 thermo-hydraulic framework. COMSOL gives analytical expressions to track the evolution of the
 225 hydrogen viscosity μ_γ , thermal conductivity Λ_γ , and heat capacity $C_{p\gamma}$ as functions of temperature (see
 226 Appendix B). Other van Genuchten, thermal, and hydraulic parameters are detailed in Table (1).

227 4. Parametric study

228 Due to the lack of any experimental data treating hydrogen invasion into the rock salt, this parametric
 229 study is presented before performing simulations on the cavern scale. The objective of this section is to
 230 investigate the effect of van Genuchten parameter (P_r) and hydrogen-brine diffusion coefficient ($\bar{D}_{h\lambda}$)
 231 on the percolation-diffusion phenomenon. The chosen van Genuchten parameter and diffusion coefficient
 232 values will then be used in a real-scale cavern simulations, and while assuming a pessimistic or an
 233 overestimating scenario with regard to the total mass of lost hydrogen. To simplify the calculations, this
 234 study is performed for a one-dimensional axisymmetric transient boundary value problem (Fig. 3(a)).

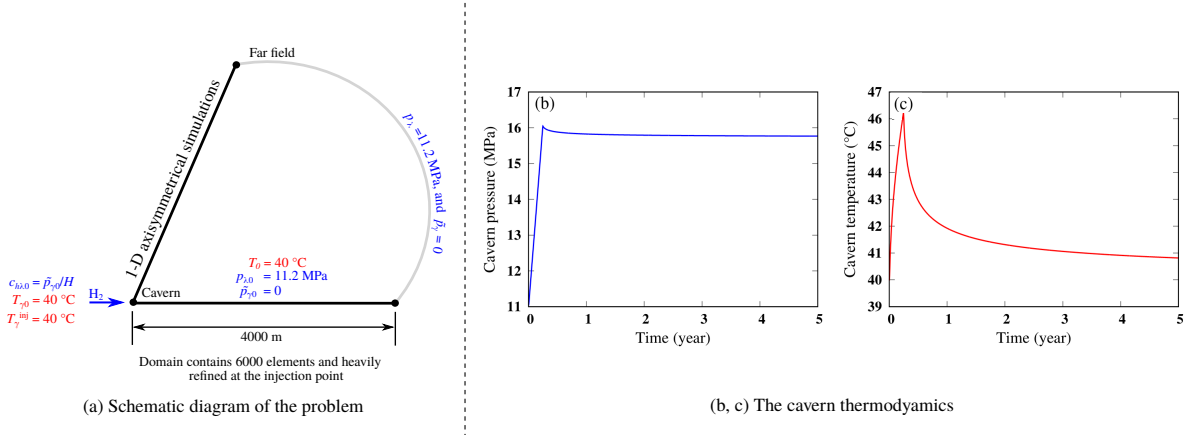


Figure 3: (a) Schematic diagram representing the transient boundary value problem to perform the parametric study of hydrogen invasion into a saturated rock salt. The cavern volume averaged (b) pressure, and (c) temperature. Injection continues through 90 days, it then stops allowing for heat transfer and hydrogen mass exchange with the rock salt.

235 Initial and boundary conditions are set similar to the working conditions of the spherical cavern (Fig.

Table 1: Hydraulic, thermal, and van Genuchten parameters to model hydrogen invasion into the rock salt.

Interpretation	Parameter (unit)	Value	Reference
Rock salt permeability	k (m ²)	1×10^{-20}	[45, 46]
Rock salt porosity	n	0.01	[45, 46]
Brine density	ρ_λ (kg/m ³)	1200	[29]
Brine isochoric compressibility	$\chi_{T\lambda}$ (1/Pa)	46×10^{-11}	[29]
Brine isobaric expansivity	$\chi_{p\lambda}$ (1/K)	45×10^{-5}	[29]
Brine dynamic viscosity	μ_λ (Pa s)	1.32×10^{-3}	[29]
Brine thermal conductivity	Λ_λ (W/m/K)	0.51	[29]
Brine heat capacity	$C_{p\lambda}$ (J/kg/K)	3300	[29]
Rock salt pore pressure	p_λ (Pa)	$-\rho_\lambda \mathbf{g} z$	Overestimating study
Rock salt density	ρ_σ (kg/m ³)	2200	[47]
Rock salt thermal conductivity	Λ_σ (W/m/K)	6	[47]
Rock salt heat capacity	$C_{p\sigma}$ (J/kg/K)	900	[47]
Maximum brine saturation	$S_{\lambda s}$	1.0	Assumed
Residual brine saturation	$S_{\lambda r}$	0.15	[39]
van Genuchten parameter	P_r (Pa)	8×10^6 or 15×10^6	Parametric study
van Genuchten parameter	ℓ	0.5	[48]
Mass creation terms	π_b and π_h (kg/m ³ /s)	0	Assumed
Hydrogen mass concentration	$c_{h\lambda}$	\tilde{p}_γ/H	Definition
Hydrogen diffusion in brine	$\bar{D}_{h\lambda}$ (m ² /s)	5×10^{-7} or 5×10^{-10}	Parametric study
Diffusion correction parameter	q	2.1	[21]
Henry's constant hydrogen-brine	K_H (L atm/mol)	1300	[49, 50]

236 2(a)). Hydrogen concentration is initially neglected in the rock domain ($c_{h\lambda} = 0$). Consequently, the
 237 initial rock salt pseudo-hydrogen pressure is assumed equal to zero ($\tilde{p}_{\gamma 0} = 0$). The initial rock salt
 238 interstitial brine pressure is set equal to the halmostatic value $p_{\lambda 0} = 11.2$ MPa. The cavern (injection
 239 point) is initially assumed in thermal equilibrium with the surrounding rock domain at $T = 40$ °C.
 240 The cavern is filled gradually with hydrogen during a 90-day time period, where the cavern pressure
 241 is increased from halmostatic to ~ 16 MPa (around the maximum cycling value of the real cavern (Fig.
 242 9(a)). Injection then stops and hydrogen is left to diffuse and/or percolate into the rock domain. Figures
 243 3(b, c) show the hydrogen pressure and temperature within the cavern during a 5-year time period.

244 During filling, the cavern averaged temperature increases from 40 °C to ~ 46.2 °C. Heat exchange
 245 with the colder surrounding rock salt is observed in Fig. 3(c) during 5 years. To simulate the two-phase

246 hydrogen percolation into the rock salt, the van Genuchten parameter $\ell = 0.5$ is used as cited in a few
 247 articles for rock salt [48]. Similar works have used a van Genuchten parameter $P_r \in [10 - 15]$ MPa
 248 for air and nitrogen percolations in concrete, granite, or crushed rock salt [39, 48, 51]. For this study,
 249 simulations are performed for $P_r = 8$ and 15 MPa. The residual saturation $S_{\lambda r} = 0.15$ is used as in
 250 *Mahjoub et al.* [39] and *Poppei et al.* [48]. The possibility to have a fully brine saturated state is taken
 251 into consideration by setting $S_{\lambda s} = 1$. To investigate the effect of Fickian diffusion on the total hydrogen
 252 mass lost into the rock salt, a wide range (3 orders of magnitude) of diffusion coefficient is considered,
 253 i.e. $\bar{D}_{h\lambda} = 5 \times 10^{-7}$ or 5×10^{-10} m²/s. Consequently, four simulations are performed: for $P_r = 8$ MPa
 254 and $\bar{D}_{h\lambda} = 5 \times 10^{-7}$ or 5×10^{-10} m²/s; and for $P_r = 15$ MPa and $\bar{D}_{h\lambda} = 5 \times 10^{-7}$ or 5×10^{-10} m²/s.
 255 Results are simultaneously correlated and analyzed.

