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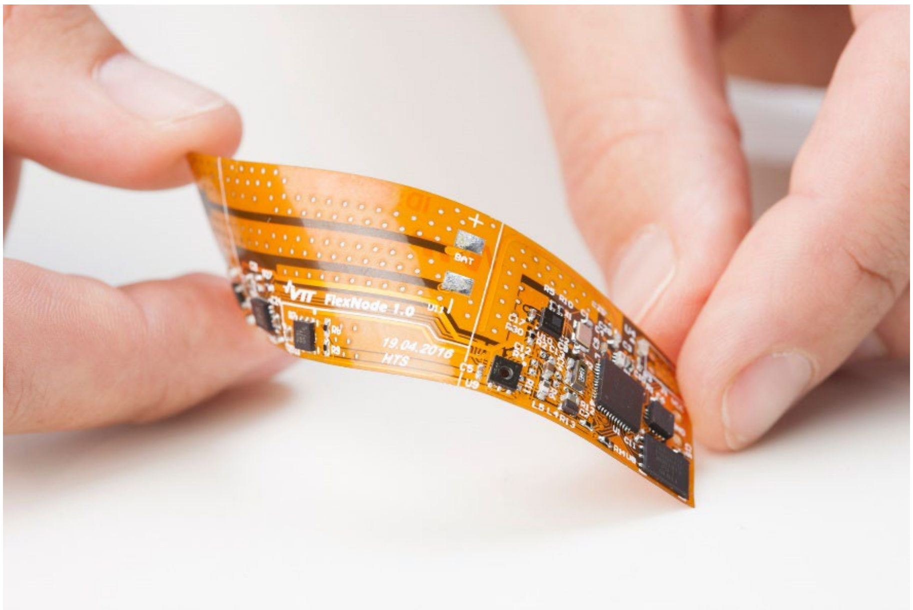

Hydrogen and Concrete - Literature review

Authors:	Pirkko Kekäläinen Yushan Gu
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Report's title

Hydrogen and Concrete - Literature review

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Summary

This work on the interactions of hydrogen with cementitious materials is conducted as a literature survey as a part of the VTT project H2Matters. The goal of this study is to summarize what is known about hydrogen behaviour, transport, and interactions with cementitious material, as well as current modelling capabilities, and highlight knowledge gaps that require further research. Preventing hydrogen leakage from underground hydrogen storage is important for preventing economic, safeguarding from hazard due to hydrogen flammability, and because of the effect of a leakage on the public opinion and acceptance of storage sites. There may be possible, but still unknown effects on atmosphere and climate change, on materials both at the storage facility or other above the ground structures, and on aquifers and biota. Concrete structures will not be the sole barrier of hydrogen, but it is important to minimize the possibility of leaks and safeguard the structural soundness.

The transport of gasses in cementitious materials is governed by the pore structure and saturation state of the material. The research on the effects of hydrogen on cementitious materials is rather scattered and concentrated on oil well cements. In this review it was found that the testing of both the hydrogen transport in cementitious materials and the hydrogen effects on cementitious materials has mostly been studied with a very limited number of binder compositions and most of the research has been done on pastes. Mortar and concrete studies, and studies where actual hydrogen is used, are either scarce or lacking altogether. There are known geochemical effects of hydrogen on rocks, but the possible implications of these studies on mortar/concrete aggregate or binder mineral phases, have not been considered in the published studies found.

Majority of the studies surveyed conclude that the effects of hydrogen on cementitious materials is insignificant, however the test durations are often very short. When planning structures with long service life, even the more subtle changes in the structural and barrier materials should be well understood. This is essential for making sound material and engineering decisions. Both the physical, chemical and thermal environment to which the materials will be exposed in a real-life storage facility have a significant effect on the possible ageing mechanisms. Material research should be done with realistic exposure conditions and on materials with actual compositions considered for these environments.

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Written by	**Reviewed by**
Pirkko Kekäläinen, Research scientist Yushan Gu, Research scientist	Miguel Ferreira, Research Team Leader

VTT's contact address
VTT Technical Research Centre of Finland Ltd, P.O. Box 1000, FI-02044 VTT, Finland

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Date:	13.8.2024
Signature:	DocuSigned by: C91D5DDA5EC5446...
Name:	Janne Pakarinen
Title:	Research Team Leader

Contents

1. Introduction

This work presents the results of a literature survey on the interactions of hydrogen with cementitious materials, conducted as part of WP1 for the VTT project H2Matters.

Concrete or other cementitious materials have been suggested being part of the underground hydrogen storage structural solution [1]. The behaviour of cementitious materials and possible interactions with hydrogen should therefore be understood to ascertain the integrity of the materials and structures and to anticipate any specific ageing phenomena related to hydrogen exposure.

2. Goal

The goal of this study is to summarize what is known about hydrogen behaviour, transport, and interactions with cementitious material, as well as current modelling capabilities, and highlight knowledge gaps that require further research. The scope of this work covers gaseous, pure hydrogen and is concentrating on possible phenomena related to its interaction with cementitious materials in underground hydrogen storage environments.

In this study the technical concepts of hydrogen storage are not considered, including the effect of possible cushion gas [2] or the effects of corrosion of metals on cementitious materials and concrete degradation.

3. Properties and Chemistry of Hydrogen

Hydrogen (H) is a non-metal with atomic number 1. In room temperature hydrogen is a colourless and odourless gas with a very low density. The essential physical characteristics of hydrogen have been summarized in Table 1. The hydrogen atom is smaller than any other element, with a covalent radius of 0.0371 nm. The bond between H-H is very strong due to intermolecular forces, so although the weak attractive forces between H_2 molecules cause a low boiling point, H_2 tends to be unreactive in room temperature. H atoms, however, are highly reactive, and are easily created through exposure to heat, irradiation, or catalysis.

Table 1 Physical characteristics of hydrogen. [3, 4, 5]

Characteristic	H_2
Molecular weight	2.016 g/mol
Density STP	0.089 g/l
Liquid density	71 LH_2
Vapour density relative to air	14 x = lighter
Boiling point	-253 °C
Minimum ignition energy	0.14 mJ
Diffusion coefficients	0.61 cm^2/s
Flammability limits (in air)	4–75 vol%
Ignition temperature	574 °C
Explosive limits	18.3–59.0

Hydrogen combines with every element, except the noble gases. It has three isotopes protium ^1H, deuterium ^2H and tritium ^3H. [3] H forms strong O-H bonds and is a good reducing agent for metals. When H_2 is dissolved in pure water, the pH of the water rises slightly. The solubility is low in normal temperatures, circa 8.65 x 10^{-7} mg/l.

Viscosity is an important property when studying fluid transport. The viscosity of hydrogen is presented in Table 2, in which it can be seen that the viscosity increases with both increasing temperature and pressure. The low viscosity, together with low molecular weight, of hydrogen makes it prone to leaking from storage structures.

Table 2 Hydrogen viscosity [6].

