



A discussion on hydrogen migration in rock salt for tight underground storage with an insight into a laboratory setup

Murad S. Abuaisha, Joel Billiotte

► To cite this version:

Murad S. Abuaisha, Joel Billiotte. A discussion on hydrogen migration in rock salt for tight underground storage with an insight into a laboratory setup. *Journal of Energy Storage*, 2021, 38, pp.102589. 10.1016/j.est.2021.102589 . hal-03210848

HAL Id: hal-03210848

<https://hal.science/hal-03210848>

Submitted on 9 May 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Marked article

A discussion on hydrogen migration in rock salt for tight underground storage with an insight into a laboratory setup

Murad AbuAisha^{a,*}, Joël Billiotte^a

^aMINES ParisTech, PSL Research University, Centre de Géosciences, 35 rue Saint Honoré, 77300, Fontainebleau, France

Abstract

Hydrogen is being regarded as a primary vector in the energy transition process towards a less polluted planet. The tremendous and increasing energy demands necessitate finding large-scale storage techniques. Underground salt caverns seem to be promising. Nevertheless, the fast solicitations (thermal and mechanical) of these caverns, to reply to the fast demands, imply damage to the ambient rock salt. There is a general scientific ambiguity about the transport mechanisms taking place in the rock salt intact/damaged, particularly for hydrogen. In this paper we provide a detailed review about these transport mechanisms while the cavern undergoes cycling. This review helped us define a mathematical approach to simulate hydrogen migration in the rock salt around underground caverns. We ended up by presenting a patent laboratory setup that we are currently using to define any required model parameters experimentally.

Keywords: Underground salt caverns; hydrogen storage; saturated rock salt; hydrogen percolation and diffusion; cavern thermodynamics

1. Introduction

In the context of energy transition, hydrogen storage in underground salt caverns is becoming a leading technique [1–5]. This is related to the tremendous research on hydrogen production which promotes future cheap and facile product [6, 7]. Moreover, the underground salt caverns offer large-scale storing techniques able reply to the intermittency problems [8–10] and the increasing demands [11–13]. Not to forget that such caverns have also low investment costs and low cushion gas requirements [13]. Nevertheless, the future increasing energy demands will necessitate almost daily solicitations of the caverns [14]. Such fast charges, mechanical and thermal, are expected to affect the transport integrity/tightness of the rock salt embracing these caverns [15, 16]. To keep precise tracks/accurate management of the cycled hydrogen quantities, the hydrogen mass exchanged with the rock salt or other phases within the underground

*Corresponding author

Email addresses: murad.abuaisha@mines-paristech.fr (Murad AbuAisha), joel.billiotte@mines-paristech.fr (Joël Billiotte)

11 caverns must be minimized [17].

12 Rock salt occurs within sedimentary rocks where it has formed from the evaporation of seawater or
13 salty lakes. Rock salt is consequently deposited in cycles which affects its directional properties like the
14 elastic modulus and the permeability. Depending on the location, the rock salt properties, mechanical
15 and hydraulic, differ as well. Most of the available literature treats rock salt as impermeable non-porous
16 halite. The tightness of the underground salt caverns needs to be further investigated. There is a general
17 ambiguity about gas, a priori hydrogen, migration in the rock salt. As hydrogen storage is becoming a hot
18 interesting research topic, its transport mechanisms in the rock salt is also getting considerable attention.
19 Even if the intact rock salt may be hydrogen tight, the severe required utilization of caverns will imply
20 damage to this rock [18]. This damage incites modification to the transport properties of the rock salt
21 and the entire tightness of the storage system [19]. There have been a few scientific articles that discussed
22 seepage around underground caverns. For instance, *Liu et al.*, [20, 21] have presented cavern scale studies
23 to investigate the underground tightness for hydrogen, natural gas, and oil. Their approach assumed that
24 these fluids filtrate through the rock salt following a Darcian one-phase flow type. They concentrated
25 their research, mainly, on seepage in the interlayers rather than the intact or the cycling-damaged rock
26 salt. Besides, rock salt contains interstitial fluids and is characterized by very low permeabilities and
27 porosities. These factors render the assumption of one-phase Darcian flow questionable. Nuclear waste
28 storage in rock salt has been also a research subject for quite few scientists [22–24]. Their works proved
29 that disposal of heat-generating nuclear waste in salt formations is attractive because the material is
30 essentially impermeable, self-sealing, and thermally conductive. However, in particular, *Ghanbarzadeh et*
31 *al.*, [25] extended their research to seek a broader understanding of fluid percolation in the deformable rock
32 salt formations used for nuclear waste storage. They concluded that the low permeability of static rock
33 salt is due to a percolation threshold. However, deformation may be able to overcome this threshold and
34 allow fluid flow. Interestingly, they observed that percolation occurred at porosities considerably below
35 the static threshold due to deformation-assisted percolation. There is, however, considerable literature
36 that treats hydrogen percolation in clay sedimentary basins in the context of radioactive waste storage
37 [26, 27].

38 The main contribution of this scientific paper is to provide a resume about hydrogen transport in rock
39 salt. This resume is gathered from the available scientific literature and our expertise of understanding
40 the problem. By firstly addressing the interactions of phases within an underground cavern, we end up
41 by discussing all possible transport mechanisms in the embracing rock salt. Eventually, we conclude by
42 providing a modeling approach that would help scientific researchers develop a comprehensive mathe-
43 matical model for hydrogen migration in the saturated rock salt. The paper seals up by providing a
44 patent laboratory setup [28] that could be used to calibrate correctly the parameters of the suggested
45 mass transport models.

46

47



52
53
54
55
56
57
58
59
60
61

temperature. Since hydrogen may be present in the non-gaseous phase in the other phases (brine and solid), its presence will be characterized by a concentration. For the rock salt which is a mixture of solid and brine, the presence of hydrogen can be characterized by an overall concentration or a pressure. It is worthwhile to mention that the definition of gas concentration is very delicate. In this research, we would chose the mass concentration ($c_{h\lambda}$), where the density of hydrogen in the liquid phase $\rho_{h\lambda}$ is defined as $\rho_{h\lambda} = c_{h\lambda} \times \rho_{\lambda}$, with ρ_{λ} being the density of the liquid phase.

While the cavern is operated, the three phases are interacting as follows (Fig. 1): water is evaporating into the stored hydrogen (F_1''); hydrogen is dissolving in the brine (F_1 and F_1') and is percolating and diffusing into the porous rock salt (F_3); brine at the cavern bottom is flowing into the rock salt (F_2).

3. Hydrogen-brine interaction

Interactions between hydrogen and brine take place at the hydrogen-brine interface in the cavern (flow F_1 in Fig. 1) and they are defined by the solubility of hydrogen in brine according to Henry's law [31]. The definitions of the Henry's law parameters must account for the temperature and pressure ranges of the storage [32–34]. The solubility induces a flow of the dissolved hydrogen in the brine (flow F_1' in Fig. 1) which globally and gradually enriches the brine according to two mechanisms:

1. diffusion, which is characterized by a diffusion coefficient of the dissolved hydrogen in the brine, of which the value is dependent on the brine state variables (pressure, temperature) as well as the NaCl concentration [35]. The works of Chabab *et al.*, [36, 37] have proven that the saturated nature of the brine may require the use of sophisticated models¹ which take into account the interactions between the solution components, i.e. pressure, temperature, and concentration [36]. One can think of this as an apparent diffusion coefficient where the value is no longer a constant but a function of the brine saturation and the cavern working conditions.
2. convection, due to the circulation induced in the brine by the heat exchanges at the brine-rock salt interface and the non-equilibrium of the temperature between these two phases. The non-equilibrium of temperature is further enhanced during the cycling of the storage process and by the differences in thermal properties of the two phases, i.e. rock salt and brine. The driving force behind this convection is mainly the variations in the brine density with temperature [38, 39].

Accounting for all these phenomena of convection, the cavern working conditions, as well as the brine saturation, leads to the definition of an apparent diffusion coefficient that can be two orders of magnitude higher than the binary diffusion coefficient [40]. It is also important to study the kinetics of diffusion as will be discussed in Sect. 8. The brine itself being an NaCl solution, the solvent (H_2O) can be exchanged

¹Comparison between models is presented in Chabab *et al.*, [36].

93 through the hydrogen–brine interface (flow F_1'' in Fig. 1). This results in an existence of a partial pressure
94 of water–vapor in the gas phase of hydrogen [41].

95 4. Brine–rock salt interaction

96 Depending on the degree of salinity of brine at the bottom of the cavern, the brine–rock salt interface
97 can move due to dissolution or precipitation. Salt can precipitate from brine onto the interface or
98 the interface can be worn away by the brine to achieve saturation continuity at the cavern working
99 temperature and pressure conditions [42–44]. Even if its natural porosity is quite low ($\sim 0.01\%$) [45, 46],
100 due to its geologic formation, the rock salt can be considered as a porous medium saturated with brine
101 [47, p. 32] with a zero concentration of hydrogen. However, traces of liquid or gaseous hydrocarbons
102 are common in rock salt [48]. Therefore, the state variables for the rock salt interstitial brine are the
103 temperature and pressure.

104 Due to the ambiguity with regard to knowing the inter–grain connectivity of rock salt, the pressure
105 of the interstitial brine is poorly defined. However, its value can be limited to two extreme values [47]:

- 106 1. the so–called halmostatic pressure, which considers that the brine occupies a totally connected
107 space in the rock mass. Consequently, this pressure is the equivalent to the hydrostatic pressure
108 calculated using the brine density ($\sim 1200 \text{ kg/m}^3$);
- 109 2. a lithostatic pressure, which considers that the brine occupies an isolated space in the rock salt
110 phase. Therefore, the brine pressure is assumed in equilibrium with the isotropic stresses of the
111 rock salt mass. This pressure extremity is calculated using the rock salt density ($\sim 2160 \text{ kg/m}^3$)
112 [49].

113 During cycling, the cavern brine pressure will be equal to that of hydrogen and its value will vary as
114 a function of time between two extreme values:

- 115 1. a minimum pressure, equal to the halmostatic pressure during the cavern leaching, but which may
116 be lower than this during its operation;
- 117 2. a maximum pressure, which will always be lower than the lithostatic pressure to preserve the
118 integrity of the rock salt mass. Usually, the maximum operation pressure of the cavern is limited
119 to 80% of the surrounding minimum horizontal stresses [50].

120 Consequently, we can consider the existence of a brine flow (flow F_2 in Fig. 1) linked to a pressure
121 difference between the cavern brine and the brine saturating the rock salt. Since the pressure in the
122 rock salt mass is not known for certain, the concept of permeation [51], flow proportional to the pressure

imposed at the interface², is often preferred to that of convection, flow proportional to the local pressure gradient. Likewise, the mechanism of movement of brine in the rock salt mass is uncertain and discussed between two hypotheses: a movement in a network of connected pores characterized by a very low permeability quantifiable by Darcy's law (Fig. 2(a)); and a movement of isolated brine masses by a process of dissolution and precipitation at the brine-rock salt interface under the effect of slight changes in stresses and/or temperature created by changes in the cavern working conditions, including the induced creep at the cavern boundary (Fig. 2(b)) [52, 53].