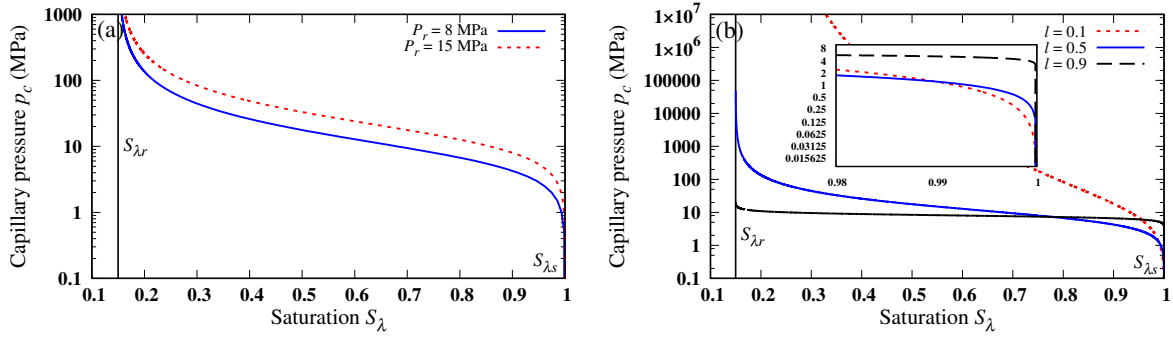


Figure 4: Capillary pressure as calculated by the van Genuchten equation (Eq. 5), (a) for $\ell = 0.5$ and $P_r = \{8, 15\}$ MPa, and (b) for $P_r = 8$ MPa and $\ell = \{0.1, 0.5, 0.9\}$.

256 Figure 4(a) shows the brine saturation evolution as function of the capillary pressure for the two
 257 values of the van Genuchten parameter P_r . It is obvious that a tremendous cavern pressure is needed
 258 for hydrogen to invade the rock salt in a pure or even a semi-pure nature ($S_\lambda < 0.15$). For typical
 259 working conditions of our typical spherical cavern, capillary pressure ranges between 0 and ~ 4 MPa.
 260 Consequently, hydrogen saturation in the pore brine is expected to be very low (< 0.05), i.e. $S_\lambda > 0.95$.
 261 It is also observed that a lower value of the parameter P_r allows for a more significant percolation of
 262 hydrogen for the the same capillary pressure.

263 Figure 5 shows the rock salt radial profiles of pseudo-hydrogen pressure, of brine pore pressure, and of
 264 temperature for the transient boundary value problem of Fig. 3(a). Hydrogen exists only in the domain
 265 where the pseudo-pressure is grater than zero ($S_\lambda < 1$). It is observed that the rock domain temperature
 266 is minimally affected by the choice of the diffusion coefficient and the van Genuchten parameter P_r (Figs
 267 5(c, f)). Figs 5(b, e) show that the rock salt brine pressure is also independent of the value of the diffusion
 268 coefficient. However, the van Genuchten definition (Eq. 5) necessitates that the brine pore pressure
 269 be dependent of the parameter P_r . Comparing Figs 5(a, d) demonstrates that the percolation is slightly
 270 affected by the value of the diffusion coefficient. For instance, for both values of $\bar{D}_{h\lambda}$, hydrogen percolates

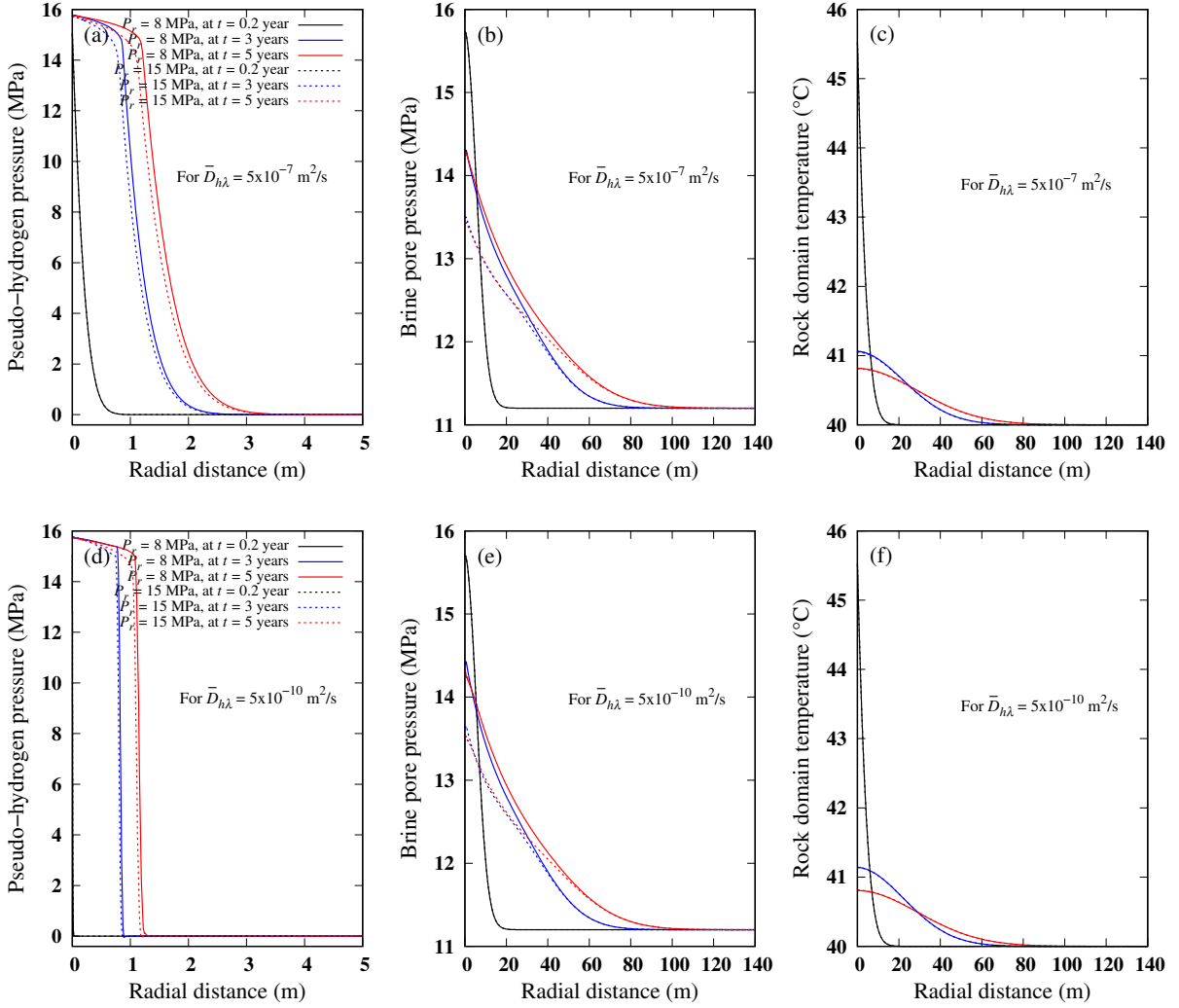


Figure 5: (a, d) Pseudo-hydrogen pressure, (b, e) brine pore pressure, and (c, f) rock salt temperature radial profiles at three distinct times of 0.2, 3, and 5 years. These profiles are traced within the rock domain and shown for the four permutations of P_r and $\bar{D}_{h\lambda}$ values.

271 to a distance of almost ~ 1.3 m after 5 years. However, when the diffusion coefficient value is significant,
 272 percolation continues to show a diffusive nature where the affected domain could reach a distance of ~ 3 m
 273 after 5 years. Before percolation takes place ($t < 89$ days (Fig. 6(a))), the chosen value of P_r has no effect
 274 on the hydrogen pressure profiles in the rock domain (see the black curves in Figs 5(a, d)). As expected,
 275 it is seen that smaller values of the parameter P_r allow for more percolation of hydrogen (compare red
 276 and blue curves of Figs 5(a, d)).

277 Figure 6 shows the histories of the brine saturation at the cavern wall, of the percolated and of the
 278 Fickian diffused hydrogen masses into the rock salt domain. The exchanged masses are calculated by
 279 integrating Eq. 9 over time and over a surface equivalent to that of the cavern in Fig. 2(a).