Hydrogen Viscosity (µPa-s) at Different Temperatures and Pressures							
Temperature (°C)	**Pressure (MPa)**						
	0,1	**1**	**5**	**10**	**30**	**50**	**100**
-150	4.8497	4.9024					
-125	5.5131	5.5568					
-100	6.1394	6.1766	6.3447				
-75	6.7366	6.7691	6.9143	7.1114	8.1266		
-50	7.3098	7.3386	7.4668	7.6363	8.5079	9.4607	
-25	7.8624	7.8883	8.0031	8.1523	8.9119	9.7489	12.209
0	8.3969	8.4205	8.5245	8.6581	9.3275	10.077	12.241
25	8.9153	8.9369	9.0321	9.1533	9.7491	10.430	12.357
50	9.4193	9.4393	9.5270	9.6380	10.173	10.797	12.532
75	9.9102	9.9287	10.010	10.113	10.597	11.172	12.750
100	10.389	10.407	10.483	10.578	11.020	11.553	12.999
125	10.858	10.874	10.945	11.034	11.440	11.935	13.271

4. Gas transport in cementitious materials and concrete

4.1 Permeability

Permeability is the ability to conduct fluid, that in this case describes the ease in which a gas penetrates through concrete or cementitious matrix under a pressure differential. It is expressed as the velocity with which a fluid of specified viscosity, under the influence of a given pressure, passes through a sample having a certain cross section and thickness. Permeability can be divided into intrinsic (or absolute permeability) in which the permeability is related to the characteristics of the pore structure, and into effective permeability which is also influenced by the presence of other fluid in the pore structure, such as free moisture. Intrinsic permeability is influenced by Klinkenberg effect, which is the frequency in which the gas molecules collide with each other and the solid pore walls. [7] In viscous flow the collisions with the wall are dominated by the molecular collisions, viscous flow is reached when the pressure of gas is high enough. [8]

4.1.1 Characteristics governing gas permeability

Cementitious materials are inherently permeable since they always have porosity. In general permeability is governed by the porosity and pore structure. When concrete is of good quality, that is properly cast and cured, the most important characteristic governing permeability is water to binder ratio (w/b). When w/b is lower, there are more cementing particles in a unit volume of the paste and therefore the capillary space in between has a smaller volume. Also, the grain size influences the porosity, smaller grain size result in smaller pores, which fill out quicker with hydration products. Curing time decreases the permeability and theoretically a fully hydrated cement paste with low enough w/b would be impermeable, but real-life concrete is never fully hydrated nor perfectly placed and finished, and the interfacial transition zones (ITZ)

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between paste and aggregate creates more permeable pathways. The amount of ITZ is to some extent linked to w/b but also to aggregate characteristics. Because of this the permeability of mortar or concrete is significantly larger than that of the paste, which should be taken into consideration when planning permeability testing. Intrinsic permeability decreases when aggregate is added because of the dilution effect and increased complexity of the pore structure. [9, 10, 11, 12, 13]

It has been found that increasing the sand content of mortar significantly decreases the permeability regardless of the composition or water to binder ratio of the mortar. Microcracking affects permeability, and therefore concrete has a larger permeability than mortar. [14]

Other factors influencing the permeability are the presence and quality of supplementary cementitious materials (SCMs) and admixtures, and the curing process and age/degree of hydration of the concrete, and deterioration. Some of these effects may be very small. The SCMs must be reactive or influence the pore structure to have significant effect. All the afore mentioned may alter the capillary porosity. [15, 16]

Although permeability is an intrinsic property of a material, the characteristics of the permeating fluid and pressure influence the permeation rate. Lamouchi *et al* [17] tested the gas permeability of CEM II/B-V concrete and found virtually no difference in the intrinsic permeability between argon and helium, despite the significant molar mass and atomic radii difference. In their study with the permeability was very homogenously circa 1.5×10^{-16} m^2. The author attributes this to low pressure used.

4.2 Absorption

Absorption describes the phenomenon in which a fluid is absorbed into the bulk of the solid concrete and resides inside the solid. The rate of absorption is not affected by temperature. In terms of concrete and gases, absorption is most likely the absorption of water in which gasses may have dissolved.

4.2.1 Characteristics governing gas absorption

Water is usually absorbed into concrete by a process called the capillary absorption. Capillary absorption is related to surface tension, which gases do not have, but gases can dissolve in water and be transported through capillary absorption. H_2 only slightly dissolves (0,142 cm^3/mol) in water at normal temperature and pressure. The solubility increases when the pressure increases and decreases with increasing temperature or salinity of the water. [18, 19, 20]

4.3 Diffusion

Diffusion is the movement of a fluid from a higher concentration to a lower concentration. This can happen for example between the interior of the concrete and the environment, or within different areas of the concrete. Diffusion can be separated into three different types: molecular diffusion, Knudsen's diffusion and surface diffusion. However, the lates research suggest only molecular diffusion and Knudsen diffusion are significant in cementitious pastes and can co-exist. [21]

In molecular diffusion the mean free path (MFP) of the gas molecules is smaller than the pore size. Diffusion is the result of molecule-molecule collision, and the driving force is the composition gradients. In Knudsen diffusion the pore walls are interacting with the diffusive agent, thus hindering the movement. Knudsen diffusion happens in pores with a diameter smaller than the distance between molecular collision, that is large to small capillary pores. [22, 23, 24]

4.3.1 Characteristics governing gas diffusion

Diffusivity of a gas in concrete has been found to be dependent on the inverse of the square root of the molecular weight of the gas. This is only true to RH below 80%, above which the gas is practically diffusing in water. [21]

Pore size affects the type of the diffusion in concrete, and different diffusion types can co-exist. In the larger air voids and large capillary pores, in which the pore size is considerably larger than MFP, molecular diffusion dominates. When the pore size decreases to similar or smaller than the MFP Knudsen diffusion co-exists with molecular diffusion or dominates. [24, 25] Pressure influences the diffusion mechanism in cement paste. Below 10 kPa virtually all diffusion is Knudsen diffusion, in higher pressure also molecular diffusion is significant. [21]

Temperature, molecular mass, and the concentration gradient influence the rate of diffusion: Increasing the temperature will increase the rate; Diffusion rate decreases while the concentration rate decreases.

Age of the material decreases the (oxygen) diffusivity, because of the reduction in capillary porosity or refinement of pore structure due to continued hydration. This has been found for both ordinary Portland cement and cement supplemented with fly ash or silica fume. The addition of SCMs also decreases diffusivity, silica fume being the most effective addition. [15]

4.4 Relative Humidity and Water Saturation

Relative humidity (RH) is the water vapor content, that can be retained by air at a given temperature and pressure without condensation. RH is expressed in percentage of the saturated state and is governed by both the water content of the concrete and the ambient conditions.

When RH is high, the gas must dissolve in water and only then be transported through the pore system. As discussed in 4.2.1, the H_2 dissolution in water is low, and therefore at humidities greater than 80% concrete appears almost impermeable to gas transport. At the 50–80% relative humidity range hydrogen permeates concrete by Knudsen and molecular diffusion. The smaller the pore size the greater the effect of RH on diffusion. When the RH is low, below 50%, the pore spaces are available and connectivity is increased, making diffusion easier for hydrogen. Relative humidity does not change the effect of pressure on diffusion. [21, 24]

Water saturation refers to the pore water content of the concrete. Saturation changes non-linearly in relation to RH. In saturated concrete permeability is referred to as effective permeability. Effective permeability increases when water saturation of the concrete reduces. [26]

4.5 Concrete deterioration and gas transport

In a gas storage system, deterioration can be caused by internal degradation process of the materials used in the structural solution for containment of gas, external degradation processes of the materials, or processes related to the normal operations and accident scenarios of the storage system. Any process, which deteriorates the concrete, especially phenomena which change the porosity of the cementitious paste can affect the gas transport. Cracking can also affect the gas transport at least locally, but also change the mechanical properties of concrete.

4.5.1 Internal material deterioration

Alkali-silica reaction (ASR) in which the silica phases of the aggregate react with the alkalis of the pore solution of the binder in non-carbonated cement paste. The reaction can cause expansion of the aggregate, resulting in cracking of the concrete, and also changes the porosity of the concrete. High temperatures, high relative humidity and external alkalis can lower the reaction threshold and speed up the expansion. Low alkali binder and supplementary cementitious materials can mitigate the reaction, and the selection of non-silica bearing aggregate may altogether prevent the problem. For further information of ASR mechanism, see [27, 28].

Internal sulfate attacks can be either caused by the aggregate or the paste. Delayed ettringite formation (DEF) is a form of paste induced internal sulfate attack, which can cause uniform paste expansion and weblike cracking throughout the concrete. For DEF to occur, elevated temperatures during the curing are necessary and in addition a later exposure to humidity. For an in-depth review on DEF, see [29].

