

Doc.nr: HyUSPre-D5.3 Version: Final 2023.11.29 Classification: Public Page: 1 of 66



# HyUSPRe

# Hydrogen Underground Storage in Porous Reservoirs

# Experimental data on reactions between hydrogen and rock samples from reservoir and geological seals and effects on fluid flow and mechanical properties of reservoir and caprock

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Please cite this report as: Soustelle, V., van Winden, J., Houben, M. 2023: Experimental data on reactions between hydrogen and rock samples from reservoir and geological seals and effects on fluid flow and mechanical properties of reservoir and caprock, H2020 HyUSPRe project report. 66 pp.

The authors would like to thank Rama Kotni (TNO), Eric Craenmehr (TNO) and Raymond Cremers (TNO) for the support on the exposure experiments, and at the Energy Transition Campus Amsterdam we are grateful on the support of our colleagues Lodi Schoon, Fons Marcelis, Arjan van der Linden, Kevin Bisdom, Elise Kwadijk and other staff that supported this work. We would like to thank the NAM for provision of samples and specifically Esther Vermolen and the support by Rene Stoffers at the NAM core shed.

This report represents HyUSPRe project deliverable number D5.3.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:2 of 66



# The HyUSPRe consortium







# Acknowledgement

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under grant agreement No 101006632. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme, Hydrogen Europe and Hydrogen Europe Research.

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Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:3 of 66



### **Executive summary**

The HyUSPRe project explores the feasibility of large-scale renewable hydrogen storage in porous reservoirs, focusing on technical challenges and risks in geochemical, microbiological, flow and transport, and geomechanical processes. This report (D5.3) describes the results from experiments performed within Task 5.3 of the HyUSPRe project. This task investigates the effect of hydrogen exposure and cyclic loading on sandstone reservoirs and their caprocks. Both mechanisms may lead to textural changes that can alter their mechanical and flow properties with consequences for the integrity of the targeted reservoirs.

This report presents innovative experiments to assess the impact of hydrogen exposure and cyclic loading on the mechanical and flow properties of porous reservoir rocks and caprocks. The experimental protocol involves hydrogen ( $H_2$ ) and nitrogen ( $N_2$ ) exposure, geochemical analysis, and subsequent mechanical and flow tests simulating seasonal injection and withdrawal cycles. They were performed on samples representative of deep hot reservoirs (samples from NAM – qas strorage operator in the Netherlands) and intermediate depth reservoirs (samples from SNAM – Italian gas storage operator), and carried out at in-situ stresses, temperatures and pressures.

In deep hot reservoirs, inconsistent changes in brine composition, particularly pH, were observed after H<sub>2</sub> exposure. Mechanical properties (notably Young's modulus, Poisson's ratio and failure strength) of NAM samples showed complexity, with H<sub>2</sub>-exposed samples exhibiting changes below 10%, suggesting limited impact on mechanical integrity of the tested reservoirs. For intermediate depth reservoirs, the mechanical properties of the H<sub>2</sub> expososed sandstones and caprocks display very small (Young's modulus) or no variation (Poisson's Ratio). Cyclic loading tests on H<sub>2</sub> exposed showed a notable increase in inelastic axial strain, but the overall impact on mechanical integrity after ten cycles was under 1%. Permeability behavior in subsequent cycles suggested a complex response to cyclic loading under H<sub>2</sub> exposure. Overall, the study indicates limited effects of H<sub>2</sub> exposure and cyclic loading on reservoir properties relevant to flow and mechanical integrity.