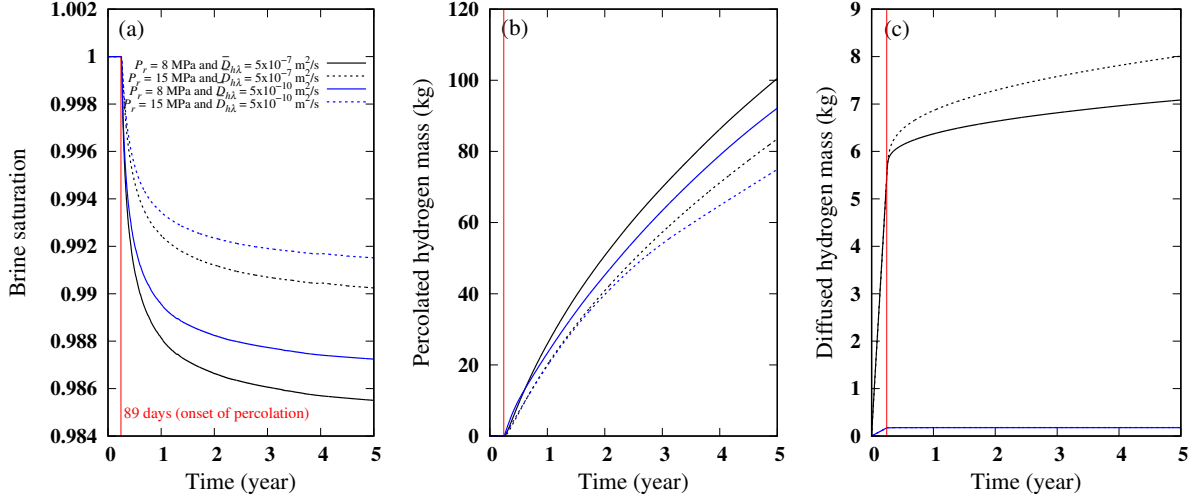


Figure 6: (a) Brine saturation history at the cavern wall, (b) two-phase percolated hydrogen mass history, and (c) Fickian diffused hydrogen mass history. Histories are shown for the four permutations of P_r and $\bar{D}_{h,\lambda}$ values.

280 Figure 6(a) shows that the two-phase percolation starts after almost ~ 89 days. Due to the low
 281 capillary pressure, i.e. $p_c \in [2 - 3]$ MPa, the brine saturation is very slightly altered (minimum of
 282 ~ 0.985). Figure 6(b) shows the hydrogen mass percolated into the rock salt domain. Obviously, a more
 283 significant diffusion coefficient and a smaller P_r value allow for a more percolated mass into the rock
 284 salt, which translates into a lesser brine saturation. Unlike percolation, hydrogen starts to diffuse into
 285 the rock salt domain as soon as a hydrogen pressure gradient is established between the cavern and the
 286 rock domain (Fig. 6(c)). It is also noticed that the Fickian diffusion is significant before percolation.
 287 However, as soon as percolation starts, hydrogen replaces brine by a certain saturation which creates two
 288 phases, and the Fickian diffusion rate becomes very slow. One can also see that hydrogen diffuses more
 289 for a greater value of the parameter P_r . Actually, a larger P_r indicates a less percolation which promotes
 290 the Fickian diffusion. This remark is strengthened by noticing that the deviation of the black curves of
 291 Fig. 6(c) takes place instantly with percolation, i.e. $t \approx 89$ days. This conclusion is less obvious when
 292 the diffusion coefficient is very low (blue curves of Fig. 6(c)).

293 Though a value of $\ell = 0.5$ has been used in literature for two-phase flow in rock salt, it is intriguing
 294 to investigate the effect of this parameter on the percolation and diffusion of hydrogen. Henceforth, for
 295 $P_r = 8$ MPa, Fig. 4(b) shows the brine saturation as function of the parameter ℓ . It is conceivable
 296 and expected that the percolation depends on the value of ℓ , however, this dependency becomes less
 297 significant for a quite low hydrogen saturation, i.e. $S_\lambda \approx 0.98$ (see the zoom-in of Fig. 4(b)). When ℓ
 298 approaches 0.9, the capillary pressure exceeds 4 MPa, which is translated into no percolation at all for
 299 the working and boundary conditions of this one-dimensional problem (Fig. 7(a)).

300 Figure 7 shows the percolated and diffused hydrogen masses for $P_r = 8$ MPa, $\bar{D}_{h\lambda} = 5 \times 10^{-7}$ m²/s,
 301 and $\ell = \{0.1, 0.5, 0.9\}$. Reducing ℓ to 0.1 increases the percolated mass by 2.65 folds. However, no
 302 percolation is observed for $\ell \approx 0.9$.

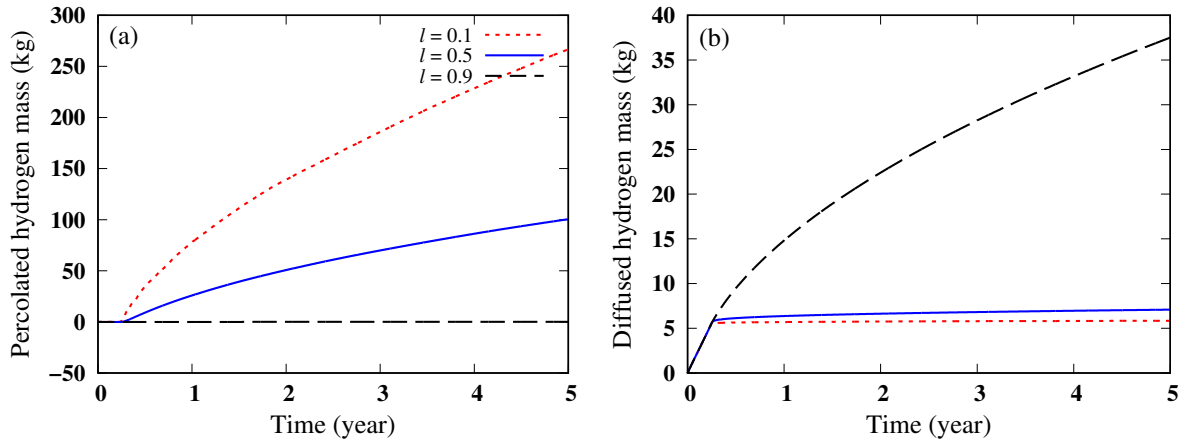


Figure 7: (a) Percolated and (b) diffused hydrogen masses through 5 years for $P_r = 8$ MPa, $\bar{D}_{h\lambda} = 5 \times 10^{-7}$ m²/s, and $\ell = \{0.1, 0.5, 0.9\}$.

303 As expected, when there is no percolation, hydrogen diffuses the most (black curve of Fig. 7(b)).
 304 For $\ell = \{0.1, 0.5\}$, Fickian diffusion gets affected by the percolation and its parabolic behavior changes
 305 as soon as percolation starts (blue and red curves of Fig. 7(b)). Percolation happens a bit earlier for
 306 $\ell = 0.1$, which is attributed to a lower capillary pressure for the same saturation (see the zoom-in of Fig.
 307 4(b) for $S_\lambda \in [0.99 - 1]$). For the coming stimulations on the cavern scale, we will assume van Genuchten
 308 parameters of $P_r = 8$ MPa, of $\ell = 0.5$, and a hydrogen-brine diffusion coefficient of $\bar{D}_{h\lambda} = 5 \times 10^{-7}$ m²/s.

309 5. Cavern-scale cycling simulations

310 A two-dimensional axisymmetric model was adopted to simulate heat and mass exchange with the
 311 surrounding rock domain during hydrogen cycling in the real cavern (Fig. 2(a)). Figure 8 shows the
 312 spatial discretization of the rock domain. The cavern is not discretized since a uniform thermodynamic
 313 state is assumed within the cavern. Initial and boundary conditions are displayed on the graph.

314 Figures 9(a, b) show the cavern averaged temperature and pressure as function of cycling. Hydrogen
 315 pressure is not showing any changes during cycling as the cavern volume is assumed constant. However,
 316 temperature is showing some changes due to the energy exchanged with the surrounding rock salt domain.

317 Figure 9(c) shows the hydrogen pseudo-capillary pressure averaged over the cavern surface during
 318 cycling. The behavior of the capillary pressure becomes almost identical after five cycles. The capillary
 319 pressure does not exceed 2 MPa for the working and boundary conditions of this typical spherical cavern.