Iron sulfide, pyrite FeS2 and pyrrhotite Fe1-x S, oxidation in aggregate can cause expansion and an internal sulfate attack (ISA) in concrete, which leads to cracking and increase in paste porosity. The expansion is caused both by the volume change of the aggregate, resulting from the oxidation process and the ISA caused by sulfuric acid released in the oxidation reaction. The process of iron sulfide oxidation is very complex but can be simplified into equations 1 and 2. In the presence of oxygen and water, the reaction continues to for goethite and iron hydroxide (equations 3 and 4).

$$2Fe_{1-x}S + 2H_2O + 4.5O_2 \rightarrow Fe_2O_3 + 2\,H_2SO_4 \qquad (1)$$

$$2FeS_2 + 4H_2O + 7.5O_2 \rightarrow Fe_2O_3 + 4H_2SO_4 \qquad (2)$$

$$Fe_2O_3 + H_2O \rightarrow 2FeO(OH) \qquad (3)$$

$$2FeO(OH) + H_2O \rightarrow 2Fe(OH)_3 \qquad (4)$$

ISA can cause secondary paste expansion, which has been thought to be the result of precipitation of secondary deposits like ettringite ($3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$), gypsum ($CaSO_4\cdot 2H_2O$) and thaumasite ($CaSiO_3\cdot CaCO_3\cdot CaSO_4\cdot 15H_2O$). The type of secondary phases depends on the pH and temperature and the original composition of the paste. The rate of oxidation depends on both the mineralogy, microstructure, and grain size of the aggregate and the exposure conditions that is temperature and pressure. Pyrite reacts to a very low degree compared to pyrrhotite. In pyrrhotite oxidation, if all pyrrhotite would oxidize to half goethite and half iron oxide, the maximum expansion of the aggregate would be 0.07%, however this does not take into consideration the secondary expansion of the paste. [30, 31, 32, 33]

4.5.2 External degradation processes

The most common phenomenon changing the porosity of the binder is carbonation in which the atmospheric CO_2 reacts with $Ca(OH)_2$ producing $CaCO_3$. Carbonation may in fact decrease the porosity, but at the same time change the mechanical properties of the paste. However, carbonation may also cause micro cracking, which may lead to higher permeability.

In saturated cementitious paste, CO_2 can be derived from fluids such as ground water. In a so called bi-carbonation reaction, the CO_2 reacts with hydroxyl ion producing HCO_3^- ions, which can continue to react with the paste. This process can lead to formation of a friable paste with a microstructure consisting of carbonate “pop corns” and gel like silica phases. A thorough review of this phenomena and its relationship to concrete degradation has been done for example by Sibbick & Crammond [34].

Carbonation changes the pH of the binder and can lead to corrosion in reinforced concrete. Another cause of corrosion is chloride ingress, for example from brine. Steel corrosion can cause expansion and result in cracking.

Deleterious external chemical attack can be caused by any substance dissolving the binder or reacting with it to form expansive secondary products. Usually, these substances are either acids or sulfates and the most corrosive agent is a sulfuric acid combining the acid and sulfate attack. Also pure water can dissolve the $Ca(OH)_2$ of the paste and change the porosity. Typically, chemical attack changes the porosity of the paste and causes surface crazing, without causing significant cracking outside the exposed zone.

However, severe sulfate attack can also cause severe surface parallel cracking traversing not just the paste but also the aggregate. For more information on chemical attack see [35].

4.5.3 Exposure caused by storage procedures

In a storage situation the materials must withstand the repetitive loading and discharging of the storage, and mechanical stresses caused by the geological processes of the surrounding country rock. This means durability in changing pressure and temperature conditions. [36, 37] When the pressure of the storage is reduced temperature will drop and may reach freezing temperatures. If the cementitious material is saturated with water, which will happen given enough time if the material is in contact with the ground water, freeze and thaw action may damage the material causing cracking. Temperature can be controlled by controlling the gas release rate, but also heating and cooling systems have been developed [38]. Freeze-thaw damage may be mitigated by using frost resistant aggregate and air entrainment [39] or synthetic fibres addition [40, 41, 42], and preventing the water saturation. In general, freeze-thaw cycles are needed to cause significant loss of mechanical strength.

Since there are several degradation processes related to the surrounding bedrock, normal operations of the storage unit or in accident scenarios, it is essential to understand the storage concept, when planning the material requirements.

5. Hydrogen and cementitious materials

5.1 Hydrogen permeability and diffusion

Hydrogen transport into and through concrete has mostly been studied through the behaviour of other gases like helium, nitrogen, or argon. The studies which actual use hydrogen as the test gas – especially in the case of permeability measurements – are rare, and sometimes the actual gas used in testing in hydrogen studies is not identified or is only mentioned when carefully reading the introduction of the methodology.

Hydrogen permeability of concrete was estimated by Gajda *et al* [43] using helium as the test gas in pulse-decay method [44] and steady-state flow method setups. Tested samples were a CEM I cement with 7% addition of limestone fines and a CEM II cement with 35% of silica fume. The pressures used for Pulse-Decay method were 2–12 MPa and the pressure gradient for the steady-state method was 1.5 MPa at the inlet and 1.0 MPa at the outlet. The results suggested, that although the permeability of concrete can be decreased with the use of SCMs, the permeability does not fall below 10^{-19} m^2. Their conclusions state, that concrete is too permeable for hydrogen storage, but that polymer modification could improve the concrete properties.

Two published hydrogen diffusion studies, using actual hydrogen as test gas were found: Sercombe *et al* [21] measured the hydrogen diffusivity of French industrial CEM I (Portland cement) and CEM V (composite cement with Portland cement, blast furnace slag and siliceous fly ash) paste samples. As expected, the average diffusivity of CEM V was lower than CEM I samples. The diffusion coefficient of hydrogen is strongly dependent on the RH within the 55–100% range, but changes in RH do not have much effect on lower the 55% RHs, which is because of the effect of capillary porosity on the diffusivity. The diffusion coefficient was found to vary between 10^{-6} m^2/s for dry paste and 10^{-10}–10^{-13} m^2/s for almost water saturated paste. Boher *et al* [45] studied the hydrogen diffusivity of CEM V/A cement (that is Portland cement, 18–30% blast furnace slag and 18–30% siliceous fly ash) samples with w/c between 0.35 and 0.50 in different saturation states and compared the results to MIP and water porosity values. They confirmed the strong link between diffusivity and saturation state. Independent of w/c, they found that between RH 60% and 80%, the H_2 diffusivity decrease linearly circa two orders of magnitude, and that the diffusivity is controlled by the smallest of pores.

In summary, the hydrogen transport properties in cementitious materials have only been tested, using hydrogen as the test gas, in CEM I and CEM V binders. Any information found on test incorporating silica fume, calcined clays or mineral fillers were conducted using other gases like helium, nitrogen, oxygen or argon. In the actual hydrogen tests a strong correlation to RH and w/b was observed. Future research needs for underground hydrogen storage include tests on binder/mortar expected to be used in UHS in realistic RH states.

5.2 Hydrogen reactions with cementitious materials

Hydrogen H_2/H_20 reduction is not considered active enough at temperatures below 60 °C to have significant impact on the cement minerals or the minerals of rocks, however in higher temperatures hydrogen may be more active in oxidation processes. [46]

5.2.1 Hydrogen and hydration

The effect of hydrogen in cement hydration may be relevant in some storage scenarios and when using slow hydrating binders. In a recent study by Ugarte *et al* [47] tested samples composed of class H oil well cement (coarser grained sulfate resistant Portland cement). The concrete samples were cured either in water or hydrogen saturated (2 ppm) water. The hydrogen cured samples consistently showed higher average compressive strength (CS) than the water cured samples. The difference in CS increased from 4.2% after 7 days to 14.3% after 168 days of curing. The increase was explained by lower porosity, caused by calcium hydroxide and ettringite deposits filling the pores. In this study Young´s modulus showed a slight, but (in the case of a UHS casing cement) unwanted increase in the H_2 cured samples.