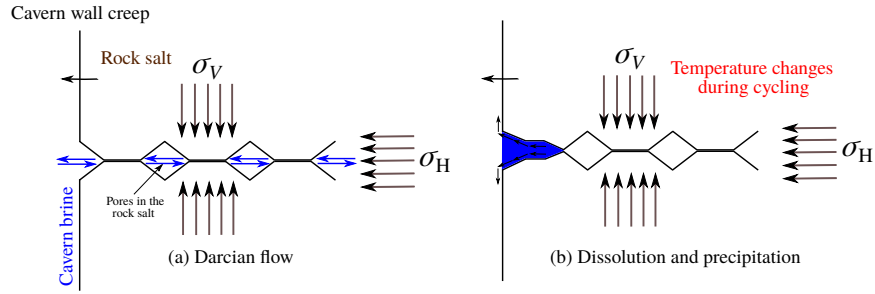


Figure 2: Schematic diagram representing the movement of brine in the rock salt domain: (a) by Darcian flow characterized by a very small permeability; (b) by dissolution and precipitation.

Depending on the value of the pressure of rock salt brine (halmostatic or lithostatic), flow F_2 can be incoming or outgoing with respect to the brine-rock salt interface. However it seems that the hypothesis of a halmostatic pressure is favored for some reasons. The first is that it leads to the most critical conditions with regard to the security of storage with maximum flow towards the surrounding rock salt. The second is that it underpins a large-scale connected porosity and therefore critical conditions for safety analysis. The assumption of halmostatic pressure allows, as well, for an assessment of fluxes by considering Darcy's law and using permeability values determined in the laboratory on test specimens [54]. For instance, authors like Bérest *et al.*, [55] have conducted *in situ* pressure monitoring tests in an idle salt cavern filled with brine at a pressure almost 4 MPa above the halmostatic pressure. They then analyzed the pressure at the head of the filled cavern. Once the effects linked to the deformation of the rock salt mass (atmospheric pressure, creep, leaks and terrestrial tides), and to the temperature were corrected [56], the pressure difference between the brine in the cavern and a halmostatic pressure in the rock salt was used to correlate to the measured flux during the test period. The measured flow was low to very low, from a few tens to a few m^3 per year, compared to the volume of the cavern (7500 to 8000 m^3). Note that the evolution of this flow was approximated using Darcy's law with a permeability

²In the permeation concept pressure is replaced by a concentration and flow is calculated using experimental permeation coefficients.

value of the rock mass of the same order of magnitude as values determined in the laboratory (order of 10^{-20} m²) for this layered rock salt (Bresse basin – France) [57]. There have been also some other *in situ* tests to investigate nitrogen and oil leaks around the cavern well and correlate them to Darcian flow [58]. Durup *et al.* [59] presented a deep cavern abandonment study. The objective was to study the pressure build-up effect on the integrity of a closed salt cavern.

In the case of hydrogen storage, hydrogen dissolved in the cavern brine can, by advection, propagate into the rock salt mass due to this permeation flow (flow F_2). Since the rock salt has very low porosity, mainly constituted by grain boundaries [60], the phenomenon of transverse dispersion can be neglected. Consequently, the penetration distance of hydrogen is calculated by considering the flow speed of the brine in the rock salt mass deduced from Darcy’s law with a pressure field characterized by spherical divergence. Henceforth, where the rock salt domain is invaded by the cavern brine, dissolved hydrogen concentration in the rock salt is equal to that in the cavern brine divided by the porosity of the rock salt, i.e. a factor of 10^{-2} to 10^{-3} , assuming that the rock salt is neither damaged nor disturbed by the creation of the cavern and/or by the operation of the repository. This evaluation of the penetration distance, which neglects the Fickian diffusion of hydrogen, can be corrected and maximized by taking into account a longitudinal diffusion with a diffusion coefficient deduced from that of hydrogen in brine. This diffusion coefficient should only consider the effects of the porous medium (porosity, tortuosity, and constrictivity) [61]. All of this leads to the fact that hydrogen concentration in the rock salt domain at the cavern bottom be much lower than that in the cavern brine. Since hydrogen concentration in the cavern brine can not be but minimal³, the entire flow F_2 seems to be negligible.

Taking into account the effects of damage and/or disturbance on the hydraulic properties of the rock salt mass also implies taking into account the distribution of fluids (brine, water vapor and possibly hydrogen) in the porosity increased by this damage and/or disturbance. These mechanisms will be analyzed in more detail in the section discussing the interaction between hydrogen and the rock salt mass.

5. Hydrogen–rock salt interaction

At the hydrogen–rock salt interface, the penetration of hydrogen into the saturated rock can take place either [62]:

1. in the solid phase itself, i.e. the halite crystals;
2. in the fluid phases occupying the rock pores (brine, water vapor, or gas).

³Available literature, for instance Chabab *et al.*, [37], proves that hydrogen dissolves in very small quantities in saturated brine compared to other gases, i.e. CO₂.

These are two different mechanisms, the first is similar to gas diffusion in solids or what is defined as permeation. The second is similar to gas diffusion in brine saturating the pores or to a two-phase flow in porous media, if the pores are not saturated, or if they are desaturated by the percolation of hydrogen.

5.1. Permeation in the halite crystals

Diffusion of gas into solids is called permeation. This phenomenon is responsible for gas permeability of polymer pipes and is particularly important in the case of hydrogen with metals [63, 64]. This permeability deficiency of metals with respect to hydrogen results from the high availability of electrons in a metal. On the metal surface, the dihydrogen molecule can dissociate and each hydrogen atom ionizes in the H^+ form, i.e. a proton. As the size of the proton is much smaller than the distance between the atoms of the crystal lattice, it moves easily through the crystallized structure of the metal, and even over significant thicknesses. The mobility of protons is greatly enhanced by the presence of vacancies in the crystal structure. This permeation mechanism is illustrated in Fig. 3 from a technical report about the problems caused by hydrogen permeation in pressure transmitters [65].

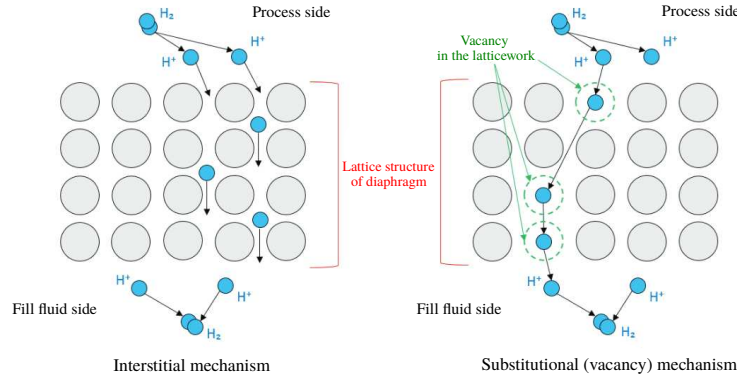


Figure 3: Mechanism of hydrogen permeation in the metallic diaphragms. Figure reproduced from Yokogawa [65].

On the other face of the diaphragm, and even if it is in contact with a liquid, the protons will recombine into dihydrogen molecules. This flow of protons will lead to the formation of hydrogen bubbles in the liquid, and this is reinforced by the significantly low solubility of hydrogen. In the case of pressure transmitters, this permeation is equivalent to a leakage in the pressure measurement of the gas phase. The formation of bubbles in the liquid phase modifies its compressibility. Therefore it causes the respiration of the pressure sensors and the deformation of the diaphragm, particularly during temperature variations. Finally the exchange of electrons in the crystal lattice weakens the metal [65].

Permeation is characterized by a coefficient whose ratio is the permeability with units as $\text{mol}/(\text{s m}^2 \text{ Pa})$ in the SI system and more practically in $\text{m}^3 \text{ (STP)}/(\text{s m}^2 \text{ Pa})$, or with more exotic units (Barrer or GPU)

[66]. The value of the permeability coefficient can be determined experimentally by measuring the flow of hydrogen through a sample of known thickness (Fig. 4) [67]. The evaluation of the flow is carried out in the downstream chamber either by measuring the evolution of the hydrogen concentration by gas chromatography, or by measuring the pressure. It can be also calculated by the measuring the pressure difference between the upstream and the downstream chambers.

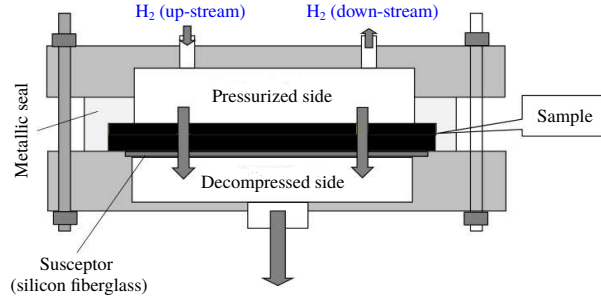


Figure 4: Schematic representation of a laboratory model to measure the hydrogen permeability coefficient [67].

The interpretation of this model measurements is made by considering that the transfer of gas into the solid is governed by diffusion according to Fick's law. Therefore, the only state variable of the gas in the solid is its concentration. At the gas-solid interface, it is generally assumed that the gas penetration is governed by Henry's law (form of solubility). The use of this law allows to relate the gas pressure applied to the sample surface to concentrations at the limits of the sample [68].

With regard to hydrogen permeation in halite lattice structure, the comparison between the size of a hydrogen atom (106 pm) and the atomic space in the crystal lattice of halite (34 pm) [69], shows that the diffusion of hydrogen in the atomic form is not possible. However, as hydrogen protons have a radius of 0.84 fm, it would be possible that hydrogen diffuses in the ionic form. Yet, since halite is already an ionic solid, ionization of hydrogen atoms is usually not possible. It follows that the phenomenon of hydrogen permeation in metals and its importance cannot be as significant in rock salt. The value of a permeability coefficient or a diffusion coefficient of hydrogen in halite crystal, which generally constitutes the solid phase of rock salt, can only be very small. It is the same with all minerals, except for ores, graphite and clay minerals, which have electrically non-neutral surfaces, and which can create preferential and rapid migration paths of protons by moving to electronegative sites on the surface of minerals [70]. This proton conduction phenomenon is usually taken into consideration in the safety analysis of radiolysis hydrogen produced by nuclear waste often stored in clayey rocks. For this particular case, this conduction mechanism is associated to water molecules saturating the space between the clay particles and the hydrogen dissolved in this interstitial fluid [71].

5.2. Diffusion in the interstitial brine

The porosity of rock salt is saturated with brine. Since brine is in equilibrium with halite (the solid phase), it is necessarily saturated with sodium chloride NaCl [47]. This porosity is formed by the joints between crystals or halite grains and the fluid inclusions. This defines a connected porosity, a priori (the grain boundaries), and an unconnected porosity (the fluid inclusions) [60]. If the fluid inclusions are very numerous (milky salt), and representing a significant relative volume (a few %), then porosity associated with the grain boundaries is low to very low (less than 1% to zero). Measuring this kind of porosity is tremendously tough, with particular difficulty with respect to eliminating the artifacts related to the sample preparation and the deconfinement of the rock salt logs [60].

Considering that hydrogen diffusion in halite crystals is very low, a preliminary approach is to consider that it will diffuse in the brine saturating the rock salt. It is then possible to carry out an evaluation of the penetration of hydrogen using Fick's law with [62]:

1. a concentration of dissolved hydrogen on the cavern surface deduced from the storage pressure and Henry's law;
2. an effective diffusion coefficient of hydrogen in the rock salt brine via its connected porosity.