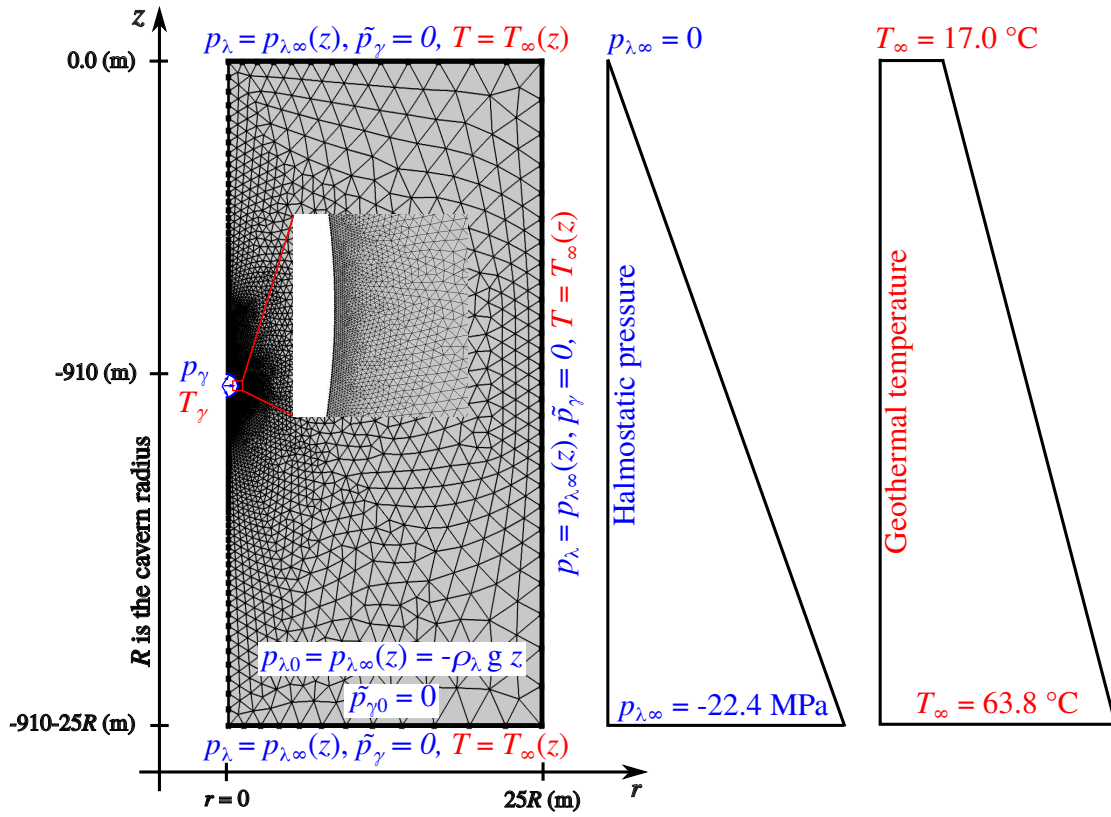


Figure 8: A two-dimensional axisymmetric discretization of the boundary value problem of Fig. 2(a). A surrounding rock volume of $25R$ is chosen around the cavern to avoid the effect of far-field boundaries. Mesh is considerably refined close to the cavern wall to account for abrupt changes/large gradients. Mesh contains 160113 triangular elements.

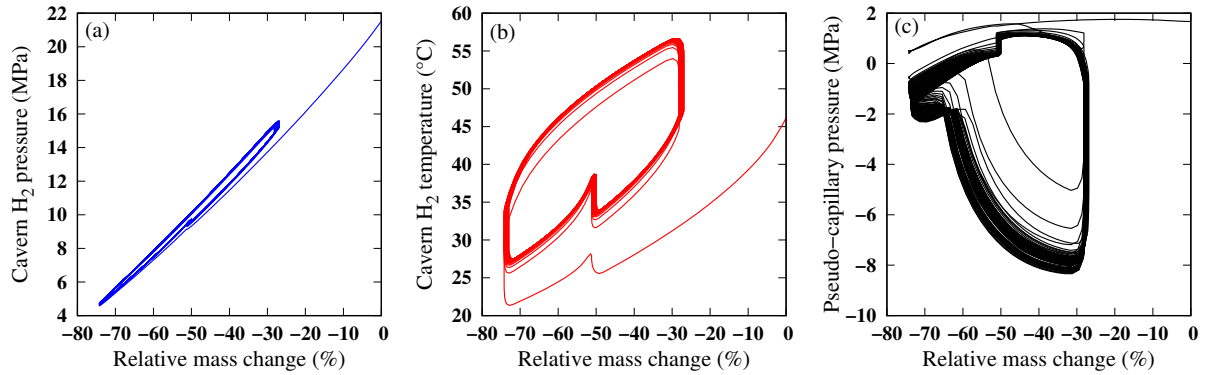


Figure 9: (a) cavern average pressure, (b) cavern average temperature, and (c) hydrogen pseudo-capillary pressure averaged over the cavern surface. The three quantities are presented as function of cycling/relative mass changes within the cavern.

320 To study the hydrogen mass exchanged with the rock domain, Fig. 10(a) shows the brine saturation,
 321 and Fig. 10(b) shows the radial component of hydrogen filtration velocity averaged over the cavern surface
 322 during the first four cycles. Other cycles are not displayed due to similarity and to avoid redundant

323 repetitions.

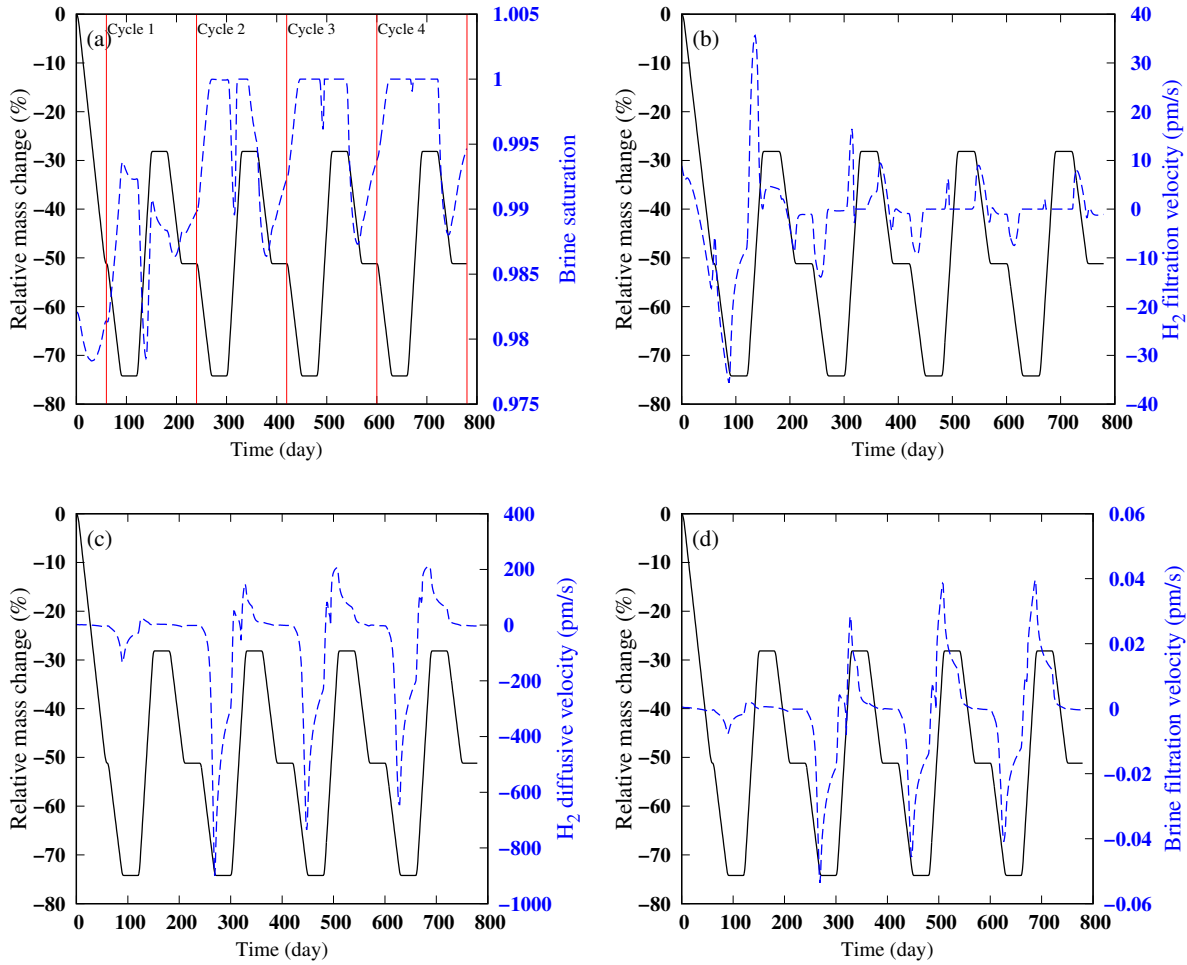


Figure 10: (a) Brine saturation at the cavern wall, as well as the surface averaged radial components of (b) the hydrogen filtration velocity, (c) the Fickian diffusive velocity, and (d) the brine filtration velocity during the first four cycles.