5.2.2 Hydrogen and hardened cementitious materials

There is a limited number of publishes studies on the effects of hydrogen on hardened concrete or other cementitious materials. Most research has been done in conjunction with oil well cements, which are composed of Portland cement only. Experiences of different binder mixtures, which may have slightly different phase composition due to use of SCMs, is lacking.

Vidic *et al* [48] exposed water saturated cement plug samples for hydrogen atmosphere (25% H_2 and 75% CH_4) for 14 months under 70 bars pressure and temperature of 40 °C. They monitored the samples periodically with permeability measurements, x-ray diffraction (XRD) analysis and with optical microscopy. There was an insignificant change in permeability, which was of the same order of magnitude as caused by exposure to methane or nitrogen. The content of vaterite ($CaCO_3$ polymorph) increased during the exposure, as a result of $Ca(OH)_2$ carbonation.

Boersheim *et al* [49] exposed class G oil well cement (fine grained Portland cement, w/c 0.44) plugs to brine and H_2 under pressure of 50 bars and temperature of 100 °C for the duration of 4 weeks. They observed a decrease in porosity and an increase in permeability. This could, however, be explained by the leaching of the cement matrix caused by the brine used as a medium. The evidence pointing to leaching was calcium in solution, as well as increased pH of the test solution.

One dry well cement sample was incubated by Shi *et al* [50] for three months in a chamber loaded with 13% H_2 and 87% NG mixture to a starting pressure on circa 26.2 MPa (i.e. 262 bars). The incubator was kept at a constant temperature of 80 °C. The permeability, porosity, and XRD phase composition was measured before and after the exposure, with significant changes observed. The permeability increased 62.5%, while the porosity decreased 0.4%. However, the authors speculated the accuracy of the results based on a single small (25 x 49 mm) sample, permeability of which could have been affected by for example cracking traversing the sample. The XRD results showed an increase in both SiO_2 and $CaCO_3$ content, and a decrease in $Ca(OH)_2$ content, which the authors were unable to explain. The possibility of carbonation and reduction of the amorphous C-S-H phase were not considered.

Al-Yaseri *et al* [51] performed a 125-day test on two class G oil well cement (fine grained Portland cement) core plugs in temperature of 75 °C and pressure of 96.5 bars (9.65 MPa). The test was performed after 30 days of curing in a reaction cell with 99.99% hydrogen. The samples were characterized pre and post testing by XRD, X-ray fluorescence spectroscopy (XRF), computerized tomography (CT) scanning and by measuring ultrasonic wave velocities. XRD and XRF revealed similar mineral phases both before and after the exposure, but in different concentrations, slight dissolution of calcium was suspected. In CT scan a minor reduction in pore volume was observed, and weight measurements revealed an increase of 4%. The exposure had a minor effect on the Poisson´s ratios and Elastic moduli, calculated from the ultrasonic wave velocities. In general, the study shows a minor reactivity of hydrogen with cement in elevated temperature and pressure, which would suggest minor impact on integrity.

Corina & ter Heege (sited in [52] p. 9) exposed class G oil well cement (fine grained Portland cement, w/c 0.38) plugs to brine and H_2 under pressure of 80–110 bars and temperature of 200 °C for the duration of 2 weeks, then tested for the compressive strength, Young’s Modulus, and Poisson’s ratio. They found higher values in all the measured parameters in comparison to a non-exposed sample.

In an investigation of hydrogen effects on wellbore cements, Hussain *et al.* [53] injected hydrogen at circa 49 °C (i.e. 120 °F) and 103.4 bars or 10.3 MPa (i.e. 1500 psi) to a cement sample of 50 x 38 mm (i.e. 2” x 1.5”) and found a significant reduction in compressive strength, which they explained by cracking found in a CT-scan. The test was only done with a single sample and the composition of the cement is not indicated.

Corina *et al* [52] exposed class G oil well cements (Portland cement, w/c 0.44) in brine and H_2 under pressure of 200 bars and temperature of 80 °C for the duration of 2 months. Samples were analyzed prior, in the middle and end the end of the exposure for phase composition (XRD), compressive strength, and cyclic loading. The differences in CS and Young’s modulus were very small between H_2 exposed samples and reference samples. Also, the changes caused by the cyclic loading were quite similar between the exposed and non-exposed samples. XRD results showed that there were no significant changes in phase composition due to the exposure.

Aftab *et al* [54] tested well cements in 207 bars (i.e. 3000 psi), 80 °C, and salinity of 35 and 250 ppt. Two of the tested binders were a Class G oil well cement, in which 40% of the Portland cement was supplemented by silica fume, one with and one without AccuSET D197 retarder. The third binder was a Polycell Polyfilla Quick Set cement, which is a quick hardening Portland cement with limestone fines. The samples were cured and then pulverized, the powder was tested in the exposure conditions and resulting solution tested with ICP. The elemental analysis showed minor differences in the concentrations between exposures to different gases, but the authors did not consider these changes significant. The test duration was 15 days and for the higher salinity 30 days.

Jacquemet *et al.* [55] studied the class G well cement (Portland cement) reactions with hydrogen through geochemical modelling. They concluded that although hydrogen may reduce the ettringite and hematite phases of the paste, the effect on the paste porosity is insignificant.

In summary, the earlier research has been concentrated on class G oil well cements and in environments typical for oil wells. The exposure test were in general rather short, from 2 to 18 weeks in duration, and the longest test duration was 14 months. The number of subsamples was often rather small, even just one sample. Also, difficulties were encountered with alteration caused by other test matrix than hydrogen, complicating the estimation of the effects of hydrogen. Still, minor interactions of hydrogen with hydration of cement and hydration phases of cement have been observed, as well as slight changes in pore structure and mechanical properties. Based on this the future research needs include: testing binders incorporating supplementary cementitious materials; testing in temperatures and pressure ranges expected for underground hydrogen storage facilities; testing with mortar and concrete at the age and noisture condition appropriate with use. The tests should be planned carefully to avoid interference from other ageing mechanisms.

5.3 Hydrogen reactions with other concrete materials

5.3.1 Aggregate

Hydrogen can react with minerals in rocks, especially those sensitive to redox reactions. In these reactions, gases like H_2S, SO_2, CO_2, may be produced. Both H_2S and SO_2 can degrade the concrete binder. CO_2 can carbonate the concrete binder, making possible steel reinforcement susceptible to corrosion [56]. These changes have been observed for interactions between hydrogen and surrounding country rocks but could geochemically be possible also for the hydrogen-aggregate interactions. Any reactions causing volume change could be deleterious. Also, any observed reactions between hydrogen and minerals similar to cement hydration products could have implications to cementitious material stability.

In alkaline environment, elevated temperatures (> 90 °C) and high H_2 partial pressure hydrogen can reduce pyrite into pyrrhotite releasing sulfides into the solution (equation 5). This could increase the risk of expansive reaction, since as pyrrhotite reacts much faster than pyrite in an alkaline environment and also the degree of reaction is much higher. [57]

$$FeS_2 + (1-x)H_2 = FeS_{1+x} + (1-x)H_2S \qquad (0 < x < 0.125) \qquad (5)$$

Anhydrite and carbonate alteration or total dissolution by H_2 has been observed in sedimentary rocks, by petrographic microscopy and computer tomography, resulting into an increase in porosity and permeability. The changes were observed only in the areas in contact with the pore structures. Alteration of silicates was not detected. [58]

In addition to anhydrite, also other sulfates like anglesite ($PbSO_4$), gypsum ($CaSO_4{:}2H_2O$), barite ($BaSO_4$) and celestine ($SrSO_4$) may also be reduced by hydrogen. [59]

In an experimental study on hydrogen effects on sandstone mineralogy in varying test environment (100-200 °C, 100 bars and H_2 partial pressure 10–50 bars, wet or dry conditions) simulating typical underground hydrogen storage environments. Microstructural changes were not detected, and no significant changes in mineralogy by XRD, apart from muscovite and hematite, were detected. [60]

Whether these findings may have implications to concrete aggregate (or binder) stability in contact with hydrogen, has not been considered according to the available literature. Further research on the geochemical and dimensional stability of the aggregate in cementitious matrixes is needed, to ensure the soundness of UHS structures including mortars or concretes. The hydrogen interactions with minerals similar to hydration phases in cementitious binders, should also be taken into careful consideration when planning testing of hydrogen and binder interactions.