The value of the effective diffusion coefficient D (m^2/s) is deduced from that of hydrogen in brine \bar{D} (m^2/s) by adjusting it using three coefficients [72]:

$$D = \bar{D} \times n \times \frac{\delta}{\tau^2}, \quad \text{with:} \quad (1)$$

- the first is equal to the porosity (n), which represents a reduction in the volume of the brine due to the presence of the solid phase;
- the second is the inverse of the square of the tortuosity (τ), which represents the relative elongation of the diffusion paths relative to a fluid due to the texture of the porosity;
- the last coefficient (δ) represents the constrictivity factor which depends on the flow regime imposed by the shape of the pores and their size. When the pore size decreases and becomes smaller than the mean free path of the solute molecules of the solvent, the diffusion regime changes from molecular to transitional, and then to slip for which the Knudsen number⁴ is less than unity. This will be discussed in details in the next section.

There is almost no available literature on hydrogen diffusion in the saturated brine. However, since hydrogen diffusion in water is well known ($\bar{D} = 6.1 \times 10^{-9} \text{ m}^2/\text{s}$ at 25 °C) [73, 74], the viscosity models

⁴The Knudsen number (K_n) is a dimensionless number defined as the ratio of the molecular mean free path length to a representative physical length scale.

for electrolyte solutions [75–77] can be used to approximately calculate its diffusion coefficient in brine. Using the Stokes–Einstein law [78], the viscosity models give $\bar{D} \approx 4.6 \times 10^{-9} \text{ m}^2/\text{s}$ at 25 °C for hydrogen in the saturated brine. Another handy way to calculate the effective diffusion coefficient is to use the relation of *Grathwohl* [79], i.e. $D = \bar{D} \times n^q$. The empirical parameter q usually lies between 1.8 and 2.4.

Regardless of the method used to determine the effective diffusion coefficient, by molecular simulations or experiments, its implementation in Fick’s law allows for possible simple analytical solutions [80]. The use of Fick’s law also permits to define a characteristic time linked to the diffusion. Such time can be compared to that calculated by convection and to have, particularly for long periods, an evaluation of a penetration distance. This distance into the rock salt mass is mathematically proportional to the square root of the product of the effective diffusion coefficient and time [80].

As stated in Sect. 4, if hydrogen concentration in the rock salt is to be considered as a state variable, we can, rigorously, assume its initial value to be zero. However, certain underground mines of evaporite rocks (potash, carnalite) and rock salt are known to have some concentrations of hydrogen in the void of their galleries. The origin of this hydrogen is linked to the radiolysis of water under the effect of radioactive minerals present in the rock salt mass [26, 42]. Consequently, hydrogen can be observable in the rock salt fluid inclusions and its release is subsequent to the creation of damaged and/or disturbed zones [81]. The creation of these zones increase the connected porosity which will be unsaturated and which will allow for a flow of hydrogen towards the farther galleries. This kind of flow drains hydrogen from the grain boundaries and the fluid inclusions [82]. The damage or disturbance of the host rock can be induced by thermal gradients and stresses [83]. Some studies have looked at the diffusion of gas, including hydrogen, contained in fluid inclusions mainly due to temperature variations. For instance, *Clark et al.*, [81] found that the migration distances were of the order of a few tens of micrometers for inclusions in quartz.

In case of rock salt, the experimental determination of the effective diffusion coefficient is challenging. This hardness is attributed to several reasons of which: 1) the difficulty to keep interstitial brine in equilibrium with the solid phase, and so that no convective movement of the brine may be induced by the field of constraints imposed; 2) preventing any water vapor exchanges with the injected gas (water vapor comes usually from the external atmosphere of the sample) [84].

5.3. Convective flow in the rock salt

Convective flow of hydrogen in the rock salt takes place due to bulk motion of the gas. This bulk motion can happen in one-phase or two-phase natures.

5.3.1. One-phase flow

In this simplistic approach, we assume that we have only one fluid filling the pores of the rock salt mass. The flow of this fluid is governed by Darcy’s law. The use of Darcy’s law requires using the fluid

281 pressure as a state variable, and to characterize the permeability of the rock salt with regard to the fluid
 282 used [85]. This gives rise to difficulties, namely, the value of the fluid pressure in the rock salt domain,
 283 i.e. halmostatic, lithostatic, or an intermediate value. The permeability of the rock salt, with regard to
 284 one-phase flow, needs to be experimentally calculated. The calculation of the permeability of rock salt
 285 is an experimental challenge. This is due to the very low values, less than 10^{-20} m² in case of the intact
 286 rock. The difficulty is also experimental, where it is almost impossible to define a representative state of
 287 the actual rock mass, not disturbed, by the sample preparation and the test conditions. Test conditions
 288 should be perfect where no parasite flows or leaks on the sample boundaries are allowed [45].

289 Due to the very low permeability of the rock salt, almost all of the measurements are carried out
 290 using gas as the measuring fluid. They are also done in transient conditions with pressures, or pressure
 291 gradients that are quite different from the *in situ* rock salt conditions. Using gas as a measuring fluid
 292 involves removing the sample brine, generally by drying, whether thermal or vacuum . Drying extracts
 293 water from brine, but the salt remains in the porosity. Therefore, the pore space that would be traveled
 294 by the measuring gas is necessarily different from that initially exited. To mimic the *in situ* rock salt
 295 stress conditions, laboratory measurements are usually performed under loads. However, rock salt is
 296 sensitive to the state of stress, particularly the deviatoric stresses, which generate creep (Fig. 5). The
 297 use of an isotropic confinement state can cancel rock salt creep globally, but not locally. Local changes
 298 include development of the grain contacts and healing of the damage defects with water vapor bubbles
 299 [86].

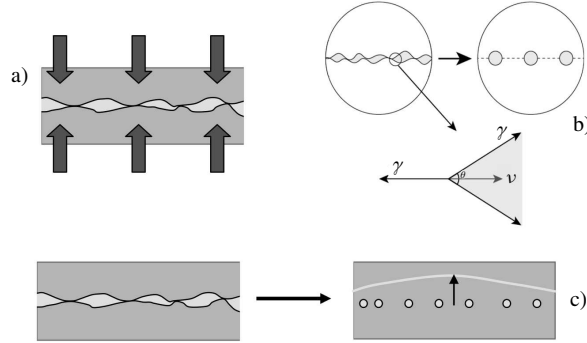


Figure 5: Crack healing/sealing and permeability reduction in rock salt. a) Mechanical closure of cracks due to compaction of the rock by elastic deformation or plastic flow. b) Necking down of cracks and pores to form arrays of disconnected tubular and spherical inclusions. Here γ denotes the surface energy vectors, θ the dihedral angle of the crack, and ν the crack migration velocity. c) Crack and pore occlusion through fluid-assisted grain boundary migration (recrystallization). Figure is modified from Koelemeijer et al., [86].

300 Due to the very low porosity of rock salt, it is difficult to define the hydromechanical coupling using

301 Biot's effective stresses [87]. However, reality shows that there is a very strong hydromechanical coupling
 302 [88, 89]. This coupling is related to the tremendous increase of the permeability with damage [19]. It
 303 is also observed during laboratory tests, where measurements made with the same difference between
 304 confining stress and upstream gas pressure were not equivalent [19]. This suggested that the upstream
 305 gas pressure was an addition to the stress in the direction of flow, where different deviatoric stress states
 306 induced different changes in porosity [45].

307 The very low value of permeability is attributed to the very low porosity and to the presence of inter-
 308 grains constrictions at their contacts (Fig. 6). Measurements showed that pore size of rock salt varies
 309 from 0.01 to 300 μm with major concentration of pore size being smaller than 1.0 μm [60, 90].

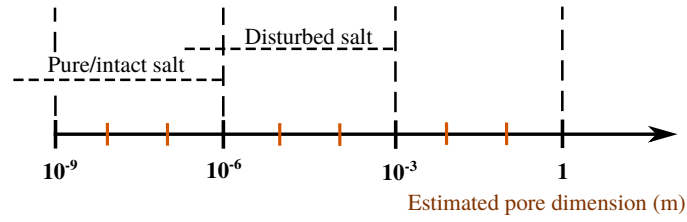


Figure 6: Estimation of the pore dimension in rock salt [19, 60, 90].

With very small pore dimensions, fluid flow is affected by the interactions between the fluid molecules and the solid surface. The importance of these interactions is assessed by comparing the mean free path of a molecule ζ (m) to that of a characteristic pore dimension (d_p) via the Knudsen number ($K_n = \zeta/d_p$). In the case of gas flow, the average free path is evaluated with the following expression [91],

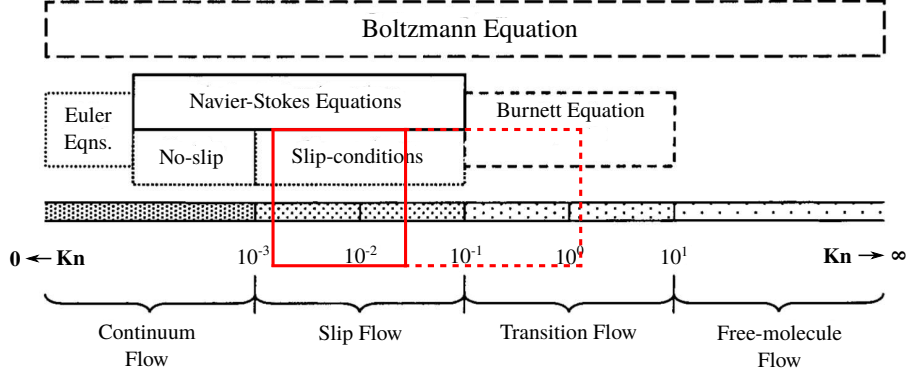
$$\zeta = \frac{RT_\gamma}{\sqrt{2}\pi d_m^2 p_\gamma N}, \quad (2)$$

310 with R (J/mol/K) being the universal gas constant, T_γ (K) the gas absolute temperature, d_m (m) the
 311 kinetic diameter of the gas (289 pm for hydrogen), p_γ (Pa) the gas pressure, and N (1/mol) the Avogadro
 312 constant. For hydrogen storage in a typical cavern at 1000 m depth, during seasonal operations, hydrogen
 313 pressure changes between 16 and 5 MPa, and the corresponding temperature ranges between 65 and 28
 314 $^\circ\text{C}$ [50]. However for extreme daily utilization of the cavern, and for the same pressure changes, the
 315 cavern average temperature ranges between 95 and -40 $^\circ\text{C}$ [14]. Table (1) shows that the mean free path
 316 of hydrogen traveling in rock salt varies between 0.86 and 1.70 nm for extreme daily utilization of a
 317 typical cavern.

318 Depending on the value of the Knudsen number (Table (1)), the equation used to describe the gas
 319 flow in the rock salt is different (Fig. 7). In case of an intact salt, most of the domain (red box) is located
 320 in the “slip flow”. However, if the rock salt pore dimensions are less than the smallest average (5×10^{-7}
 321 m of Fig. 6), transition flow may take place.

Table 1: Mean free path of hydrogen traveling in rock salt under daily cavern utilization.

Pressure (MPa)	Temperature (°C)	ζ (nm)	K_n for		
			$d_p = 10^{-6}$ m	$d_p = 5 \times 10^{-7}$ m	$d_p = 10^{-9}$ m
16	95	0.86	0.86×10^{-3}	0.17×10^{-2}	0.86
5	-40	1.70	1.70×10^{-3}	0.35×10^{-2}	1.70


 Figure 7: Flow type and associated equation based on the Knudsen number, modified from *Roy et al.*, [92].