While the study indicates limited effects of  $H_2$  exposure and cyclic loading on sandstones reservoir and caprock properties within the tested conditions, it highlights the necessity for further research. Extended exposure durations and varied geological settings should be considered to comprehend the long-term impacts. In addition, experimentally validated models can provide insights into injectivity, productivity, and geological seal integrity over longer timescales relevant to Underground Hydrogen Storage (UHS) sites.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:4 of 66



### About HyUSPRe

Hydrogen Underground Storage in Porous Reservoirs

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

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





# Document information, revision history, approval status

### Document information

Title:	Experimental data on reactions between hydrogen and rock samples from reservoir and geological seals and effects on fluid
	flow and mechanical properties of reservoir and caprock
Lead beneficiary:	TNO
Contributing beneficiaries:	Shell
Due date:	2023.11.30
Dissemination level:	Public
Published where:	HyUSPRe website
Recommended citation:	Soustelle, V., van Winden, J., Houben, M. 2023: Experimental data on reactions between hydrogen and rock samples from reservoir and geological seals and effects on fluid flow and mechanical properties of reservoir and caprock, H2020 HyUSPRe project report. 66 pp.

### **Revision history**

Version	Name	Delivery date	Summary of changes
V01	HyUSPRe_report_D5.3_V01	2023.11.05	First draft report (internal TNO)
V02	HyUSPRe_report_D5.3_V02	2023.11.07	First draft report (to Shell)
V03	HyUSPRe_report_D5.3_V03	2023.11.15	Second draft report with Shell's contribution
V04	HyUSPRe_report_D5.3_V04	2023.11.20	Second draft report (annotated)
V05	HyUSPRe_report_D5.3_V05	2023.11.20	Final draft for review HyUSPRe consortium
V06	HyUSPRE_WP5D5.3_v2023.11.29	2023.11.29	Definitive layouted report

### **Approval status**

Role	Name	Delivery date
Deliverable responsible:	TNO	
Task leader:	J. ter Heege	
WP leader:	J. ter Heege	2023.11.29
HyUSPRe lead scientist	R. Groenenberg	2023.11.29
HyUSPRe consortium manager:	H. Cremer	2023.11.29



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:6 of 66





# **Table of Content**

Executive summary	3
1 Introduction	7
1.1 Deliverable context	7
1.2 Scientific background	7
1.2.1 Hydrogen-fluid-rock reactions	7
1.2.2 Effects of cyclic loading on the mechanical properties of sandstones and caprocks	9
1.3 Description of the work	10
2 Materials and Methods	11
2.1 Sample selection	11
2.2 Sample description	12
2.3 Exposure tests	15
2.3.1 At TNO	15
2.3.2 At the Energy Transition Campus Amsterdam	18
2.4 Inaxial tests at TNO	18
2.4.1 Experimental setup	10
2.4.3 Static elastic moduli	23
2.4.4 Dynamic elastic moduli	24
2.4.5 Permeability measurements	25
2.5 Technical Challenges	25
3 Results	27
3.1 NAM samples	27
3.1.1 Chemical reactions in autoclave setup used by TNO	27
3.1.2 Chemical reactions, autoclave setup used at ETCA	28
3.1.3 Mechanical properties measured at TNO	30
3.2 SNAM samples	
4 Discussion	38
4.1 Effect of H <sub>2</sub> Exposure on Flow and Mechanical Properties	
4 1 1 Deep hot reservoirs (NAM Samples)	
4.1.2 Intermediate depth reservoirs (SNAM Samples)	40
4.2 Effect of H <sub>2</sub> Cyclic Loading on Flow and Mechanical Properties	40
5 Conclusions	42
6 References	44
Appendix A: Mineral compositions	47
Appendix B: Experimental data	49
Appendix C: Flow tests	65



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:7 of 66



# 1 Introduction

### **1.1 Deliverable context**

In the context of the HyUSPRe project, we are actively exploring the feasibility of implementing large-scale renewable hydrogen storage in porous reservoirs. Our investigation encompasses a comprehensive assessment of technical challenges and associated risks. Specifically, our research delves into key areas, including geochemical (WP2), microbiological (WP3), flow and transport (WP4), and geomechanical (WP5) processes. These processes dictate the behavior of subsurface porous reservoir storage systems when subjected to cyclic injection and withdrawal of hydrogen-rich gas streams. Our approach combines laboratory-scale experiments and integrated modeling to evaluate system responses comprehensively.

In WP5, our primary focus is on geomechanical processes, specifically examining the impact of cyclic injection and withdrawal of hydrogen-containing gas streams on the durability and integrity of well systems and reservoir rocks and caprocks.