5.4 Hydrogen, bacterial growth, and integrity of cementitious materials

In oil wells and mining environments, sulfur reducing bacteria are known to occupy a wide range of temperatures and salinities. Bacterial communities in hydrogen storage facilities may cause serious problems for cementitious materials. One of the identified problems is growth of sulfidogenic bacteria resulting in release of hydrogen sulfide (H_2S) as a metabolism product. H_2S can in the presence of humidity oxidize into sulfuric acid, which is very aggressive towards cementitious binders. It has been recognized that microbes may be involved in a variety of geochemical processes, but the magnitude of the effects is not well understood. Deeper review of the possible microbially induced deterioration of cementitious materials is out of the scope of this study, but for example Doppfel *et al* [61] have done a recent review on the topic.

5.5 Hydrogen absorbing materials in concrete

It is unlikely that cementitious materials can me made impermeable to hydrogen, and therefore the possibility of improving the hydrogen absorption properties of concrete to prevent leakages to the environment is interesting.

Porous carbon has been tested as a H_2 storage medium and biochar has been tested for gaseous emissions filtering. Whether biochar incorporated into a concrete material would have H_2 adsorbing/absorbing properties has not been investigated. [62, 63, 64] Supplementing cement and/or aggregate in mortars/concrete has been studied in recent years, and can be done while retaining the wanted properties of the material. Biochar has been observed, in 1–2% additions and below 500 °C heat exposure, to decrease the permeability and strength loss. [65, 66]

Clay minerals have been shown to adsorb hydrogen. There are differences between different clay minerals: the more complex the pore structure and the larger the specific surface area, the larger the adsorption of H_2. Sepiolite and palygorskite are the most absorptive ones, because they absorb hydrogen both on the bulk phase and the external surfaces. [67, 68, 69] No published information on whether this is true for calcined clays (CC) and if adding CC to concrete binder would improve the H_2 storage properties was found. Supplementing cement with calcined clays is a rising trend in binder production. [70, 71]

5.6 Materials suitable for hydrogen storage

Material suitability is largely governed by the exposure conditions, the planned service life, structural concept and operational criteria. This is true to all cementitious materials in all structures. Some specific recommendations for cementitious materials in hydrogen environments have been made:

- Low addition of silica fume to the binder has been suggested by several authors. [56, 46, 72] Silica fume is a side product of ferrosilicon alloys form electrical arc furnaces, which improves the reactivity of cement-based binders and also effects as a filler, refining the pore structure and decreasing the permeability. [73, 74]
- Addition of organic admixtures, such as synthetic resins or rubber powders, have been suggested to reduce shrinkage cracking and expansion. [46, 72, 75]

In Sweden the first underground hydrogen storage has already been built following the in the HYBRIT project. In their final report a lining concept including a concrete layer is discussed, but the composition of the concrete is not published. However, the importance of the correct thickness and casting quality of the concrete was emphasized in the pre-study. [37]

It was, however, not possible to find research verifying the suitability of these suggestions. More research is needed to evaluate which materials are least reactive with hydrogen and have the lowest permeability to hydrogen.

5.7 Test methods and laboratory safety considerations

5.7.1 Testing hydrogen transport in cementitious materials

Measuring gas permeability in concrete, albeit rather simple, presents some difficulties related to both the type of the flow and the moisture content of the pore system. The gas flow within the pore structure is not strictly laminar and thence does not follow Darcy´s law. As a result, the coefficient of permeability will change when pressure changes. The amount of moisture and the distribution of moisture within the pores will also affect the permeability significantly. This effect is more pronounced when the pores are close to dry. This reliable comparison between different materials is only possible if conditioning (moisture content), applied pressure and gas flow are kept constant. It is also essential to keep the preconditioning gentle as not to alter the characteristics of the sample materials. [24, 76, 77]

The importance of sample preparation is further emphasized by the observation, that the thickness of the sample influences the permeability results. It has been suggested based on mortar studies, that the thickness should be at least ten times the largest aggregate size. Shrinkage cracking always present to some extent, may traverse the thinner samples fully, increasing the permeability. [14] The surface area of the tested samples has also been found to influence the permeability results, with increasing surface producing decreasing permeability compared to smaller samples. [77]

Since testing gas permeability is time consuming, and porosity is the main factor in permeability, efforts have been made to link porosity (measured for example by mercury intrusion porosimetry or nuclear magnetic resonance) to permeability. It has been shown that 2D back scatter electron analysis of the pore structure can be correlated to the gas diffusivity and permeability, both in high w/b and low w/b samples. [78]

Permeability of concrete is measured with steady flow and transient flow methods, some of the most common methos are steady state method Cembureau [79], and transient methods Torrent [80] and Oxygen permeability index [81]. RILEM recommends the Cembureau method, which is developed for oxygen permeability. The method or it´s quasi-steady flow modifications have been used also for testing with air, argon, helium and hydrogen (in carrier gas).

The inlet gas pressure and confining pressure may influence the permeability measurements and should be carefully chosen. Qian *et al* [82] found in concrete permeability measurements with the Cembureau method a steady zone of 15-30 bars of inlet pressure for optimal measurements. They also observed a decrease in intrinsic permeability when confined pressure was increased and suggested 50 bars as optimum.

5.7.2 Testing hydrogen interactions with cementitious materials

Hydrogen exposure tests are usually static tests, in which the samples are placed in a pressure chamber / test cell either in wet or dry conditions. Different types of test setups can be found in references [50-53]. When planning a hydrogen exposure test, the research results in 5.1 and 5.2 emphasize the need for a test setup, which reliably measures the hydrogen effects only, without the interference of other factors, for example, leaching. The sample size and number of subsamples should also be carefully considered.

5.7.3 Laboratory safety

There is no specific legislation for hydrogen in Finland, but it is considered under the dangerous chemicals legislation. The hazard classification for hydrogen is extremely flammable gas. Hydrogen is tasteless, odourless, and colourless. Odorization of the H_2-gas is not possible due to the large density differences between the odorant gases and H_2. Hydrogen is significantly lighter than air. In ventilated areas hydrogen gas will disperse, but liquid hydrogen may form a pool before reverting into the gaseous state and dispersing. The flammability range is very high, but in ventilation areas accumulating the necessary concentration to reach the flammability range is difficult if not impossible. If the flammability range is reached hydrogen may catch fire extremely easily even from static electricity. The flame is almost invisible and will cause serious burns. [4, 83, 84]

Due to the small molecular size of H_2, it may permeate through materials and cause embrittlement especially in metal materials, which should be taken into consideration when choosing storage and testing media. The inability of human senses to detect hydrogen together with the high tendency of hydrogen to leak requires accurate monitoring during both storage and operations. [85, 86, 87]

Some of the safety considerations in exposure testing using hydrogen have been outlined by [54]. These include using 316 stainless steel, with high manganese content and below 13% nickel concentration for the equipment and ensuring, limiting the pressure below 65 MPa and regulating the rate of hydrogen injection to prevent thermal excursion, as well as using hydrogen detectors to notify of potential leaks.

5.8 Open questions and research needs

Preventing hydrogen leakage from underground hydrogen storage is not only important for the economical effects of the loss in leakage. The most imminent potential effect of the leak is accumulation of the hydrogen below infrastructure and its flammability. Any possibility for a leak could severely affect the public opinion and acceptance of storage sites. Other issues caused by a leakage are the possible effects on atmosphere and climate change, the effects on materials both at the storage facility or other above the ground structures, as well as the possible unknown effects on aquifers and biota. [88, 89] Even though concrete structures will not be the sole barrier for containing hydrogen, it is important to prevent or minimize the possibility of leaks also with careful planning of the cementitious materials working as a part of the barrier systems. In addition to leak prevention, the structural soundness of any cementitious materials should also be safe guarded to insure the safe functioning of a storage facility.