It is, therefore, quite probable that hydrogen will flow in a slip regime in the rock salt. The interaction **gas-solid** in this regime is characterized by the Klinkenberg effect [93]. Consequently, the apparent permeability of gas k_a (m²) flowing in a porous medium is related to the intrinsic permeability k (m²) via the following relation,

$$k_a = k \left(1 + \frac{b}{\langle p_\gamma \rangle} \right), \quad (3)$$

with b (Pa) being an empirical parameter (usually called the slip factor), $\langle p_\gamma \rangle$ (Pa) the mean pressure at which the apparent permeability is calculated. The influence of gas on the calculated permeability is related to the size of the molecules. Thus, for the same tested sample, the slip factor b depends on the measurement gas. Besides, the influence of the sample, i.e. the porous medium, is not explicit, as it depends on the testing conditions as well. Empirical relations, such as proportionality with an inverse power of the permeability, are usually proposed to calculate the slip factor [45, 94].

5.3.2. Two-phase flow

In this approach we assume the effective penetration of hydrogen into the rock salt porosity to imply a displacement of the brine. It is a two-phase immiscible flow in a porous medium. In this flow the hydrogen constitutes the non-wetting displacing phase and the brine the wetting displaced phase.

332 In a porous medium, these two immiscible phases are separated by an interface characterized by
 333 surface energy or surface tension. In case of air and saturated brine, this energy is 1.13 times greater
 334 than in the case of water, i.e. 82 mN/m at 25 °C and at the atmospheric pressure [95]. Studies have shown
 335 that increasing temperature from 27 to 100 °C increased the surface energy by 17%. However, increasing
 336 pressure from 5 to 25 MPa reduced it by 28% [96, 97]. Since in underground caverns, increasing pressure is
 337 associated with increasing temperature, changes in surface tension could be crucially neglected. *Fukuzawa*
 338 *et al.*, [98] have shown that the hydrogen–water surface tension is equal to 74.81 mN/m at temperature
 339 4.7 °C and atmospheric pressure. At this particular temperature, the surface tension barely showed any
 340 pressure dependency. We could not find in literature any studies on hydrogen–brine surface tension.
 341 However, if we assume the same increase as in water–brine surface energy, we will find an approximate
 342 value of 84.5 mN/m at 25 °C and at the atmospheric pressure. We still could assume a further increase at
 343 normal temperature conditions of 25 °C. Based on the curvature of the gas–liquid interface, the surface
 344 energy results in a positive pressure difference between the two phases. This pressure difference can be
 345 quantified using Jurin’s law, or directly using the Young–Laplace equation [99]. Both equations indicate
 346 that the interfacial pressure difference is proportional to the surface tension and inversely proportional
 347 to the characteristic size of the pores. To give an order of magnitude for hydrogen–brine interface, a
 348 pore radius of 1 μm corresponds to a pressure difference of ~ 0.1 MPa, meanwhile a pore radius of 1 nm
 349 corresponds to a pressure difference of ~ 85 MPa. The interfacial pressure difference defines a condition
 350 called the entry pressure. The gas pressure in contact with the porous medium must exceed the pressure
 351 of the interstitial fluid and the entry pressure so that gas may invade the medium and replace the pore
 352 liquid. Penetration is conditioned by the size of the largest pores on the surface of the porous medium,
 353 meanwhile invasion is linked to the average radius. If we assume the rock salt to be intact at the end of
 354 the cavern leaching, for a pore size of 1×10^{-8} m, the required entry pressure is around 34 MPa. This
 355 value is very approximative, as for intact rock salt the pore size varies widely (Fig. 6). For applications
 356 with regard to hydrogen storage in porous media, and hydrogen production in underground repositories
 357 of radioactive waste, researchers have assigned values of 2 to 5 MPa to the pressure entry in the case of
 358 argillite repositories [27, 100] (with relatively large porosities), and up to 15 MPa in the case of shale
 359 [101].

360 Hydrogen distribution in the partially desaturated pore space depends on two dimensionless numbers.
 361 The first is called the capillary number Ca , which represents the relative effect of viscous drag forces versus
 362 surface tension forces acting across the gas–liquid interface. The second number defines the mobility M ,
 363 which represents the viscosity ratio of the displaced fluid to the displacing gas [102, 103]. Depending
 364 on the values of these two dimensionless numbers, the flow will have different morphologies and will
 365 require different simulation methods to quantify the penetration distance (Fig. 8). In case of hydrogen–
 366 brine flow, the mobility number is important. Besides, the high capillary pressure, linked to the small

pore size, makes the application of Darcian approaches quite inaccurate. Therefore, only percolation
 type approaches, with or without gradient, should be used. These approaches are characterized by the
 absence of a finite size of a representative elementary volume. Henceforth, at the percolation threshold,
 even-though the over all saturation of hydrogen is quite small, its penetration distance could still be
 considerable [17].

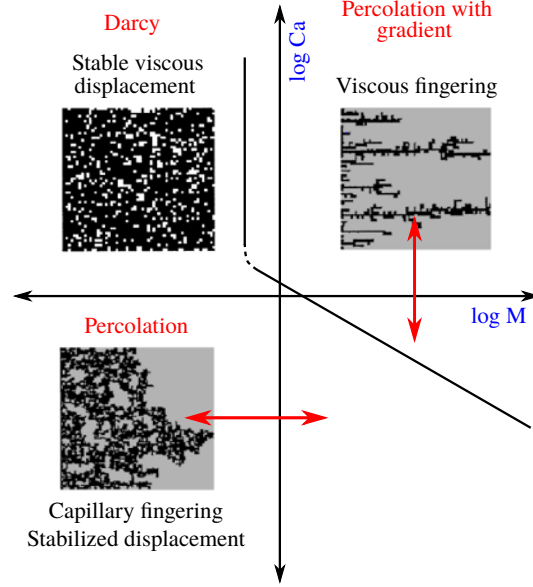


Figure 8: Lenormand diagram [103] describing the reasons of drainage in a porous medium. The non-wetting phase (hydrogen μ_1) is replacing the wetting phase (brine μ_2) as a function of the capillary number Ca and the mobility number $M = \mu_2/\mu_1$.

Under the conditions of hydrogen storage in underground salt caverns, the $\log(M)$ is always positive,
 and the capillary number is quite insignificant due to the small viscous forces of hydrogen. This neces-
 sitates that hydrogen flow in rock salt to be located in the lower right quarter of Fig. 8. Consequently,
 a flow pattern of either viscous fingering (percolation with gradient), capillary fingering (percolation),
 or intermediate of the two is expected. It is the same domain usually used to model the migration of
 radiolysis hydrogen in the clay rock hosting a repository of radioactive waste [26, 27]. Lefort [104] defined
 this flow pattern or domain as a hyper-slow drainage, and he found that a flow of viscous fingering (per-
 colation with gradient) would stabilize after a distance of a few thousand pores. The gas invasion then
 continued over a stable front which made it possible to describe it either by a generalized Darcian flow
 or a Buckley-Leverett model. However, these models require establishing, experimentally or conceptually
 (by using van Genuchten and/or Brooks-Corey models [105, 106]), hydraulic parameters that take into

account the local hydrogen saturation. Yet, if we consider a steep desaturation front, the flow can be reduced to a piston type flow [107]. With all the cited references, the relevance of these models and their applicability to the salt rock can not be solidly established, including *Lefort* [104] analysis. This is attributed to the very low porosity and morphology of the rock salt pores, which are grain boundaries, therefore of crack type with contact points [60].

Whatever approach is chosen to model hydrogen–salt rock exchanges (diffusion, single–phase, or two–phase flow), the transient modeling as a function of the cavern pressure cycles requires the determination of additional parameters. These parameters include the effective porosity for the diffusion, the storage coefficient for the single–phase flow and the capillary pressure–saturation and relative permeability–saturation relationships for the two–phase flow. The experimental determination of such parameters is very delicate, especially under the *in situ* conditions. A transient approach would be necessary to estimate the hydrogen quantity exchanged with the rock salt mass and to obtain a transient spatial distribution. However, one would anticipate that due to the very low permeability of the rock salt, hydrogen pressure cycles might have very small influence distances. Therefore, it might be possible to consider a constant value of the pressure or of the concentration at the solid rock salt–hydrogen interface. This value could be the average or even the maximum storage pressure to maximize the determined penetration, and which allows to determine a characteristic speed for each of the modes of movement. In case of Fickian diffusive movement, the penetration distance is directly quantifiable as function of the effective diffusion coefficient. In case of a single–phase or a two–phase flow, we can consider the flow to be governed by the displacement of the brine, which depends only on the permeability of the rock salt mass and the pressure difference.

All of these approaches consider a displacement of the fluid molecules with regard to a fixed solid surface. The calculated penetration distance must be corrected by the displacement of the rock salt towards the cavern. Such displacement is induced by the creep of the rock salt under the effect of mechanical stresses. The creep stresses are, themselves, induced by the leaching and the operation of the cavern. If the cavern wall displacement is considered, the effective penetration distance will be less than those determined by previous approaches.

6. Influence of the damaged zone

Under the effect of stresses induced by leaching and operation of underground caverns, the damage criteria can be met which may modify the rock salt hydraulic properties [50]. This phenomenon leads to the creation of a damaged zone which extends from the cavern surface to a certain distance beyond which the rock retains its initial properties, particularly the hydraulic ones. **The rock salt damage results in the development of microcracks or cracks which can develop on different scales.** This causes an increase in the

rock porosity which can range from very large, say five-fold the initial value, to a few milli-percents [18]. Likewise, the permeability of rock salt samples taken from damaged areas in the vicinity of underground galleries showed considerable increase in their permeability, i.e. more than three orders of magnitude [19, 54].

The intrinsic permeability of the intact or *in situ* rock salt is extremely low, less than 10^{-20} m², and its porosity is saturated with brine. As a result, any damage induced porosity cannot be saturated by an overall displacement of the brine. It will, therefore, be occupied by a gas phase composed of water vapor from brine at a partial pressure in accordance with the brine-gas interface determinable by the Kelvin equation. This mass transfer of water vapor can create a local over-saturation of the brine and a localized precipitation of halite. Likewise, damage can connect fluid inclusions to the defects created and bring the content of these inclusions, i.e. liquid or gaseous hydrocarbons and gases (nitrogen, CO₂, and hydrogen) into the connected porous network. On the other side, some oxide inclusions maybe reduced to metal or even form metal hydrides. The formation of methane is most likely due to the reaction between Na₂CO₃ and hydrides or metal as reported in *Zhu et al.*, [7]. Meanwhile, CO₂ methanation *in situ* formed from LaNi₅H₅ catalyzed via Metallic as reported in *Zhong et al.*, [108].

Even if the permeability of the damaged zone is much higher than that of the intact rock salt, any displacement of brine out of the damaged zone necessarily implies a flow of brine into the farther intact rock salt. This means that the occupation of the damage-created unsaturated porosity happens as result of increasing the partial or total pressure of hydrogen, and by the flow of the initial brine towards the intact rock salt mass. To estimate the hydrogen penetration into the rock salt as part of a safety analysis, it is possible to decouple these modes. Therefore, it will be acceptable to consider the whole damaged area to be invaded and pressurized by hydrogen with a uniform representative pressure. However, at the edge of the damaged zone, hydrogen applies a pressure to the brine of the intact rock salt. The analysis of hydrogen penetration and displacement of brine could be described using the methods mentioned in Sect. 5.