324 The debrining and the standstill phases of 180 days (Sect. 3.3) have led the brine saturation at
 325 the cavern wall to decrease to ~ 0.981 before any cycling (Fig. 10(a)). The subsequent withdrawal has
 326 counteracted this reduction in the brine saturation by allowing the percolated hydrogen to leave back to
 327 the cavern volume, and again a full brine saturation is reached. Furthermore, hydrogen would percolate
 328 into and leave from the rock domain as a function of the cavern hydrogen pressure (Fig. 10(b)). This
 329 allows for a reduction in the brine saturation at the cavern wall before it sustains the full saturation state
 330 (Fig. 10(a) and Fig. 11(a)).

331 The Fickian diffusive velocity resembles the brine filtration velocity (Figs 10(c, d)). Depending on the
 332 direction of hydrogen pressure gradient, hydrogen may diffuse into the rock domain, or pour down the
 333 cavern wall along with the leaving brine. The surface averaged radial component of the brine filtration

334 velocity is show in Fig. 10(d). It is observed that brine moves into the cavern volume when the percolated
 335 hydrogen leaves the rock domain and vice versa. Besides, the thermal effects are noticed on the behavior
 336 of the brine filtration and the Fickian diffusive velocities due to the hydro–thermal coupling, especially
 337 during the standstill phases.

338 To understand how the rock domain interstitial brine gets drained by the invading hydrogen, Fig.
 339 11(a) shows the time variations of the brine saturation and the pseudo–capillary pressure at the cavern
 340 wall for the first four cycles.

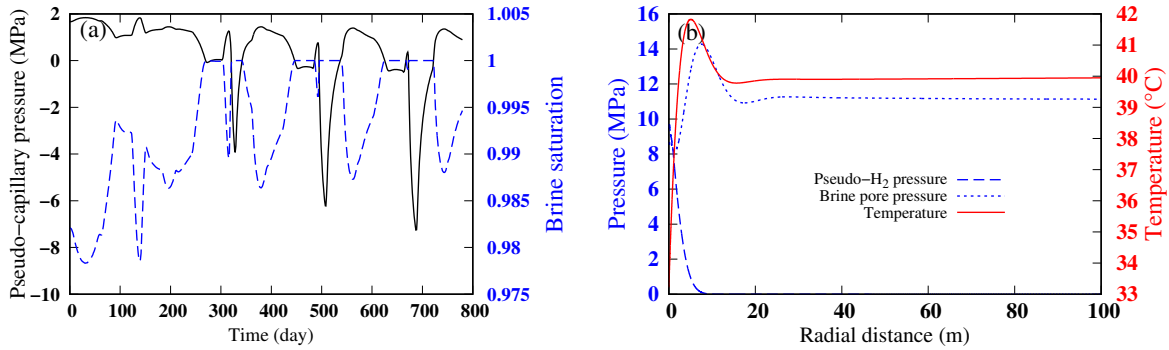


Figure 11: (a) Time variations of the cavern surface averaged brine saturation and pseudo–capillary pressure for the first four cycles. (b) Radial profiles of interstitial brine pressure, of hydrogen pseudo–pressure, and of temperature within the rock domain at the end of cycling/at 40 years.

341 One can see that hydrogen percolates into the rock domain when the capillary pressure is positive.
 342 Besides, the hydrogen saturation rate (increasing or decreasing) has the same sign as the capillary pressure
 343 rate.

344 To study the zone disturbed by brine pore pressure changes, hydrogen pseudo–pressure and temper-
 345 ature fluctuations, Fig. 11(b) shows the radial profiles of these variables at the end of cycling, i.e. 40
 346 years. The altered zone due to hydrogen invasion into the rock domain has not exceeded ~ 15 m after 40
 347 years of seasonal cycling. However, this zone extends to ~ 40 m due to brine pore pressure and rock do-
 348 main temperature changes. Knowing the range of these distances helps design a network of underground
 349 caverns while avoiding harmful interactions.

350 Figure 12 shows the hydrogen mass exchanged with the surrounding rock domain due to two–phase
 351 percolation and the Fickian diffusion. Figure 12(a) is a zoom–in of Fig. 12(b) for the first four cycles/800
 352 days.

353 Both the percolated and diffused hydrogen masses tend to reduce during withdrawal in accordance
 354 with Figs 10(b, c). Even–though the Fickian diffused mass is initially smaller than the percolated mass,
 355 after ~ 25 years of cycling, the diffused mass becomes more significant than the two–phase percolated
 356 mass (Fig. 12(b)). Eventually, the percolated and the diffused hydrogen masses summed up to ~ 93 kg

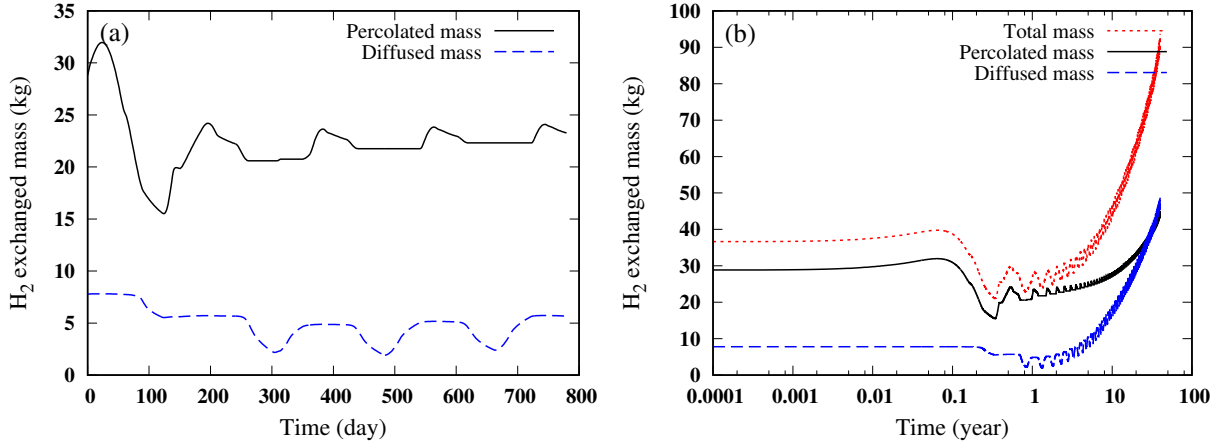


Figure 12: Darcian percolated and Fickian diffused hydrogen masses during 40 years of cycling. Figure (a) is a zoom-in of figure (b) for the first four years. The debrining and the standstill phases of 180 days (Sect. 3.3) have led to the initial percolated and diffused masses observed in figure (a).

357 after 40 years of the cavern operation.

358 6. Discussion

359 For a P_r range that resembles the hydrogen invasion into the rock salt, Sect. 4 has shown that the
 360 Darcian percolation has a slight dependency on the value of P_r . The parameter ℓ has been assigned a
 361 value of 0.5 for rock salt in a few research papers. However, possible high values ($\ell \sim 0.9$) can increase
 362 considerably the capillary pressure at full brine saturation leading to a naught percolation. A value of
 363 $\ell = 0.1$, close to the lowest limit, has increased the hydrogen mass percolated into the rock salt domain
 364 by 3 folds (Fig. 7(b)).

365 The value of the diffusion coefficient $\bar{D}_{h\lambda}$ does not affect directly the Darcian percolation, but rather
 366 its diffusive nature. Percolation becomes more of a piston-like for very small values. Consequently,
 367 hydrogen mass lost due to percolation differed a little bit depending on the diffusion coefficient value
 368 (Fig. 6(b)). However, it is natural that the hydrogen mass lost due to Fickian diffusion is almost 50
 369 times larger for a 3-order of magnitude higher diffusion coefficient (Fig. 6(c)).