The research on the effects of hydrogen on cementitious materials is rather scattered and concentrated on oil well cements. Several authors have recognized the need for further research: Considering the effect of temperature and pressure in hydrogen-cement interactions is needed [47], further research on possible hydrogen embrittlement of cement [88], effect of hydrogen on cement mechanical and poroelastic properties [90], to name a few.

In this review it was found that the testing of both the hydrogen transport in cementitious materials and the hydrogen effects on cementitious materials has mostly been studied with a very limited number of binder compositions and most of the research has been done on pastes. Mortar and concrete studies are either scarce or lacking altogether. The gas used for studies is not necessarily hydrogen. There are known geochemical effects of hydrogen on rocks, but the possible implications of these studies on mortar/concrete aggregate or binder mineral phases, have not been considered in the published studies found.

Many of the small number of existing studies conclude, that the effects of hydrogen on cementitious materials is insignificant, however the test durations are often very short. Even though the hydrogen interactions with cementitious materials may not be fast, dramatic, or unexpected, when planning structures with long service life, even the more subtle changes in the structural and barrier materials should be well understood. This is essential for making sound material and engineering decisions.

Both the physical, chemical and thermal environment to which the materials will be exposed in a real-life storage facility have a significant effect on the possible ageing mechanisms. Material research should be done with realistic exposure conditions and on materials with actual compositions considered for these environments.

The knowledge gaps and research need in short:

- most testing has been done on pastes, testing should be done on mortars and concretes to take into consideration the effects of aggregate
- different binder types, realistic for use in UHS applications, should be exposed to hydrogen
- carbonate and sulfate minerals have been found sensitive to hydrogen in caprock studies, whether the same reactions are significant in cementitious matrix or aggregate should be investigated

- testing for longer duration in exposure conditions realistic to UHS applications is still lacking, and needed if facilities are planned for long service life, to be able to do this more detailed information on the structural concept, operation and planned materials are needed

6. Modelling of hydrogen in cementitious materials

6.1 General hydrogen storage conceptions

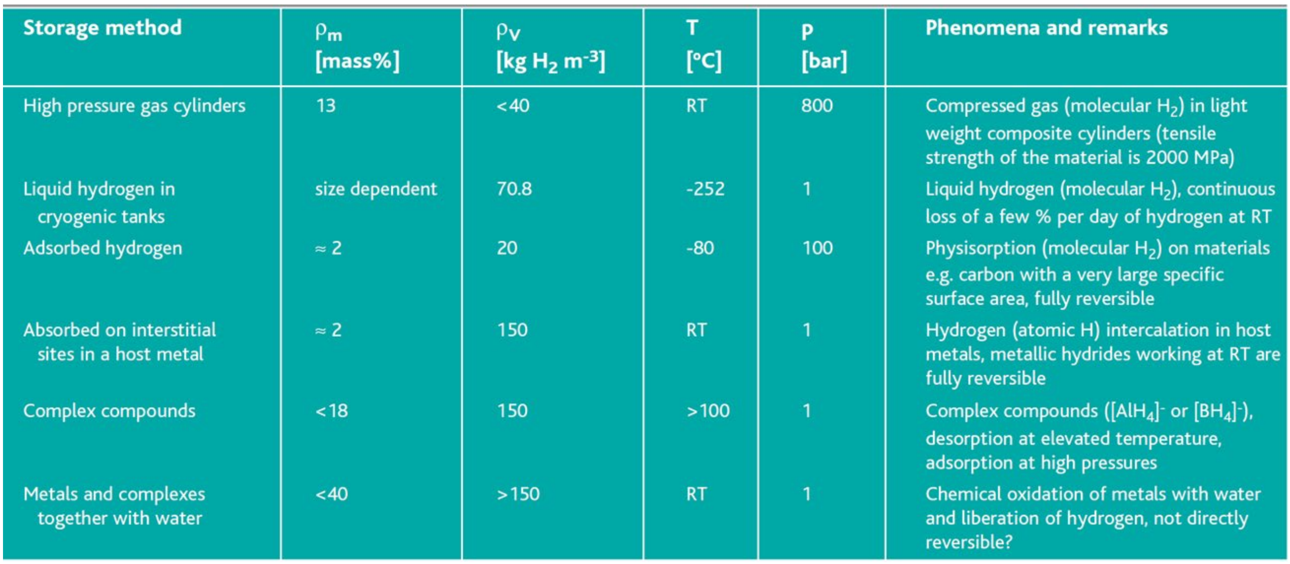
As the simplest and most abundant element on the planet and clean energy without producing CO_2 during combustion, hydrogen has been widely discussed and promoted to replace fossil fuels [91]. Hydrogen is a naturally occurring gas, abundant in the universe, thus it is a primary sustainable renewable energy source. Hydrogen is rarely found in its pure form, but usually in a wide variety of inorganic and organic chemical compounds, the most common being water (H_2O) [92]. Though hydrogen has advantages as an alternative energy, its properties bring challenges, especially for its storage [37], including (i) light density, which implies its higher requirement for spacious volumetric storage capacity than natural gas to produce the same energy [93]; (ii) small molecules, which enables it to diffuse easily in any porous media; (iii) wide flammable concentration varying between 4–75%, against 5–15% of the natural gas, which means that the operational area should be free of heat flames and sparks; (iv) Joule-Thomson effect, i.e., H_2 heats up due to expansion, and it needs to be cooled down below -71 degrees to behave like most other gases; (v) hydrogen embrittlement, during which hydrogen atoms may promote localized plastic processes and enhance crack propagation in the steel [94].

Based on these characteristics, hydrogen is mainly stored in four basic storage methods: gas storage in depleted oil/gas reservoirs or excavated caverns in hard rock; compressed hydrogen gas (CGH2), liquid hydrogen (LH2), and solid storage of hydrogen (SSH2):

1) Gas storage in depleted reservoirs and lined rock caverns: Depleted oil/gas reservoirs and lined rock caverns are geological traps that serve as a hydrocarbon storage medium. They are usually overlaid with an impermeable layer that is generally aquifer-supported from the bottom or edges [95].
2) CGH2: high-pressure gas steel cylinders [96]; operated at a maximum pressure of 20 MPa. The ideal material for a high-pressure cylinder has a very high tensile strength, a low density, and does not react with hydrogen or allow hydrogen to diffuse into it. Hydrogen atoms may promote localized plastic processes and enhance crack propagation in the steel, which is called hydrogen embrittlement; austenitic stainless steel is less susceptible to hydrogen embrittlement.
3) LH2: Liquid hydrogen is stored in cryogenic tanks at -252 degrees at ambient pressure [96].
4) SSH2 [96]: Solid storage of hydrogen can be further divided into categories: physisorption in porous materials; absorbed on interstitial sites in a host metal, complex compounds, metals and complexes with water. Physisorption of hydrogen [97], the interaction is composed of two terms: an attractive term and a repulsive term. Materials with a large specific surface area like activated or nanostructured carbon and carbon nanotubes (CNTs) are possible substrates for physisorption.

Following similar conceptions, Table 3 lists the innovative methods [78] of hydrogen storage in high-pressure gas, liquid, and complex solids.

Table 3 Summarised hydrogen storage methods and phenomena reported in [78].



Storage method	ρ_m [mass%]	ρ_V [kg H_2 m^{-3}]	T [°C]	p [bar]	Phenomena and remarks
High pressure gas cylinders	13	<40	RT	800	Compressed gas (molecular H_2) in light weight composite cylinders (tensile strength of the material is 2000 MPa)
Liquid hydrogen in cryogenic tanks	size dependent	70.8	-252	1	Liquid hydrogen (molecular H_2), continuous loss of a few % per day of hydrogen at RT
Adsorbed hydrogen	≈ 2	20	-80	100	Physisorption (molecular H_2) on materials e.g. carbon with a very large specific surface area, fully reversible
Absorbed on interstitial sites in a host metal	≈ 2	150	RT	1	Hydrogen (atomic H) intercalation in host metals, metallic hydrides working at RT are fully reversible
Complex compounds	<18	150	>100	1	Complex compounds ($[AlH_4]^-$ or $[BH_4]^-$), desorption at elevated temperature, adsorption at high pressures
Metals and complexes together with water	<40	>150	RT	1	Chemical oxidation of metals with water and liberation of hydrogen, not directly reversible?