The estimation of the size of the damaged zone necessitates the development of sophisticated models to describe creep in rock salt due to pressure and temperature cyclings [109–111]. The model/material parameters are usually determined experimentally [15, 112]. However, this zone is sometimes considered as disturbed and not damaged. The stress induced microcracks and cracks might have developed, but the density, and especially the connectivity, of these defects do not lead to an increase in permeability (Fig. 5). As a result, this zone would have a hydraulic behavior similar to the intact rock salt, since the changes in porosity do not intervene. This needs to be investigated by laboratory tests which will be highlighted in Sect. 8

7. Influence of temperature

Pressure variations induced during gas cycling generate temperature variations at the cavern surface. In the context of hydrogen transport in rock salt, these temperature variations may have transport effects that must be taken into account. These effects can be divided into two main groups: the first is related to the modification of hydrogen and brine viscosities; the second is attributed to the modification of the rock salt hydraulic properties. Thermal changes usually cause an increase in the permeability due to the presence of insolubles that have different expansion coefficients than that of halite. We can cite the case of anhydrite and calcite nodules which represent dilation anisotropies unlike those of halite. With a temperature increase, the dilation anisotropies cause local deformation incompatibilities generating thermal damage. *Le Guen et al.*, [113] have experimentally measured a permeability increase of approximately 1.7 times due to a temperature increase of 34 °C.

Temperature changes also induce migration of fluid inclusions, therefore of elements of non-connected porosity. The inclusions migrate towards the hot zones under a dissolution effect on their hot side and a precipitation effect on the cold side. The speed of migration depends on the importance of the temperature gradient, the size of the inclusion, and of its content. In the case of strong gradients, close to a heating element of 150 °C, this migration can generate significant disturbances with the creation of tubes resulting from the coalescence of the migrating inclusions, and with a supply of brine from the grain boundaries (Fig. 9) [114]. Figure 9 is deduced from a study that concerned a thermal test performed in the Amélie mine (Haut-Rhin France).

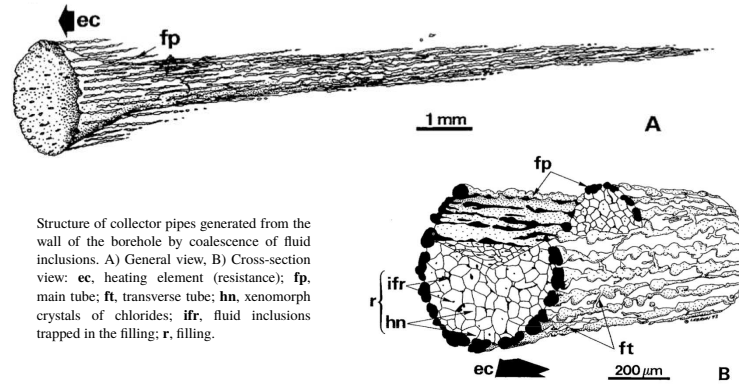


Figure 9: Schematic diagram of a tube created by fluid inclusions migration in the vicinity of a heating element. Figure is reproduced from *Lebrun et al.*, [114].

More generally, the migration of fluid inclusions goes through the redistribution of the inter-crystalline brine in the connected porosity inducing a set of mechanisms and reactions which can modify the hydraulic

properties of the rock salt. For instance, Fig. 10 shows that conduits in rock salt can be created by several driving forces. Such driving forces can include temperature changes or mineral vapor pressure. The result is a displaced pore fluid or vapor that goes into the creation of a new connected porosity (inter-crystalline redistribution) that is also altered by the external stresses or the induced pore pressure gradient itself.

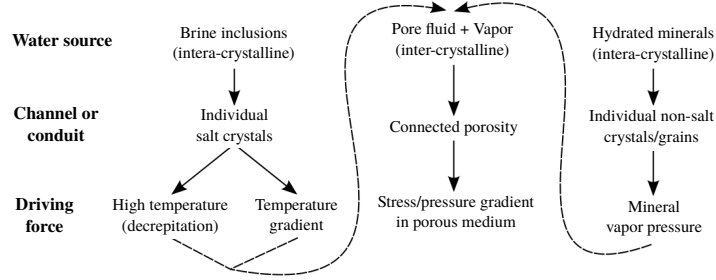


Figure 10: Relations between mechanisms and brine movements induced by temperature gradients. Figure is reproduced from Kuhlman and Malama [115].

In the case of hydrogen storage, the temperature variations of the stored hydrogen can be significant, i.e. -40 to 95 °C (considering fast and excessive utilization). We recommend that these effects be accounted for in the models describing rock salt creep [109], as well as in the fluid phases hydraulic properties and densities. However, temperature related mechanisms are expected to be located in the vicinity of the cavern wall, therefore in the damaged area. Consequently, the temperature related modifications of hydraulic properties of the rock salt of the damaged zone would probably have no influence compared to the mechanical or pressure effects

8. Modeling approach with perspectives

The previous literature review helps understand all possible transport mechanisms of hydrogen gas in the rock salt surrounding an underground cavern during cycling. Deploying this study, we can come out with the following modeling scenario:

1. the assumption that the surrounding rock salt domain is saturated with brine at the halmostatic pressure is favored. It leads to the most critical conditions with regard to the security of storage with maximum flow towards the rock salt (Sect. 4);
2. Hydrogen Fickian diffusion in the rock salt lattice is tremendously small and can be neglected (Sect. 5.1);
3. One-phase convective flow hypothesis of hydrogen in the saturated rock salt is dubious. This is attributed to the presence of the liquid phase in the *in situ* rock salt, as well as the difficulties to define the flow nature and the hydraulic parameters (Sect. 5.3.1);

493 4. assuming two-phase transport of hydrogen into the ambient rock salt mass seems to be the com-
 494 prehensive or the most convincing theory (Fig. 11). However, this transport should address: the
 495 Fickian diffusion of hydrogen into the saturating brine (Sect. 5.2); and the percolation of the drying
 496 phase (hydrogen) by displacing the wetting phase (brine) (Sect. 5.3.2);

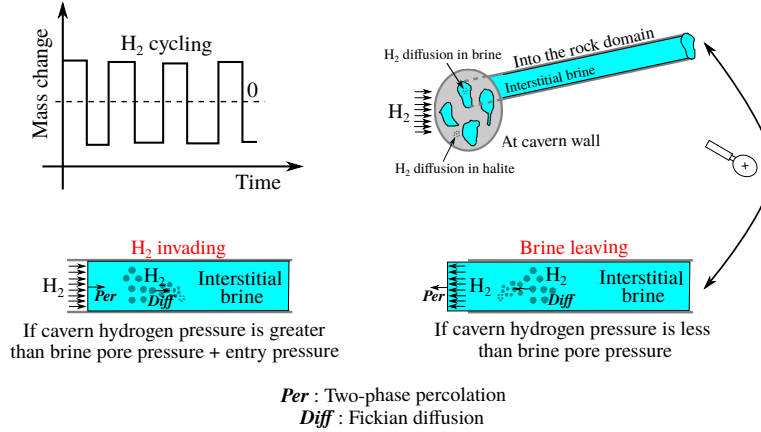


Figure 11: Schematic diagram illustrating the migration of hydrogen into the saturated rock salt during cycling in underground caverns.

497 5. accounting for rock salt creep or damage during cycling is very important. The created disturbed
 498 zone might be the only place where hydrogen can migrate (Sect. 6);
 499 6. As rock salt has relatively high thermal transport properties (compared to other rocks), non-
 500 isothermal models need to be considered for hydrogen migration into it (Sect. 7).

501 Consequently, to thoroughly describe hydrogen transport in the saturated rock salt, the developed
 502 mathematical model must strongly couple: the cavern thermodynamics (p_γ and T_γ); the development
 503 of the disturbed or damaged zone; the transfer of heat into the rock salt domain, and the two-phase
 504 percolation with the Fickian diffusion. This mathematical model is already developed and published in
 505 the work of *AbuAisha et al.*, [17]. Figure 8 shows all the transport mechanics of hydrogen that take place
 506 within an underground cavern. The figure also presents our research methodology to consider the most
 507 convincing and influential mechanisms.

508 It is worthwhile to mention that our previous research focuses on the flux F_3 of Fig. 1. To ensure the
 509 hydrogen-tightness of the entire storage system, the other fluxes, particularly F_1 should be quantified⁵.
 510 Hydrogen dissolution in the saturated brine has been a very interesting research subject recently [37, 116,
 511 117]. Even-though these articles present hydrogen dissolution at different pressures and temperatures,

⁵Flux F_2 is deemed negligible compared to other fluxes (see the argument of Sect. 4).

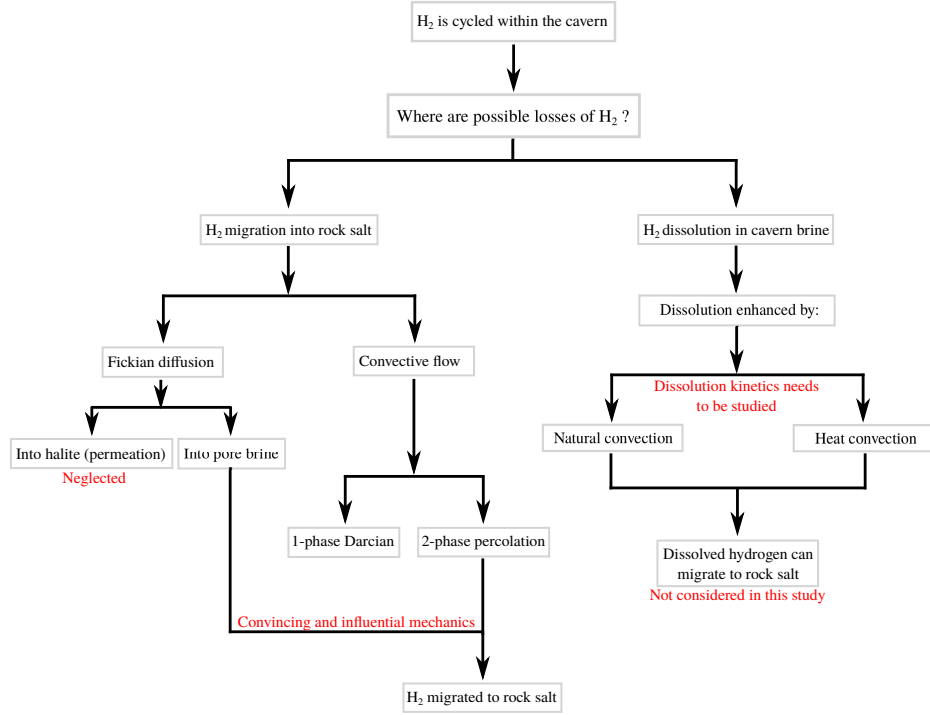


Figure 12: Our research methodology presenting the transport mechanisms of hydrogen that happen within an underground cavern.

none of them treats the kinetics of the dissolution as function of time. Another challenging task to this framework, is the determination of the two-phase percolation-diffusion model parameters. A van-Genuchten type model seems interesting (Sect. 5.3.2), however, an experimental approach must be conceived to calibrate its parameters. We provide the following patent laboratory setup (Fig. 13) [28] to evaluate the van Genuchten model parameters, as well as to study the Kinetics of hydrogen dissolution. This laboratory setup consists of a hydrogen-tight steel cell of 110 mm height and 55 mm diameter.