This report (D5.3) describes the results from experiments performed within Task 5.3 of the HyUSPRe project. This task describes the effect of hydrogen exposure and cyclic loading on sandstone reservoirs and their caprocks. Both mechanisms may lead to textural changes that can alter their mechanical and flow properties with consequences for the integrity of the targeted reservoirs. The new experimental data presented here simultaneously investigate the effect of H<sub>2</sub> exposure and pressure cyclic loading on a selected combination of representative porous reservoirs in Europe. The experiments presented in this report constitute an innovative workflow and a unique and new dataset to assess the integrity of porous reservoirs in a UHS context.

### **1.2 Scientific background**

The injection of hydrogen in porous reservoirs induces changes in pressure, temperature and potential dissolution of hydrogen in the formation fluids, which can react with minerals. These reactions may lead to dissolution/precipitations and result in mechanical and flow properties variations. In this section, we are summarizing the extensive literature reviews conducted in task T5.1 of HyUSPRe (Corina et al., 2022) and the TCP-Task 42 technology monitor report (IEA, 2023).

### 1.2.1 Hydrogen-fluid-rock reactions

Hydrogen injection into dry reservoir rocks or caprocks generally exhibits minimal to no reactivity with minerals, making it appear inert (Yekta et al., 2018). However, when hydrogen dissolves in the formation fluid, limited interactions occur with silicate and clay minerals, characterized by slow kinetic rates (Hassannayebi et al., 2019; Hassanpouryouzband et al., 2022; Labus & Tarkowski, 2022). For instance, Labus and Tarkowski (2022) predict minor silicate mineral dissolution of approximately 0.001% volume over eight years. The limited hydrogen reactivity originates from its strong H-H bond, which requires a high activation energy



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:8 of 66



to be broken and its non-polar nature that lowers its solubility in formation fluids. The solubility and the rate of the geochemical reactions being temperature dependent, abiotic reactions are rarely expected at low-medium temperature (< 80 °C) on timescales relevant to seasonal hydrogen storage (IEA, 2023).

Dissolution of hydrogen in brine initiates redox equilibration in the fluid-rock system, leading to redox reactions affecting various minerals, such as iron oxides (goethite, hematite, magnetite), iron sulfides (pyrite, pyrrhotite), and iron-bearing clays and minerals (Hassannayebi et al., 2019; Henkel et al., 2014; Labus & Tarkowski, 2022; Truche et al., 2013). These reactions, influenced by rock composition, may increase or reduce porosity. Sandstones and some claystones tend to experience increased porosity, while other claystones and mudstones may undergo reduction. These variations in porosity can impact rock strength, elastic properties, and, consequently, the mechanical integrity of the reservoir. Notably, claystones and mudstones may also see alterations in their sealing properties.

Furthermore, hydrogen-induced redox reactions with iron-bearing clays can lead to the reduction of Fe(III), causing hydrogen sorption in swelling clay-rich reservoirs, caprocks, and fault gouges (Didier et al., 2012; Mondelli et al., 2015). Hydrogen adsorption and desorption at grain contacts can induce local stress fluctuations, potentially promoting mechanical fatigue and permanent deformation within UHS operations lifespans (Heinemann et al., 2021). Heinemann et al. (2021) argue that despite hydrogen's lower sorption capacity in swelling clays compared to other fluids like CO<sub>2</sub>, the stress-strain-sorption behavior remains relevant for UHS reservoir integrity, caprocks and adjacent faults. Clay swelling might induce fault stressing, triggering slip and potentially enhancing hydrogen's lubrication effect, resulting in fault reactivation and potential leakage through geological seals (Heinemann et al., 2021).

Moreover, carbonate- and sulfate-bearing minerals prove sensitive to hydrogen dissolution in formation fluids. Hydrogen-induced pH decrease triggers the dissolution of carbonate (calcite, dolomite) and sulfate (anhydrite) minerals, with rapid processes noted in sandstone reservoirs (Bo et al., 2021; Flesch et al., 2018; Henkel et al., 2014). These dissolution reactions can be swift, potentially leading to the near disappearance of calcite or anhydrite cement in sandstone reservoirs within decades (Bo et al., 2021). However, over time, the increase in pH due to carbonate dissolution and redox reactions may mitigate further dissolution (Labus and Tarkowski, 2022).