6.2 Interaction with concrete

The hydrogen interaction with cement is not well understood, and the concern is regarding whether cement can provide proper containment as a cement barrier. Concluding the conceptions mentioned in section 6.1, cementitious material/concrete is mainly used in two cases: (i) concrete is one of the main hydraulic barriers used to isolate hydrogen storage from the surrounding fluid, e.g., the conception in the HYBRIT project [37]; and (ii) cementitious materials are used for injection well grouting. A direct interaction between hydrogen and cementitious materials is foreseen when hydrogen leakage occurs. The concrete may be further exposed to high pressure and low temperature when hydrogen is stored as compressed gas or liquid. The low temperature may freeze the groundwater or the pore solution in concrete, which further damages the material.

Hydrogen storage in depleted reservoirs is the easiest way to develop, operate and maintain. However, hydrogen interactions in underground gas storage sites are a complex topic, which has not been studied comprehensively and is difficult to predict. Changes regarding the mineral precipitation and dissolution in cement, reservoir, caprock etc. are foreseen. A thermodynamic study investigating the interaction between cement and hydrogen has been done [98] and the transformation of Fe_2O_3 into Fe_3O_4 was observed. Due to the low content of Fe_2O_3 in cement, the impact of the reaction on the cement system is limited. A similar conclusion was drawn [55], where thermodynamic calculation, with software PHREEQC, has been used to simulate the chemical reactions between hydrogen and cementitious materials. It has proved that reductive dissolutions occur in ettringite and hematite due to the sulphate and ferric iron reactions with hydrogen. The so-produced sulphides and ferrous iron precipitated as iron sulphide and oxide minerals. However, the phase changes do not significantly affect the microstructure of cement due to the minor volume of the involved minerals in cement.

In addition to thermodynamic calculations, experimental studies to investigate the hydrogen interaction with cement have been conducted. Visual observations and measurements of dimensions and weight on the cement samples have shown no changes before and after when they were exposed to hydrogen [98]. Moreover, the chemical composition of samples related to the pre- and post-H_2 remains the same, which indicates that H_2 does not alter the characteristics of cement and acts in a way as an inert gas for cement. An experiment to investigate the impact of hydrogen interacting with the cement sheath was performed [53], and it was concluded that hydrogen bubbles were trapped in the wet cement during the setting phase of a new well in a hydrogen storage reservoir. It results in a change in the mechanical property and microstructure of cement, e.g., lower strength, higher porosity, etc. Contrary to these results, an increase in compressive strength, a lower porosity, and a finer microstructure of cement paste cured in water that is saturated with molecular hydrogen rather than in distilled water were observed [99]. The longer the curing time, the higher porosity difference was observed. The amount of hydrated cement products in samples exposed to hydrogen was higher, e.g., C-S-H, and a continuous formation of ettringite and portlandite were detected.

In addition to the hydrogen interaction with concrete, hydrogen might damage materials of other types [100]: hydrogen embrittlement; hydrogen-induced cracking; and high-temperature hydrogen attack. Furthermore, hydrogen attack from high pressure and low temperature is also possible, as indicated in Table 3. Among them, hydrogen embrittlement is the most serious, and the second is somehow accompanied by stress corrosion cracking. However, the last damage is more relevant to concrete performance. In addition, the impact of temperature and pressure also brings concerns to the concrete resistance. Based on the information collected from the literature, it was concluded that the direct interaction between concrete and H_2 is limited and its impact on concrete properties and performance is negligible. However, understanding the transport of hydrogen in cementitious material is important, in simulating the scenario when hydrogen leakage occurs. Moreover, the impact of pressure and temperature on hydrogen interaction with concrete also requires our attention.

6.3 Existing models

Different hydrogen storage conceptions have been presented above, where hydrogen is stored in gas, liquid, and solid phases. In underground hydrogen storage, hydrogen is mainly stored as a gas phase because its solubility in water is very low. Hydrogen interaction with surrounding material changes the chemical equilibrium between the formation water, the dissolved gases and rock minerals. The involved phenomenon may include:

- Microbial activity [101, 102]
- Loss of hydrogen due to diffusion [46]
- Precipitation/dissolution of minerals in the surrounding material/caprock [107]
- Consequent mechanical property and porosity changes [103, 104]

In the case that hydrogen is stored in a steel tank, one more phenomenon needs to be considered:

- Hydrogen embrittlement [105]

Multiple models have been proposed to solve one or several involved processes among gas/water/metal/rock interactions. This subsection only lists some models that may be relevant to the study regarding hydrogen interaction with concrete.

6.3.1 Chemical reactions modelling

The thermodynamic dataset PHREEQC [106] has been widely used to represent the involved chemical processes and reaction kinetics. The database includes data to allow solubility computation of gases at high pressure and various temperatures. Also, specific volumes of aqueous species are calculated as a function of the dielectric properties of water and the ionic strength of the solution, which allows the calculation of pressure effects on chemical reactions and solution density, potentially significant at the high pressures relevant for hydrogen storage. The information on kinetic rates regarding mineral dissolutions and precipitations can be referred to [107].

In addition to the chemical reactions of hydrogen with the surrounding environment, the oxidation of hydrogen itself is one of the main hydrogen reactivities in underground hydrogen storage. Thus, the aqueous redox reactions have been modelled in the literature. Typically, four different approaches have been considered [108], redox reactions at equilibrium, abiotic reactions without reactivity of hydrogen, redox reactions controlled by kinetics and threshold energy thermodynamic constraints, and redox reactions controlled by a microbial kinetic model.

6.3.2 Transport modelling of hydrogen

Numerical simulations of hydrogen diffusion through the cement sheathes of oil and gas wells have been performed [91], which is based on Fick's second law of diffusion for fixed-concentration boundary conditions. A modified effective diffusion coefficient considering the presence of other substances in the cement pores has been introduced into the calculation. The results have shown that the hydrogen takes about 7.5 days to fully penetrate a 35 cm cement sheath, where a diffusion coefficient of 1.9×10^{-3} cm^2/s, a porosity of 0.35, and water saturation in cement pores of 0.7 were considered.

Pore-scale modelling on hydrogen transport in a pore network in a sandstone porous media was proposed by [109], where the impact of sandstone porous media at strongly water-wet and weakly water-wet (hydrogen-wet) on transport behaviour was investigated. Multiphase simulations and brine-hydrogen two-phase flow were used to simulate hydrogen transport in hydrogen injection and extraction processes. The results showed that increasing hydrogen wetting during the hydrogen injection process enabled a greater pore space for hydrogen storage, while it unfavoured the hydrogen extraction process by promoting the size and stability of hydrogen clusters. Thus, storing hydrogen in depleted gas reservoirs under irreducible water saturation was recommended. The study also indicated the impact of water saturation in porous media on the transport of hydrogen during the storage period. Consequently, sensitivity studies are necessary.

A mathematical model, a compositional two-phase flow model has been proposed to simulate the flow of gas and water, where the flow was considered one-dimensional, composition at an equilibrium state, capillary pressure and molecular diffusion were neglected [110]. Mass balance equations for each component were considered. The study showed the impact of water flow on the transport of hydrogen, which indicated the importance and necessity of simulating water flow, especially in the case where the hydraulic pressure is high.