370 The simulations on the cavern scale have been performed such that an overestimating/a pessimistic
 371 scenario of lost hydrogen is considered. Therefore, while setting $\ell = 0.5$, values of $P_r = 8$ MPa and
 372 $\bar{D}_{h\lambda} = 5 \times 10^{-7}$ m²/s have been chosen. Cycling simulations prove that percolation happens mostly
 373 when the cavern pressure is close to the maximum cycling value, i.e. $p_\gamma \approx 16$ MPa. Yet, depending on
 374 the sign of the pressure gradient, hydrogen may percolate into/leave from the rock domain. The Fickian
 375 diffusion resembles the brine filtration, following the pressure gradient direction, hydrogen tends to diffuse
 376 into the rock domain or pours down the cavern wall along with the leaving brine. Eventually, the total

377 mass of lost hydrogen sums up to ~ 93 kg. This mass is extremely negligible compared to the hydrogen
378 mass manipulated during one cycle ($\mathcal{M} = 2.05$ Mkg), i.e. the percentage of the lost mass to one cycle
379 mass is $\sim 0.005\%$.

380 Though a wide range of model parameters is studied, our research rests limited to its numerical nature.
381 A laboratory validation is needed. We assume a homogeneous rock salt all around the spherical cavern.
382 However, rock salt can be widely heterogeneous. Besides, this research does not introduce any permeable
383 interlayers, nor does it account for damaged zones. The implementation of heterogeneities in rock salt,
384 whether in the mechanical or the hydraulic properties, affects the transported/exchanged quantity of
385 hydrogen. This effect can be direct as in the case of increased permeability, or indirect as in the case of
386 weaker or more damageable rock salt.

387 The available research concerning gas migration in rock salt promotes the results found in our research.
388 For instance *Jockwer and Wieczorek* [53] have stated that the presence of a damaged zone (DRZ) is the
389 main factor for gas transport in rock salt. They conducted experiments and simulations concerning
390 helium, neon, and butane. They found that the diffusion coefficient of these gases increased by two
391 orders of magnitude in the DRZ. Out of the DRZ, the measured permeabilities were in the order of 10^{-19}
392 and 10^{-20} m², and the pseudo gas pressure slightly penetrated the rock salt in a two-phase psiton-like
393 flow (compare to Fig. 5(d)). *Senger et al.* [51] studied gas (particularly air) migration in concrete. They
394 have found that the gas penetrated distances were limited to 1.5 m after 4 years of injection (compare to
395 Fig. 5(a, d)). The two-phase gas saturation depended on the permeabilities, yet it was less than 0.1 for
396 permeabilities in the order of 10^{-19} m². Generally, the existed literature already confirms that permeable
397 interlayers are the main transport conduits around salter caverns [10, 11].

398 7. conclusion and perspectives

399 In general, for an overly assumed diffusion of hydrogen in brine ($\bar{D}_{h\lambda} = 5 \times 10^{-7}$ m²/s) [52], a null
400 pressure entry, and overestimating van Genuchten parameters, the hydrogen mass lost to the rock do-
401 main remains very negligible. Yet, increasing energy demands necessitate fast utilization of underground
402 caverns. The severe utilization of salt caverns exposes them to considerable pressure and temperature
403 changes throughout short periods, which may affect the development of the damaged zones . The in-
404 troduction of a damaged zone, during cycling and at the end of leaching, can affect the total mass of
405 the lost hydrogen. Future studies will include, in a first step, laboratory work to develop mass transport
406 laws that would describe precisely hydrogen migration into the rock salt. In a second step, constitutive
407 laws that quantify the permeability and porosity evolutions of rock salt due to mechanical, hydraulic and
408 thermal charges would be needed. Once these transport and constitutive laws are developed, they can
409 be integrated in our current frame work to estimate their effect on hydrogen percolation and diffusion

410 during rock salt damaging/severe exploitation of caverns.

411 Though our simulations have demonstrated that cycling reduces the total amount of transported
412 hydrogen (Fig. 12(b)), the role of heterogeneities, whether mechanical or hydraulic, needs also to be
413 investigated in a future research. Moreover, in a laboratory hydrogen storage model, we are currently
414 investigating the importance of other fluxes, F_2 , F_3 , and F_1 of Fig. 1; F_1 is expected to have an impact
415 on the hydrogen thermodynamic behavior. Once these fluxes are quantified, their payoffs should be
416 compared and/or added to the flux F_4 , presented in this research, to draw a general conclusion about
417 the hydrogen-tightness of salt caverns.

418 **8. Acknowledgment**

419 Authors would like to thank Géodénergies and the French Association Nationale de Recherche (ANR)
420 for their financial support via the two projects: ROSTOCK-H; and STOPIL-H.

421 **Appendix A.**

422 **Real hydrogen state law**

423 A real gas behavior is assumed in our simulations of hydrogen storage and migration into the rock salt.
 424 The hydrogen state equation can be completely described using two state functions; the mass density
 425 $\rho_\gamma(p_\gamma, T_\gamma)$, and the heat capacity $C_{p_\gamma}(T_\gamma)$ at a given pressure [37]. The thermodynamic variables are
 426 related to each other through the formula,

$$\rho_\gamma = \frac{p_\gamma}{T_\gamma Z}, \quad (\text{A.1})$$

with Z being the hydrogen compressibility factor. Equation A.1 can be written in a derivative form as,

$$\frac{d\rho_\gamma}{\rho_\gamma} = \chi_{T_\gamma} dp_\gamma - \chi_{p_\gamma} dT_\gamma, \quad (\text{A.2})$$

with χ_{T_γ} being the hydrogen isochoric compressibility and χ_{p_γ} the hydrogen isobaric thermal expansivity. Integrating Eq. A.2 gives,

$$\ln\left(\frac{\rho_\gamma}{\rho_{\gamma 0}}\right) = \int_{p_{\gamma 0}}^{p_\gamma} \chi_{T_\gamma} dp_\gamma - \int_{T_{\gamma 0}}^{T_\gamma} \chi_{p_\gamma} dT_\gamma, \quad (\text{A.3})$$

which can be written as,

$$\rho_\gamma = \rho_{\gamma 0} \exp\left(\int_{p_{\gamma 0}}^{p_\gamma} \chi_{T_\gamma} dp - \int_{T_{\gamma 0}}^{T_\gamma} \chi_{p_\gamma} dT_\gamma\right), \quad (\text{A.4})$$

with $\rho_{\gamma 0}$, $p_{\gamma 0}$, and $T_{\gamma 0}$ being the hydrogen density, pressure, and temperature at the reference state. Both χ_{T_γ} and χ_{p_γ} are functions of the thermodynamic variables, i.e. $\chi_{T_\gamma} = \chi_{T_{\gamma 0}}(p_\gamma/p_{\gamma 0})^{b_T}$, and $\chi_{p_\gamma} = \chi_{p_{\gamma 0}}(T_\gamma/T_{\gamma 0})^{a_p}$, with $\chi_{T_{\gamma 0}}$ and $\chi_{p_{\gamma 0}}$ being the values of χ_{T_γ} and χ_{p_γ} at the reference state respectively, and b_T and a_p are dimensionless constants. Once the reference state is fixed, Eq. A.4 can be extended to,

$$\rho_\gamma = \rho_{\gamma 0} \exp\left(p_{\gamma 0} \frac{\chi_{T_{\gamma 0}}}{1 + b_T} \left[\left(\frac{p_\gamma}{p_{\gamma 0}}\right)^{1+b_T} - 1\right] - T_{\gamma 0} \frac{\chi_{p_{\gamma 0}}}{1 + a_p} \left[\left(\frac{T_\gamma}{T_{\gamma 0}}\right)^{1+a_p} - 1\right]\right). \quad (\text{A.5})$$

427 A high accuracy equation of state was used in our simulations [54]. Once the model parameters are
 428 known, Eq. A.5 can be fed to COMSOL where a real thermodynamic behavior of hydrogen is solved for.