8.1. The permeation laboratory test

In the first approach, a saturated rock salt sample (dimensions are displayed on Fig. 13(a)) is placed within the cell in away it occupies most of the void. The entire cell is placed in a water basin of a certain temperature. Non-damaged as well as damaged (by creep laboratory tests) samples can be studied. The goal is to reduce as much as possible the hydrogen volume around the sample so that any tiny pressure changes can be measured. The pressure of hydrogen is then increased by injection. Injection in this case is translated by a valve opening, where a flow between this cell and a pressurized reserve takes place

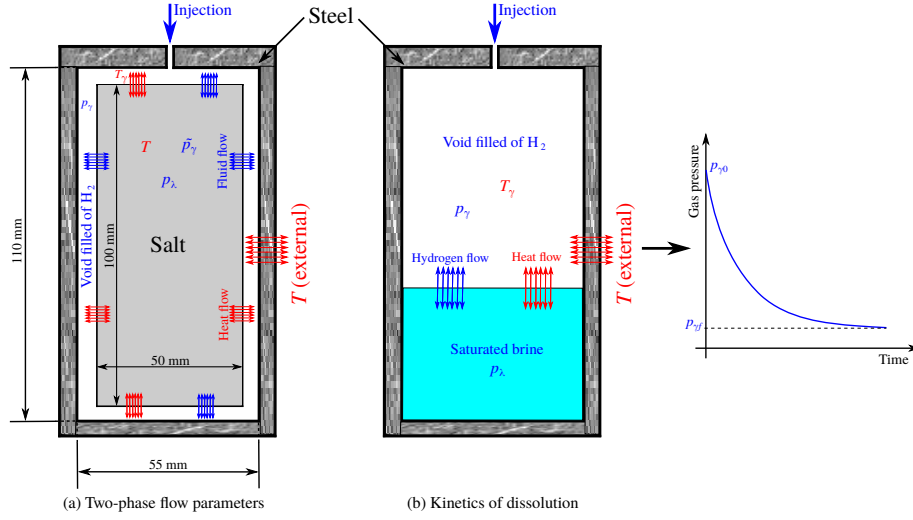


Figure 13: A schematic diagram of our proposed laboratory setup to study hydrogen permeation in the saturated rock salt as well as the kinetics of its dissolution in the saturated brine. In figure (a), the quantities p_λ and \tilde{p}_γ represent the initial brine pore pressure within the saturated sample (atmospheric), and the initial hydrogen pseudo-pressure (zero initially), see *AbuAisha et al.*, [17] for details. In figure (b), p_λ is the saturated brine pressure (atmospheric).

almost instantly. The entire cell is then left for stabilization. The void hydrogen pressure will drop from its initial value $p_{\gamma 0}$ to its final value $p_{\gamma f}$ over a time period Δt .

Fast injection of hydrogen will increase its temperature T_γ . Consequently, there will be heat exchange between hydrogen and the rock salt sample, as well as between hydrogen and the steel. Hydrogen will also invade the sample in a two-phase type flow and in Fickian diffusion. The quantity p_λ represents the initial brine pore pressure within the sample, and \tilde{p}_γ the pressure of hydrogen invading the sample. The two pressures are distinguished as two-phase percolation is accounted for. Solution starts by integrating all this physics in our mathematical model and numerically solve it. This will help determine the van Genuchten parameters and the diffusion coefficient that mostly fit the experimental curve of pressure drop. However, injected pressure values need to be so high (around 20 MPa) to allow for hydrogen entry into the saturated rock salt. This laboratory test can be conducted on intact and damaged rock salt samples. Damaged samples would have undergone creep conditions, due to thermo-mechanical charges, similar to rock salt around real caverns. The objective is to compare the transport properties of intact and damaged rock salt samples.

8.2. The dissolution laboratory test

In the second approach, the same cell is filled with NaCl saturated brine to a certain volume and is submerged in bathtub to insure a fixed temperature. Hydrogen is injected in the left void to a certain

initial pressure value $p_{\gamma 0}$. The system is then left to stabilize over time until a final hydrogen pressure value is reached $p_{\gamma f}$. This test can be run at different pressure and temperature values to study the effect of cavern working conditions on the dissolution kinetics. As in the first test, injection is expected to increase the void hydrogen temperature. Therefore, it is conceivable that there will be heat exchange between the void hydrogen and the steel, as well as between the void hydrogen and the brine.

In a real caver, usually there is a thermal gradient over the cavern brine volume. Due to the limited size of our laboratory cell, the effect of a temperature gradient may be difficult to tackle. We are currently conducting such laboratory tests to evaluate the van Genuchten model parameters along with Fickian diffusion, as well as the kinetics of hydrogen dissolution.

9. Conclusion

Due to the present-day ambiguity with regard to gas transport in rock salt, this article provides a detailed literature review about hydrogen migration in the saturated rock salt. This review is outlined in the context of underground energy storage, where precise tracks and management of the stocked hydrogen quantities are of significant importance. The objective is to draw a general scheme that can be used in developing a mathematical model for this type of gas migration.

It was indispensable to firstly understand how all phases of an underground cavern interact. Then to address the migration of hydrogen into the embracing rock salt, we needed to conceive the hydraulic nature and properties of this rock salt, i.e. porosity, permeability, and the *in situ* pore pressure or stresses. Rock salt is mostly seen as an impermeable medium. However, this is not necessarily the case, especially, when it undergoes creep due to thermo-mechanical charges from the cavern it surrounds. We sought to understand all possible transport mechanisms when hydrogen is pushed into damageable saturated rock salt. These mechanisms included the Fickian diffusion into the halite structure, into the pore brine as well. They also included the convective flow of the gas itself, where the one-phase approach was compared to the two-phase drainage. We emphasized on the necessity to consider the effect of temperature in the damaged zone of the rock salt, as well as the hydraulic properties of the fluid phases. This article aims at helping researchers find direct and concise answers to their questions with regard to hydrogen, and generally gas, transport in rock salt. We will use it to enhance our mathematical-numerical model already published in *AbuAisha et al.*, [17]. It serves as well for our future publications about hydrogen permeation in the saturated rock salt, and the kinetics of its dissolution in the saturated brine.

Though the available literature concerning gas migration in rock salt is very scarce, it promotes the research outline of this article. For instance *Jockwer and Wieczorek* [118] have stated that the presence of a damaged zone (DRZ) is the main factor for gas transport in rock salt. They conducted experiments and simulations concerning helium, neon, and butane. They found that the diffusion coefficient of these

575 gases increased by two orders of magnitude in the DRZ. Out of the DRZ, the measured permeabilities
576 were in the order of 10^{-19} and 10^{-20} m², and the pseudo gas pressure slightly penetrated the rock salt
577 in a two-phase piston-like flow. *Senger et al.* [119] studied gas (particularly air) migration in concrete.
578 They have found that the gas penetrated distances were limited to 1.5 m after 4 years of injection. The
579 two-phase gas saturation depended on the permeabilities, yet it was less than 0.1 for permeabilities in
580 the order of 10^{-19} m². Generally, the existed literature already confirms that permeable interlayers are
581 the main transport conduits around salter caverns [20, 21].

582 The current developments include the utilization of the suggested laboratory setup to calibrate the
583 two-phase percolation-diffusion model parameters for intact and damaged rock salt. Once these model
584 parameters are known, they can be transfered to real scale prototype caverns where hydrogen percolation
585 in rock salt is investigated. There is currently a European project of a prototype salt cavern (EZ53) where
586 the percolation and diffusion of hydrogen in the rock salt is studied on the real scale. The objective is
587 to quantify the amount of hydrogen lost into the rock domain during cycling, and see if it affects the
588 management of the cycled masses.

589 10. Acknowledgement

590 Authors would like to thank Géodénergies and the French Association Nationale de Recherche (ANR)
591 for their financial support via the three projects: ROSTOCK-H, STOPIL-H, and HyTrend. We are, as
592 well, expressing a deep feeling of gratitude to Prof. Christophe Coquelet and Dr. Faouzi Hadj-Hassen
593 (MINES ParisTech) for their efforts in bringing out this work.

References

- [1] 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.
- [2] 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.
- [3] 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.
- [4] 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.
- [5] Klumpp F. (2016). Comparison of pumped hydro, hydrogen storage and compressed air energy storage for integrating high shares of renewable energies–Potential, cost-comparison and ranking. *Journal of Energy Storage*, 8: 119–128.
- [6] Holladay J. D., Hu J., King D. L., Wang Y. (2009). An overview of hydrogen production technologies. *Catalysis Today*, 139(4): 244–260.
- [7] Zhu Y., Ouyang L., Zhong H., Liu J., Wang H., Shao H., Huang Z., and Zhu M. (2020). Closing the Loop for Hydrogen Storage: Facile Regeneration of NaBH_4 from its Hydrolytic Product. *Angewandte Chemie International Edition*, 59(22): 8623–8629.
- [8] Koohi-Fayegh S. and Rosen M. A. (2020). A review of energy storage types, applications and recent developments. *Journal of Energy Storage*, 27: 101047.
- [9] Demirel T., and Deveci M., and Vardar G. (2017). Location selection for underground natural gas storage using Choquet integral. *Journal of Natural Gas Science and Engineering*, 45: 368–379.
- [10] Deveci M., Demirel Ç. N., John R., and Özcan E. (2015). Fuzzy multi-criteria decision making for carbon dioxide geological storage in Turkey. *Journal of Natural Gas Science and Engineering*, 27(2): 692–705.
- [11] Matos C. R., Carneiro J. F., and Silva P. P. (2019). Overview of large-scale underground energy storage technologies for integration of renewable energies and criteria for reservoir identification. *Journal of Energy Storage*, 21: 241–258.

- [12] Ozarslan A. (2012). Large-scale hydrogen energy storage in salt caverns. *International Journal of Hydrogen Energy*, 37(19): 14265–14277.
- [13] 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.
- [14] AbuAisha M. and Rouabhi A. (2019). On the validity of the uniform thermodynamic state approach for underground caverns during fast and slow cycling. *International Journal of Heat and Mass Transfer*, 142: 118424.
- [15] Khaleli K., Mahmoudi E., Datcheva M., and Schanz T. (2016). Stability and serviceability of underground energy storage caverns in rock salt subjected to mechanical cyclic loading. *International Journal of Rock Mechanics and Mining Sciences*, 86: 115–131.
- [16] Labaune P. and Rouabhi A. (2019). Dilatancy and tensile criteria for salt cavern design in the context of cyclic loading for energy storage. *Journal of Natural Gas Science and Engineering*, 62: 314–329.
- [17] AbuAisha M., Rouabhi A., Billiotte J., and Hadj-Hassen F. (2021). Non-isothermal two-phase hydrogen transport in rock salt during cycling in underground caverns. *International Journal of Hydrogen Energy*, 46(3): 6632–6647.
- [18] Popp T., Kern H., and Schulze O. (2001). Evolution of dilatancy and permeability in rock salt during hydrostatic compaction and triaxial deformation. *Journal of Geophysical Research – Solid Earth*, 106(B3): 4061–4078.
- [19] Stormont J. C. (1997). *In-situ* gas permeability measurements to delineate damage in rock salt. *International Journal of Rock Mechanics and Mining Sciences*, 34(7): 1055–1064.
- [20] 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.
- [21] 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.
- [22] Hansen F. D. and Leigh C. D. (2011). Salt disposal of heat-generating nuclear waste. Sandia Report: SAND2011-0161, Sandia National Laboratories, Albuquerque, New Mexico 87185 and Livermore, California 94550.