6.3.3 Geochemical modelling of hydrogen

Geochemical modelling to examine the hydrogen loss due to hydrogen dissolution and fluid-rock interactions using PHREEQC, considering the impact of temperature and pressure was performed in [111]. The impact of increasing pressure and temperature was found to be limited on hydrogen solubility in brines without minerals. Almost no reactions of the saturated hydrogen aqueous solution with silicate and clay minerals were found, while carbonates trigger up to 9.5% hydrogen loss due to the calcite dissolution-induced hydrogen dissociation process. Similar to this conclusion, geochemical modelling investigating the impact of geochemical reactions on the uncertainties of hydrogen underground storage [112, 113] has shown the risk of hydrogen loss due to bacterial conversion to CH_4(g) and H_2S(g) when CO_2(g) and sulfate were available in the system. The loss of aqueous hydrogen by diffusion and related effects on the cap rock mineralogy was found negligibly. The findings indicate the potential chemical reaction between hydrogen and carbonate when concrete is employed as a surrounding barrier for storage.

Geochemical modelling studying the fluid-rock interactions using equilibrium and kinetic batch simulations at constant pressure and temperature was performed [114]. The kinetic models were used to investigate the interactions between hydrogen and the formation. The results show that reactions of hydrogen with minerals only become relevant over timescales much longer than the considered storage cycles that are typically limited to seasons, 1 year. The final kinetic model considers both mineral reactions and hydrogen dissolution to be kinetically controlled based on a typical storage cycle. Interactions among hydrogen and aqueous-phase components are dominant within the storage-relevant period.

A hydrogeochemical model to simulate the gas-water-rock interactions resulting from hydrogen storage in depleted gas fields was proposed [112], following a one-dimensional reactive mass transport model. The mineral compositions of the rock system were defined by PHREEQC [106]. The fluid flow was not considered in the model due to the lack of information regarding the hydraulic head differences. It was found that hydrogen storage causes a slight decrease in the porosity of the reservoir rock after 30 years of storage, the loss of hydrogen by bacterial activities highly depends on the exposure condition, and the loss of aqueous hydrogen by diffusion was negligibly small.

6.3.4 Models regarding high-pressure leaking

High-pressure leaking hydrogen is susceptible to spontaneous combustion due to its combustion characteristics, which may cause jet fire or explosion accidents, resulting in serious damage [100]. As the density of hydrogen is much lower than that of air, hydrogen diffuses upward rapidly under the action of air buoyancy after leakage. Hydrogen has many risks in application, compared to natural gas, such as easy leakage, low minimum ignition energy, wide flammable range (in air), wide explosion range (volume ratio of 11–59%), and embrittlement effects [115]. Because of these risks and high costs, large-scale utilization of hydrogen still needs detailed investigations. High-pressure storage tank/pipe leakage generally forms a high-pressure underexpanded jet. The concentration field of a high-pressure underexpanded jet is usually studied by simplifying it with the virtual nozzle method. The diffusion process of liquid hydrogen after it overflows from the leak source mainly includes two parts: the pool formation process of liquid hydrogen on the ground and the expansion and dilution process of low-temperature hydrogen clouds in the atmospheric environment.

6.4 Conclusions and perspectives

This section summarises the properties of hydrogen and the basic hydrogen storage conceptions according to its characteristics. Hydrogen gas storage in depleted reservoirs or lined rock caverns is the most popular and easiest method. Geochemical modelling has been proposed to simulate the gas/water/metal/rock interactions, where the thermodynamic database PHREEQC has been used to represent the mineral system. The hydrogen transport and the chemical interactions with the surrounding minerals in the reservoir are the processes that have been studied most, then followed by hydrogen loss due to either the dissolution in aqueous or the diffusion. The mineralogical changes influence the porosity of the surrounding material. The increase in porosity accelerates the transport process and further affects the chemical reactions. Among others, the impact of pressure and temperature on hydrogen diffusion is also an important factor to be considered, especially in the case when hydrogen is stored as compressed air or liquid in a tank. The operational condition generates a unique environment that requires further research.

Geochemical modelling or reactive-transport modelling has been an effective method of investigating the hydrogen interaction with the material surrounding the hydrogen. To implement geochemical modelling, the required input includes (i) hydrogen storage conceptions, e.g., gas storage in lined rock caverns or in a metal tank; (ii) transport properties of the barrier material; (iii) mineralogical phases of the surrounding material; (iv) exposure conditions of the storage structure, e.g., hydraulic pressure, composition of the groundwater, etc. The models can assess the mineralogical and microstructural evolutions/profiles in the surrounding material based on the considered scenarios, which serves to predict the service life of the operational structures.

Concrete has been limitedly used as the first barrier material for hydrogen storage due to its high permeability. However, it is still widely used as a mechanical supporting layer in the underground storage structure. Understanding the transport of hydrogen in cementitious materials is important and necessary. Some knowledge gaps in the perspective of modelling to fill are summarised as:

- Transport performance of hydrogen in cementitious materials at multiple scales, i.e., cement paste, mortar, and concrete;
- Hydrogen interactions with cementitious materials in the aspects of chemical reactions in the long-term;
- Coupling simulation of the transport performance of hydrogen and the chemical reactions in cementitious materials;

- Assessment of the hydrogen interaction with concrete under high pressure and low temperature simulating the accident scenario of hydrogen leakage;
- Extension of the above-mentioned investigations to other types of barrier materials, e.g., rock;
- A full model, which couples chemical reactions, physical property variations, and mechanics is needed.
- Existing models are mainly for hydrogen storage in depleted gas fields, and the models for other storage conceptions are missing.

7. Summary and Conclusions

This work on the interactions of hydrogen with cementitious materials is conducted as a literature survey as a part of the VTT project H2Matters. The goal of this study is to summarize what is known about hydrogen behaviour, transport, and interactions with cementitious material, as well as current modelling capabilities, and highlight knowledge gaps that require further research. Preventing hydrogen leakage from underground hydrogen storage is not only important for the economic loss in leakage. The most imminent potential effect is the safety hazard due to hydrogen flammability. Any possibility for a leak could severely affect the public opinion and acceptance of storage sites. Other issues are the possible effects on atmosphere and climate change, the effects on materials both at the storage facility or other above the ground structures, as well as the possible unknown effects on aquifers and biota. Even though concrete structures will not be the sole barrier of hydrogen, it is important to prevent or minimize the possibility of leaks also with careful planning of the cementitious materials working as a part of the barrier systems. In addition to leak prevention, the structural soundness of any cementitious materials should also be safe guarded to insure the safe functioning of a storage facility.

The transport of gasses in cementitious materials is governed by the pore structure and saturation state of the material. The research on the effects of hydrogen on cementitious materials is rather scattered and concentrated on oil well cements. In this review it was found that the testing of both the hydrogen transport in cementitious materials and the hydrogen effects on cementitious materials has mostly been studied with a very limited number of binder compositions and most of the research has been done on pastes. Mortar and concrete studies, and studies where actual hydrogen is used, are either scarce or lacking altogether. There are known geochemical effects of hydrogen on rocks, but the possible implications of these studies on mortar/concrete aggregate or binder mineral phases, have not been considered in the published studies found.

Majority of the studies conclude that the effects of hydrogen on cementitious materials is insignificant, however the test durations are often very short. When planning structures with long service life, even the more subtle changes in the structural and barrier materials should be well understood. This is essential for making sound material and engineering decisions. Both the physical, chemical and thermal environment to which the materials will be exposed in a real-life storage facility have a significant effect on the possible ageing mechanisms. Material research should be done with realistic exposure conditions and on materials with actual compositions considered for these environments.

The main conclusions are:

- transport of hydrogen in cementitious materials is governed by the pore structure and saturation state of the material
- testing of hydrogen transport and effects has been done on limited number of binder designs and mostly on paste samples, often using another gas than hydrogen
- mortar and concrete studies with hydrogen are extremely few
- hydrogen effects on rocks have been reported, but no information was found on effect on similar phases in cementitious materials or concrete aggregate
- most studies conclude the effect of hydrogen on cementitious materials is limited, but are based on short exposures

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- future research should be done with realistic exposure conditions and on materials with actual compositions considered for these environments

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