429 The reference state is set to $(p_{\gamma 0}, T_{\gamma 0}, \rho_{\gamma 0}) = (1.0 \text{ MPa}, -100 \text{ }^\circ\text{C}, 1.391 \text{ kg/m}^3)$, then for a tem-
 430 perature range of $T_\gamma \in [-100 \text{ to } 100] \text{ }^\circ\text{C}$, and a pressure range of $p_\gamma \in [1 \text{ to } 25] \text{ MPa}$, the following
 431 values of model parameters fitted best the data of *Kunz and Wagner* [54]: $\chi_{T_{\gamma 0}} = 1.04562 \text{ (1/MPa)}$;
 432 $\chi_{p_{\gamma 0}} = 5.4738 \times 10^{-3} \text{ (1/K)}$; $b_T = -1.05526$; and $a_p = -1.002851$. Figure A.1 shows the relative error
 433 (ε_ρ) in the hydrogen density as calculated by *Kunz and Wagner* [54] and by Eq. A.5.

434 The range of pressure and temperature changes during the cavern cycling (Figs 9(a, b)) is displayed
 435 on Fig. A.1, where the error percentage in the calculated hydrogen density does not exceed 5.0%.

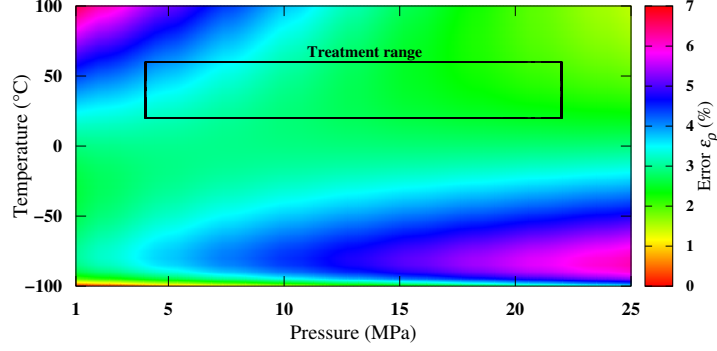


Figure A.1: Relative error (ϵ_ρ) in the hydrogen density as calculated by *Kunz and Wagner* [54] and by Eq. A.5.

436 **Appendix B.**

437 **COMSOL equations**

COMSOL gives analytical expressions to track the evolution of hydrogen dynamic viscosity μ_γ , thermal conductivity Λ_γ , and heat capacity $C_{p\gamma}$ as functions of temperature. During hydrogen cycling, for $T_\gamma \in [290 - 235]$ K, the dynamic viscosity changes as,

$$\mu_\gamma = 2.14524642 \times 10^{-6} + 2.54245 \times 10^{-8} T_\gamma - 1.0235587 \times 10^{-11} T_\gamma^2 + 2.80895021 \times 10^{-15} T_\gamma^3, \quad (\text{B.1})$$

the thermal conductivity changes as,

$$\Lambda_\gamma = 0.00517975922 + 6.72778 \times 10^{-4} T_\gamma - 3.0388973 \times 10^{-7} T_\gamma^2 + 6.58874687 \times 10^{-11} T_\gamma^3, \quad (\text{B.2})$$

and the heat capacity changes as,

$$C_{p\gamma} = 10808.501 + 21.5799904 T_\gamma - 0.0444720318 T_\gamma^2 + 3.85401176 \times 10^{-5} T_\gamma^3 - 1.14979447 \times 10^{-8} T_\gamma^4. \quad (\text{B.3})$$

References

- [1] Lattin C. W. and Utgikar P. V. (2007). Transition to hydrogen economy in the United States: A 2006 status report. *International Journal of Hydrogen Energy*, 32: 3230–3237.
- [2] McPherson M., Johnson N., and Strubegger M. (2018). The role of electricity storage and hydrogen technologies in enabling global low-carbon energy transitions. *Applied Energy*, 216: 649–661.
- [3] Caglayan D. G., Weber N., Heinrichs H. U., Linßen J., Robinius M., Kukla P. A., and Stolten D. (2020). Technical potential of salt caverns for hydrogen storage in Europe. *International Journal of Hydrogen Energy*, 45: 6793–6805.
- [4] Deveci M. (2018). Site selection for hydrogen underground storage using interval type-2 hesitant fuzzy sets. *International Journal of Hydrogen Energy*, 43(19): 9353–9368.
- [5] Lehner M., Tichler R., Steinmüller H., and Koppe M. (2014). *Power-to-gas: technology and business models*. Springer.
- [6] Götz M., Lefebvre J., Mörs F., Koch A. M., Graf F., Bajohr S., Reimert R., and Kolb T. (2016). Renewable Power-to-Gas: A technological and economic review. *Renewable Energy*, 85: 1371–1390.
- [7] Iordache M., Schitea D., Deveci M., Akyurt I. Z., and Iordache I. (2019). An integrated ARAS and interval type-2 hesitant fuzzy sets method for underground site selection: Seasonal hydrogen storage in salt caverns. *Journal of Petroleum Science and Engineering*, 175: 1088–1098.
- [8] Ozarslan A. (2012). Large-scale hydrogen energy storage in salt caverns. *International Journal of Hydrogen Energy*, 37(19): 14265–14277.
- [9] Pamucar D., Deveci M., Schitea D., Erişkin L., Iordache M., and Iordache I. (2020). Developing a novel fuzzy neutrosophic numbers based decision making analysis for prioritizing the energy storage technologies. *International Journal of Hydrogen Energy*, 45(43): 23027–23047.
- [10] Liu W., Zhang Z., Chen J., Jiang D., Wu F., Fan J., and Li Y. (2020). Feasibility evaluation of large-scale underground hydrogen storage in bedded salt rocks of China: A case study in Jiangsu province. *Energy*, 198: 117348.
- [11] Liu W., Chen J., Jiang D., Shi X., Li Y., Daemen J.J.K., and Yang C. (2016). Tightness and suitability evaluation of abandoned salt caverns served as hydrocarbon energies storage under adverse geological conditions (AGC). *Applied Energy*, 178: 703–720.
- [12] Bechtel A., Savin S. M., and Hoernes S. (1999). Oxygen and hydrogen isotopic composition of clay minerals of the Bahloul Formation in the region of the Bou Grine zinc-lead ore deposit (Tunisia):

- 468 evidence for fluid–rock interaction in the vicinity of salt dome cap rock. *Chemical Geology*, 156: 191–
469 207.
- 470 [13] Amaziane B., Keko A. Ž., and Jurak M. (2014). Modeling compositional compressible two–phase flow
471 in porous media by the concept of the global pressure. *Computational Geosciences*, 18(3–4): 297–309.
- 472 [14] Yortsos Y. C., Xu B., and Salin D. (1997). Phase diagram of fully developed drainage in porous
473 media. *Physical Review Letters*, 79(23): 4581–4584.
- 474 [15] Lenormand R. (1989). Flow through porous media: limits of fractal patterns. *Proceedings of the*
475 *Royal Society A*, 423(1864): 159–168.
- 476 [16] Charnavel Y., Leca D., and Poulain F. (1983). Advanced geometrical modelling of salt dissolution
477 during cavern leaching – illustration with a case study. *In: The SMRI Meeting, Las Vegas, Nevada,*
478 *USA.*
- 479 [17] Pernette E. and Dussaud M. (1983). Underground storages at Tersanne and Etrez: prediction and
480 simulation of cavity leaching in a salt layer charged with insoluble materials. *In: The sixth International*
481 *Symposium on Salt, Toronto, Canada.*
- 482 [18] Caglayan D. G., Weber N., Heinrichs H. U., Linßen J., Robinius M., Kukla P. A., and Stolten D.
483 (2020). Technical potential of salt caverns for hydrogen storage in Europe. *International Journal of*
484 *Hydrogen Energy*, 45(11): 6793–6805.
- 485 [19] Wang T., Yang C., Wang H., Ding S., and Daemen J. J. K. (2018). Debrining prediction of a salt
486 cavern used for compressed air energy storage. *Energy*: 147: 464–476.
- 487 [20] Jaffré J. and Sboui A. (2010). Henry’s law and gas phase disappearance. *Transport in Porous Media*,
488 82: 521–526.
- 489 [21] Grathwohl P. (1998). *Diffusion in natural porous media: contaminant transport, sorption/desorption*
490 *and dissolution kinetics.* Springer US, New York.
- 491 [22] Pray A., Schweickert E. C., and Minnichi H. B. (1952). Solubility of Hydrogen, Oxygen, Nitrogen,
492 and Helium in Water at elevated temperatures. *Industrial and Engineering Chemistry*, 44(5): 1146–
493 1151.
- 494 [23] Diaz–Viera M. A., Lopez–Falcon D. A., Moctezuma–Berthier A., and Ortiz–Tapia A. (2008). COM-
495 SOL implementation of a multiphase flow model in porous media. *In the Proceedings of the COMSOL*
496 *conference, Boston, New York, USA.*