- [23] Ślizowski J. and Lankof L. (2003). Salt–mudstones and rock–salt suitabilities for radioactive–waste storage systems: rheological properties. *Applied Energy*, 75(1–2): 137–144.
- [24] Johnson K. S. and Gonzales S. (1978). Salt deposits in the United States and regional geologic characteristics important for storage of radioactive waste. Earth Resource Associates, INC., Athens, Georgia, the USA.
- [25] Ghanbarzadeh S., Hesse M. A., Prodanović M., Gardner J. E. (2015). Deformation–assisted fluid percolation in rock salt. *Science (Geology)*, 350(6264): 1069–1072.
- [26] 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): evidence for fluid–rock interaction in the vicinity of salt dome cap rock. *Chemical Geology*, 156: 191–207.
- [27] Amaziane B., Keko A. Ž., and Jurak M. (2014). Modeling compositional compressible two–phase flow in porous media by the concept of the global pressure. *Computational Geosciences*, 18(3–4): 297–309.
- [28] Hannon M. J. (2016). Full immersion pressure–pulse decay. United States Patent PCT/US2016/031502. International Publication Number: WO 2016/179593A1, 10 November 2016.
- [29] Charnavel Y., Leca D., and Poulain F. (1999). Advanced geometrical modelling of salt dissolution during cavern leaching – illustration with a case study. *In: The SMRI Meeting, Las Vegas, Nevada, USA.*
- [30] Pernette E. and Dussaud M. (1983). Underground storages at Tersanne and Etrez: prediction and simulation of cavity leaching in a salt layer charged with insoluble materials. *In: The sixth International Symposium on Salt, Toronto, Canada, May 26–27.*
- [31] Jaffré J. and Sboui A. (2010). Henry’s law and gas phase disappearance. *Transport in Porous Media*, 82: 521–526.
- [32] Geng M. and Duan Z. (2010). Prediction of oxygen solubility in pure water and brines up to high temperatures and pressures. *Geochimica et Cosmochimica Acta*, 74: 5631–5640.
- [33] Barrett T. J., Anderson G. M., and Lugowski J. (1988). The solubility of hydrogen sulphide in 0–5 m NaCl solutions at 25°–95°C and one atmosphere. *Geochimica et Cosmochimica Acta*, 52: 807–811.
- [34] Crozier T. E. and Yamamoto S. (1974). Solubility of hydrogen in water, seawater, and NaCl solutions. *Journal of Chemical and Engineering Data*, 19(3): 242–244.

- [35] Gossett J. M. (1987). Measurement of Henry’s law constants for C₁ and C₂ chlorinated hydrocarbons. *Environmental Science and Technology*, 21: 202–208.
- [36] Chabab S., Théveneau P., Corvisier J., Coquelet C., Paricaud P., Houriez C., and El Ahmar E. (2019). Thermodynamic study of the CO₂ – H₂O – NaCl system: Measurements of CO₂ solubility and modeling of phase equilibria using Soreide and Whitson, electrolyte CPA and SIT models. *International Journal of Greenhouse Gas Control*, 91: 102825.
- [37] Chabab S., Théveneau P., Coquelet C., Corvisier J., and Paricaud P. (2020). Measurements and predictive models of high-pressure H₂ solubility in brine (H₂O+NaCl) for underground hydrogen storage application. *International Journal of Hydrogen Energy*, 45(56): 32206–32220.
- [38] Beckermann C., Ramadhyani S., and Viskanta R. (1986). Natural convection flow and heat transfer between a fluid layer and a porous layer inside a rectangular enclosure. *Journal of Heat Transfer*, 109: 363–370.
- [39] Bergholz R. F. (1978). Instability of steady natural convection in a vertical fluid layer. *Journal of Fluid Mechanics*, 2(84): 743–768.
- [40] Soubeyran A., Rouabhi A., and Coquelet C. (2019). Thermodynamic analysis of carbon dioxide storage in salt caverns to improve the Power-to-Gas process. *Applied Energy*, 242: 1090–1107.
- [41] Singh D. and Sirkar K. K. (2012). Desalination of brine and produced water by direct contact membrane distillation at high temperatures and pressures. *Journal of Membrane Science*, 389: 380–388.
- [42] Kloppmann W., Négrel P. H., Casanova J., Klinge H., Schelkes K., and Guerrot C. (2001). Halite dissolution derived brines in the vicinity of a Permian salt dome (N German Basin). Evidence from boron, strontium, oxygen, and hydrogen isotopes. *Geochimica et Cosmochimica Acta*, 65(22): 4087–4101.
- [43] Hassanizadeh S. M. and Leijnse T. (1988). On the Modeling of Brine Transport in Porous Media. *Water Resources Research*, 24(3): 321–330.
- [44] Johnson K. S. (1981). Dissolution of salt on the east flank of the permian basin in the southwestern U.S.A. *Journal of Hydrology*, 54: 75–93.
- [45] Schlichtenmayer M. and Bannach A. (2015). Renewable energy storage in salt caverns – A comparison of the thermodynamics and permeability between natural gas, air, and hydrogen. RR2015-1 Research Project Report, prepared for Solution Mining Research Institute, D-095596 Freiberg, Germany.

- [46] Popp T. and Kern H. (1998). Ultrasonic wave velocities, gas permeability and porosity in natural and granular rock salt. *Physics and Chemistry of the Earth*, 23(3): 373–378.
- [47] Gevantman L. H. (1981). Physical properties data for rock salt. U.S. Department of Commerce/National Bureau of Standards. U.S. Government Printing Office, Washington, D.C. 20402.
- [48] Hammer J., Pusch M., Häher C., Ostertag-Henning C., Thiemeyer N., and Zulauf G. (2015). Hydrocarbons in rock salt of the Gorleben salt dome—amount, origin and influence on geomechanical properties. *In: Roberts, L., Mellegard, K., Hansen, F. (Eds.), The Mechanical Behavior of Salt VIII.* Taylor & Francis Group, London, pp. 69–75.
- [49] Bradley J. S. (1975). Abnormal Formation Pressure. *AAPG Bulletin*, 59(6): 957–973.
- [50] Rouabhi A., Hévin G., Soubeyran A., Labaune P., and Louvet F. (2017). A multiphase multi-component modeling approach of underground salt cavern storage. *Geomechanics for Energy and the Environment*, 12: 21–35.
- [51] Rutherford S. W. and Do D. D. (1997). Review of time lag permeation technique as a method for characterisation of porous media and membranes. *Adsorption*, 3(4): 283–312.
- [52] Martin B., Röller K., and Stöckhert B. (1999). Low-stress pressure solution experiments on halite single-crystals. *Tectonophysics* 308: 299–310.
- [53] Spiers C. J. and Schutjens P. M. T. M. (1999). Intergranular Pressure Solution in NaCl: Grain-to-Grain Contact Experiments under the Optical Microscope. *Oil & Gas Science and Technology*, 54(6): 729–750.
- [54] Cosenza P. H. and Ghoreychi M. (1999). Effects of very low permeability on the long-term evolution of a storage cavern in rock salt. *International Journal of Rock Mechanics and Mining Sciences*, 36: 527–533.
- [55] Bérest P., Brouard B., and Hévin G. (2011). Twelve-year monitoring of the idle Etrez salt cavern. *International Journal of Rock Mechanics and Mining Sciences*, 48: 168–173.
- [56] Bérest P., Bergues J., and Brouard B. (1999). Review of static and dynamic compressibility issues relating to deep underground salt caverns. *International Journal of Rock Mechanics and Mining Sciences*, 36: 1031–1049.
- [57] Bérest P., Bergues J., Brouard B., Durup J. G., and Guerber B. (2001). A salt cavern abandonment test. *International Journal of Rock Mechanics and Mining Sciences*, 38: 357–368.

- [58] Bérest P., Brouard B., and Durup J. G. (2001). Tightness Tests in Salt-Cavern Wells. *Oil & Gas Science and Technology – Rev. IFP*, 56(5): 451–469.
- [59] Durup J. G., Vidal F., and Rolin C. (2007). Pilot Abandonment Test of a Very Deep Gas Storage Salt Cavern. *Oil & Gas Science and Technology – Rev. IFP*, 62(3): 287–296.
- [60] Jianwen C., Erbing L., and Jin L. (2018). Characterization of microscopic pore structures of rock salt through mercury injection and nitrogen absorption tests. *Geofluids*, <https://doi.org/10.1155/2018/9427361>.
- [61] Van Brakel J. and Heertjes P. M. (1974). Analysis of diffusion in macroporous media in terms of a porosity, a tortuosity and a constrictivity factor. *International Journal of Heat and Mass Transfer*, 17(9): 1093–1103.
- [62] Ho C. K. and Webb S. W. (2006). *Gas Transport in Porous Media*. Springer, 3300 AA Dordrecht, The Netherlands.
- [63] Wipf H. (2001). Solubility and Diffusion of Hydrogen in Pure Metals and Alloys. *Physica Scripta*, T94: 43–51.
- [64] Hempelmann R. (1984). Diffusion of hydrogen in metals. *Journal of the Less-Common Metals*, 101: 69–96.
- [65] Yokogawa (2018). Hydrogen permeation. Application note, Yokogawa Corporation of America.
- [66] Malykh O. V., Golub Yu. A., and Teplyakov V. V. (2011). Polymeric membrane materials: New aspects of empirical approaches to prediction of gas permeability parameters in relation to permanent gases, linear lower hydrocarbons and some toxic gases. *Advances in Colloid and Interface Science* 164: 89–99.
- [67] Eschbach H. L., Gross F., and Schulien S. (1963). Permeability measurements with gaseous hydrogen for various steels. *Vacuum*, 13: 543–547.
- [68] Yukawa H., Zhang G. X., Watanabe N., Morinaga M., Nambu T., and Matsumoto Y. (2009). Analysis of hydrogen diffusion coefficient during hydrogen permeation through niobium and its alloys. *Journal of Alloys and Compounds*, 476: 102–106.
- [69] Aquilano D., Otálora F., Pastero L., and García-Ruiz J. M. (2016). Three study cases of growth morphology in minerals: Halite, calcite and gypsum. *Progress in Crystal Growth and Characterization of Materials*, 62(2): 227–251.

- 771 [70] Ortiz L., Volckaert G., and Mallants D. (2002). Gas generation and migration in Boom Clay, a
772 potential host rock formation for nuclear waste storage. *Engineering Geology* 64: 287–296.
- 773 [71] Jacobs E., Wouters K., Volckaert G., Moors H., Maes N., Bruggeman C., Swennen R., and Littke
774 R. (2015). Measuring the effective diffusion coefficient of dissolved hydrogen in saturated Boom Clay.
775 *Applied Geochemistry*, 61: 175–184.
- 776 [72] Webb S. W. and Pruess K. (2003). The use of Fick’s law for modeling trace gas diffusion in porous
777 media. *Transport in Porous Media*, 51: 327–341.
- 778 [73] Ferrell T. R. and Himmelblau M. D. (1967). Diffusion Coefficients of Hydrogen and Helium in Water.
779 *AIChE Journal*, 13(4): 702–708.
- 780 [74] Pray A., Schweickert E. C., and Minnichi H. B. (1952). Solubility of Hydrogen, Oxygen, Nitrogen,
781 and Helium in Water at elevated temperatures. *Industrial and Engineering Chemistry*, 44(5): 1146–
782 1151.
- 783 [75] Cadogan S. P., Hallett J. P., Maitland G. C., and Trusler J. P. M. (2015). Diffusion coefficients of
784 carbon dioxide in brines measured using ^{13}C pulsed-field gradient nuclear magnetic resonance. *Journal*
785 *of Chemical and Engineering Data*, 60(1): 181–184.
- 786 [76] AspenTech. (2001). Physical property methods and models. Aspen Reference Manual, no. 11.1: 2–18.
- 787 [77] Breslau B. R. and Miller F. (1972). On the viscosity of concentrated aqueous electrolyte Solutions.
788 *The Journal of Physical Chemistry*, 74(5): 1056–1061.
- 789 [78] Cadogan P. S., Hallett P. J., Maitland C. G., and Martin Trusler P. J. (2015). Diffusion Coefficients
790 of Carbon Dioxide in Brines Measured Using ^{13}C Pulsed-Field Gradient Nuclear Magnetic Resonance.
791 *Journal of Chemical and Engineering Data*, 60: 181–184.
- 792 [79] Grathwohl P. (1998). Diffusion in natural porous media: contaminant transport, sorption/desorption
793 and dissolution kinetics. Springer US, New York.
- 794 [80] Crank J. (1973). The mathematics of diffusion. Second edition. Oxford University Press, Walton
795 street, Oxford OX2 6DP, UK.
- 796 [81] Clark G. J., White C. W., Allred D. D., Appleton B. R., and Tsong I. S. T. (1978). Hydrogen
797 concentration profiles in quartz determined by a nuclear reaction technique. *Physics and Chemistry of*
798 *Minerals*, 3(2): 199–211.
- 799 [82] Mello U. T., Karner G. D., and Anderson R. N. (1995). Role of salt in restraining the maturation of
800 subsalt source rocks. *Marine and Petroleum Geology*, 12(7): 697–716.

- [83] Fournier R. O. (1991). The transition from hydrostatic to greater than hydrostatic fluid pressure in presently active continental hydrothermal systems in crystalline rock. *Geophysical Research Letters*, 18(5): 955–958.
- [84] Sutherland H. J. and Cave S. P. (1980). Argon gas permeability of new mexico rock salt under hydrostatic compression. *International Journal of Rock Mechanics and Mining Sciences and Geomechanics Abstracts*, 17(5): 281–288.
- [85] Wu Y. S., Pruess K., and Persoff P. (1998). Gas Flow in Porous Media with Klinkenberg Effects. *Transport in Porous Media*, 32: 117–137.
- [86] Koelemeijer P. J., Peach C. J., and Spiers C. J. (2012). Surface diffusivity of cleaved NaCl crystals as a function of humidity: Impedance spectroscopy measurements and implications for crack healing in rock salt. *Journal of Geophysical Research*, 117: B01205.
- [87] Mahjoub M., Rouabhi A., Tijani M., Granet S., M’Jahad S., and Talandier J. (2018). Numerical study of Callovo-Oxfordian argillite expansion due to gas injection. *International Journal of Geomechanics*, 18(1): 04017134.
- [88] Kim K. and Makhnenko R. Y. (2020). Coupling Between Poromechanical Behavior and Fluid Flow in Tight Rock. *Transport in Porous Media*, 135: 487–512.
- [89] Zhang D., Jeannin L., Hevin G., Egermann P., Potier L., Skoczylas F. (2018). Is Salt a Poromechanical Material? *In: the 52nd U.S. Rock Mechanics/Geomechanics Symposium*, Seattle, the USA.
- [90] De Las Cuevas C. (1997). Pore structure characterization in rock salt. *Engineering Geology*, 47(1–2): 17–30.
- [91] Ziarani A. S. and Aguilera R. (2012). Knudsen’s Permeability Correction for Tight Porous Media. *Transport in Porous Media*, 91(1): 239–260.
- [92] Roy S., Raju R., Chuang H. F., Cruden B. A., and Meyyappan M. (2003). Modeling gas flow through microchannels and nanopores. *Journal of Applied Physics* 93(8): 4870.
- [93] Klinkenberg L. (1941). The permeability of porous media to liquids and gases. Paper API41200 Presented at the Drilling and Production Practice, New York, 1 January.
- [94] Zisser N. and Nover G. (2009). Anisotropy of permeability and complex resistivity of tight sandstones subjected to hydrostatic pressure. *Journal of Applied Geophysics* 68(3): 356–370.

- [95] Ozdemira O., Karakashev S. I., Nguyen A. V., and Miller J. D. (2009). Adsorption and surface tension analysis of concentrated alkali halide brine solutions. *Minerals Engineering*, 22(3): 263–271.
- [96] Liu Y., Li H. A., and Okuno R. (2016). Measurements and modeling of interfacial tension for $\text{CO}_2/\text{CH}_4/\text{Brine}$ Systems under Reservoir Conditions. *Industrial and Engineering Chemistry Research*, 55(48): 12358–12375.
- [97] Aggelopoulos C. A., Robin M., and Vizika O. (2011). Interfacial tension between CO_2 and brine ($\text{NaCl} + \text{CaCl}_2$) at elevated pressures and temperatures: The additive effect of different salts. *Advances in Water Resources*, 34(4): 505–511.
- [98] Fukuzawa K., Watanabe K., Yasuda K., and Ohmura R. (2018). Interfacial tension measurements in the ($\text{CO}_2 + \text{H}_2$) gas mixture and water system at temperatures from 271.2 K to 280.2 K and pressures up to 7.0 MPa. *The Journal of Chemical Thermodynamics*, 119: 20–25.
- [99] Rodríguez-Valverde M. A. and Miranda M. T. (2011). Derivation of Jurin’s law revisited. *European Journal of Physics*, 32: 49–54.
- [100] Ern A. and Mozolevski I. (2012). Discontinuous Galerkin method for two-component liquid–gas porous media flows. *Computational Geosciences*, 16(3): 677–690.
- [101] Pfeiffer W. T., al Hagrey S. A., Köhn D., Rabbel W., and Bauer S. (2016). Porous media hydrogen storage at a synthetic, heterogeneous field site: numerical simulation of storage operation and geophysical monitoring. *Environmental Earth Sciences*, 75:1177.
- [102] Yortsos Y. C., Xu B., and Salin D. (1997). Phase diagram of fully developed drainage in porous media. *Physical Review Letters*, 79(23): 4581–4584.
- [103] Lenormand R. (1989). Flow through porous media: limits of fractal patterns. *Proceedings of the Royal Society A*, 423(1864): 159–168.
- [104] Lefort P. (2014). Étude des déplacements gaz–eau dans les argilites du Callovo–Oxfordien à l’aide de la théorie de la percolation en gradient. Ph.D. thesis, INP Toulouse.
- [105] Akhmetzyanova A. V., Kushner A. G., and Lychagin V. V. (2017). Mass and heat transport in the two-phase Buckley–Leverett model. *Journal of Geometry and Physics*, 113: 2–9.
- [106] Morel-Seytoux H. J., Meyer P. D., Nachabe M., Tourna J., van Genuchten M. T., and Lenhard R. J. (1996). Parameter equivalence for the Brooks–Corey and van Genuchten soil characteristics: preserving the effective capillary drive. *Water Resources Research banner*, 32(5): 1251–1258.

- [107] Sukhija B. S., Reddy D. V., Nagabhushanam P., and Hussain S. (2003). Recharge processes: piston flow vs preferential flow in semi-arid aquifers of India. *Hydrogeology Journal*, 11(3): 387–395.
- [108] Zhong D., Ouyang L., Liu J., Wang H., Jia Y., and Zhu M. (2019). Metallic Ni nanocatalyst *in situ* formed from LaNi₅H₅ toward efficient CO₂ methanation. *International Journal of Hydrogen Energy*, 44(55): 29068–29074.
- [109] Khaledi K., Mahmoudi E., Datcheva M., and Schanz T. (2016). Analysis of compressed air storage caverns in rock salt considering thermo-mechanical cyclic loading. *Environmental Earth Sciences*, 75: 1149.
- [110] Deng J. Q., Yang Q., and Liu Y. R. (2014). Time-dependent behaviour and stability evaluation of gas storage caverns in salt rock based on deformation reinforcement theory. *Tunnelling and Underground Space Technology*, 42: 277–292.
- [111] Moghadam S. N., Mirzabozorg H., and Noorzad A. (2013). Modeling time-dependent behavior of gas caverns in rock salt considering creep, dilatancy and failure. *Tunnelling and Underground Space Technology*, 33: 171–185.
- [112] Wang G., Guo K., Christianson M., and Konietzky H. (2011). Deformation characteristics of rock salt with mudstone interbeds surrounding gas and oil storage cavern. *International Journal of Rock Mechanics and Mining Sciences*, 48(6): 870–877.
- [113] Le Guen C., Deveughèle M., Billiotte J., and Brulhet J. (1993). Gas permeability changes of rock salt subjected to thermo-mechanical stresses. *Quarterly Journal of Engineering Geology*, 26: 327–334.
- [114] Lebrun P., Billiotte J., Deveughèle M., and Le Cléac’h J. M. (1995). Local increase of rock salt porosity by coalescence of fluid inclusions under the effect of a thermal gradient. *Comptes Rendus de l’Academie des Sciences*, 320(7): 555–561.
- [115] Kuhlman K. L. and Malama B. (2013). Brine flow in heated geologic salt. Sandia report SAND2013-1944, 128 pages.
- [116] Pinto J. S. R., Bachaud P., Fargetton T., Ferrando N., Jeannin L., and Louvet F. (2021). Modeling phase equilibrium of hydrogen and natural gas in brines: application to storage in salt caverns. *International Journal of Hydrogen Energy*, 46(5): 4229–4240.
- [117] Li D., Beyer C., and Bauer S. (2018). A unified phase equilibrium model for hydrogen solubility and solution density. *International Journal of Hydrogen Energy*, 43(1): 512–529.

- 888 [118] Jockwer N. and Wieczorek K.(2008). ADDIGAS. Advective and diffusive gas transport in rock salt
889 formations. GRS-234, contact number: 02 E 9824 project final report, Gesellschaft fuer Anlagen- und
890 Reaktorsicherheit mbH (GRS), Berlin, Germany.
- 891 [119] Senger R., Lanyon B., Marschall P., and Vomvoris S. (2008). Numerical modeling of the gas migra-
892 tion test at the Grimsel test site (Switzerland). Nuclear Technology, 164(2): 155–168.

- Hydrogen storage in underground salt caverns is presented;
- Transport mechanisms between the cavern phases are discussed;
- A detailed review about hydrogen migration in rock salt is provided;
- The review is used to define a comprehensive mathematical model;
- A patent laboratory setup is furnished to calibrate any required parameters;

Author statement

Both authors AbuAisha M. and Billiotte J. contributed equally to the scientific content of this paper. AbuAisha M. wrote down the ideas of this paper in the final form.