- 497 [24] Beckermann C., Ramadhyani S., and Viskanta R. (1986). Natural convection flow and heat transfer
498 between a fluid layer and a porous layer inside a rectangular enclosure. *Journal of Heat Transfer*, 109:
499 363–370.
- 500 [25] Bergholz R. F. (1978). Instability of steady natural convection in a vertical fluid layer. *Journal of*
501 *Fluid Mechanics*, 2(84): 743–768.
- 502 [26] Kloppmann W., Négrel P. H., Casanova J., Klinge H., Schelkes K., and Guerrot C. (2001). Halite
503 dissolution derived brines in the vicinity of a Permian salt dome (N German Basin). Evidence from
504 boron, strontium, oxygen, and hydrogen isotopes. *Geochimica et Cosmochimica Acta*, 65(22): 4087–
505 4101.
- 506 [27] Hassanizadeh S. M. and Leijnse T. (1988). On the Modeling of Brine Transport in Porous Media.
507 *Water Resources Research*, 24(3): 321–330.
- 508 [28] Johnson K. S. (1981). Dissolution of salt on the east flank of the permian basin in the southwestern
509 U.S.A. *Journal of Hydrology*, 54: 75–93.
- 510 [29] Gevantman L. H. (1981). Physical properties data for rock salt. U.S. Department of Com-
511 merce/National Bureau of Standards. U.S. Government Printing Office, Washington, D.C. 20402.
- 512 [30] Bradley J. S. (1975). Abnormal Formation Pressure. *AAPG Bulletin*, 59(6): 957–973.
- 513 [31] Ho C. K. and Webb S. W. (2006). *Gas Transport in Porous Media*. Springer, 3300 AA Dordrecht,
514 The Netherlands.
- 515 [32] Wipf H. (2001). Solubility and Diffusion of Hydrogen in Pure Metals and Alloys. *Physica Scripta*,
516 T94: 43–51.
- 517 [33] Hempelmann R. (1984). Diffusion of hydrogen in metals. *Journal of the Less-Common Metals*, 101:
518 69–96.
- 519 [34] Pfeiffer W. T., al Hagrey S. A., Köhn D., Rabbel W., and Bauer S. (2016). Porous media hydro-
520 gen storage at a synthetic, heterogeneous field site: numerical simulation of storage operation and
521 geophysical monitoring. *Environmental Earth Sciences*, 75: 1177.
- 522 [35] Morel–Seytoux H. J., Meyer P. D., Nachabe M., Tournia J., van Genuchten M. T., and Lenhard R. J.
523 (1996). Parameter equivalence for the Brooks–Corey and van Genuchten soil characteristics: preserving
524 the effective capillary drive. *Water Resources Research banner*, 32(5): 1251–1258.

- 525 [36] AbuAisha M. and Rouabhi A. (2019). On the validity of the uniform thermodynamic state approach
526 for underground caverns during fast and slow cycling. *International Journal of Heat and Mass Transfer*,
527 142: 118424.
- 528 [37] Rouabhi A., Hévin G., Soubeyran A., Labaune P., and Louvet F. (2017). A multiphase multi-
529 component modeling approach of underground salt cavern storage. *Geomechanics for Energy and the*
530 *Environment*, 12: 21–35.
- 531 [38] Angelini O., Chavant C., Chénier E., Eymard R., and Granet S. (2011). Finite volume approximation
532 of a diffusion–dissolution model and application to nuclear waste storage. *Mathematics and Computers*
533 *in Simulation*, 81(10): 2001–2017.
- 534 [39] Mahjoub M., Rouabhi A., Tijani M., Granet S., M’Jahad S., and Talandier J. (2018). Numerical
535 study of Callovo-Oxfordian argillite expansion due to gas injection. *International Journal of Geome-*
536 *chanics*, 18(1): 04017134.
- 537 [40] Xu W. J., Shao H., Hesser J., Wang W., Schuster K., and Kolditz O. (2013). Coupled multiphase
538 flow and elasto–plastic modelling of in–situ gas injection experiments in saturated claystone (Mont
539 Terri Rock Laboratory). *Engineering Geology*, 157: 55–68.
- 540 [41] Côté J. and Konrad J. M. (2005). A generalized thermal conductivity model for soils and construction
541 materials. *Revue Canadienne de Géotechnique*, 42(2): 443–458.
- 542 [42] van Genuchten M. T. (1980). A closed–form equation for predicting the hydraulic conductivity of
543 unsaturated soils. *Soil science society of America journal*, 44(5): 892–898.
- 544 [43] Mualem Y. (1978). Hydraulic conductivity of unsaturated porous media: generalized macroscopic
545 approach. *Water Resources Research*, 14(2): 325–334.
- 546 [44] Rebour V., Billiotte J., Deveughèle M., Jambon A., and Le Guen C. (1997). Molecular diffusion in
547 water–saturated rocks: A new experimental method. *Journal of contaminant hydrology*, 28(1): 71–93.
- 548 [45] Cosenza Ph., Ghoreychi M., Bazargan–Sabet B., and de Marsily G. (1999). In situ rock salt perme-
549 ability measurement for long term safety assessment of storage. *International Journal of Rock Mechanics*
550 *and Mining Sciences*, 36: 509–526.
- 551 [46] Schulze O., Popp T., and Kern H. (2001). Development of damage and permeability in deforming
552 rock salt. *Engineering Geology*, 61: 163–180.
- 553 [47] Bannach A., Wagler T., Walden S., and Klafki M. (2005). Technology enhancement for 1) inventory
554 assessment and mechanical integrity testing of gas–filled solution mined caverns and 2) mechanical

- 555 integrity tests of solution mines and liquid storage caverns. GRI-05/0175 project final report, prepared
556 for Gas Research Institute (contract number 8750), D-095596 Freiberg, Germany.
- 557 [48] Poppei J., Mayer G., Hubschwerlen N., and Resele G. (2006). Flooding of an abandoned salt mine
558 modeling two-phase flow in complex mine structures. . *In* the Proceedings of the TOUGH Symposium,
559 Lawrence Berkeley National Laboratory, Berkeley, California, May 15–17.
- 560 [49] Crozier T. E. and Yamamoto S. (1974). Solubility of hydrogen in water, seawater, and NaCl solutions.
561 *Journal of Chemical and Engineering Data*, 19(3): 242–244.
- 562 [50] Lopez-Lazaro C., Bachaud P., Moretti I., and Ferrando N. (2019). Predicting the phase behavior of
563 hydrogen in NaCl brines by molecular simulation for geological applications. *BSGF – Earth Sciences*
564 *Bulletin* 190, 7.
- 565 [51] Senger R., Lanyon B., Marschall P., and Vomvoris S. (2008). Numerical modeling of the gas migration
566 test at the Grimsel test site (Switzerland). *Nuclear Technology*, 164(2): 155–168.
- 567 [52] Ferrell T. R. and Himmelblau M. D. (1967). Diffusion Coefficients of Hydrogen and Helium in Water.
568 *AIChE Journal*, 13(4): 702–708.
- 569 [53] Jockwer N. and Wieczorek K.(2008). ADDIGAS. Advective and diffusive gas transport in rock salt
570 formations. GRS-234, contact number: 02 E 9824 project final report, Gesellschaft fuer Anlagen- und
571 Reaktorsicherheit mbH (GRS), Berlin, Germany.
- 572 [54] Kunz O., and Wagner W. (2012). The GERG-2008 Wide-Range Equation of State for Natural Gases
573 and Other Mixtures: An Expansion of GERG-2004. *Journal of Physical and Chemical Reference Data*,
574 57(11): 3032–3091.