Flesch et al. (2018) found that carbonate and anhydrite dissolution is localized along a reaction zone at the hydrogen-formation fluid interface with a location that evolves during the injection-production cycles. This reaction front moves through the reservoir and can result in heterogeneous displacement of formation fluid by hydrogen, with a preference for migrating through zones of elevated reservoir permeability.

Studies on reactions in the hydrogen-natural gas-rock system are mainly considering the common scenario of simultaneous hydrogen and natural gas storage. (Shi et al., 2020) investigated such a scenario involving a sandstone gas reservoir, caprock, and well cement, revealing reactions similar to those described earlier. While sandstone porosity and



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:9 of 66



permeability experienced slight changes, caprocks exhibited substantial permeability reduction, which is advantageous for sealing.

Microbial activity within the hydrogen-fluid-rock system, contingent on pressure, temperature, rock, fluid composition, and microorganism population, was reviewed by (Dopffel et al., 2021; Ahn et al., 2022). Microbial effects align with and enhance the reactions described above, contributing to porosity increase in UHS reservoirs. These complex chemical reactions, contingent on rock and pore fluid compositions, give rise to varying alterations in mechanical properties. Nevertheless, an increase in permanent (inelastic) deformation is a common outcome, significantly impacting hydrogen injectivity, productivity, fault reactivation, caprock and fault sealing capacity, and ultimately, subsidence and induced seismicity (e.g., Pijnenburg et al., 2019). These effects will be further elaborated in the following section.

# 1.2.2 Effects of cyclic loading on the mechanical properties of sandstones and caprocks.

The injection of cold, pressurized fluids into porous subsurface reservoirs induces a thermoporoelastic response, affecting the stress state in the rock mass and surrounding faults. This response, well-documented in studies like Segall, 1989; Rutqvist, 2012; Candela et al., 2018, is a critical aspect of hydrogen storage investigations besides hydrogen-fluid-rock reactions. Hydrogen injection or production typically results in modest temperature variations in the reservoir, especially compared to natural gas operations due to its lower Thomson-Joule effect (Klell, 2010). However, pressure fluctuations from the injection of pressurized hydrogen/natural gas mixtures can yield stress changes beyond the immediate injection zone, bringing stresses closer to failure for both rocks and faults.

The mechanical properties of rocks play a crucial role in how they respond to stress changes and propagate stress variations within the rock mass. These properties influence the spatial distribution of stress changes, compaction, and their impact on surrounding faults during cyclic hydrogen injection/extraction. Understanding how these rock property transformations interact with poroelastic stresses during cyclic hydrogen injection/extraction is vital for predicting changes in reservoir flow, compaction, injectivity/productivity, and fault stability around the underground hydrogen storage (UHS) system.

Schimmel et al., 2021 conducted cyclic compaction experiments on quartz aggregates under various pH conditions, revealing that most permanent deformation occurs during initial cycles. Cumulative grain cracking and reorientation increase grain contact and reduce intergranular stress, impeding crack growth and grain failure. Scaling this to UHS porous reservoirs suggests that hydrogen injection can trigger responses like carbonate and sulfate dissolution, grain crushing, and local compaction, altering porosity, mechanical properties, and flow behavior.

Clay-rich caprocks, such as claystones and shales, exhibit anisotropic elastoplastic behavior, with mechanical properties influenced by bedding orientation (Zhang et al., 2019). Cyclic compaction experiments on claystone show hardening behavior, potentially influenced by clay swelling in wet conditions. Mineralogical reactions within the hydrogen-brine-rock system can



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:10 of 66



alter porosity and permeability, necessitating a case-specific assessment of their impact on mechanical properties due to the highly variable mineral composition of caprock.

Heinemann et al. (2021) suggest that repetitive injection of dry hydrogen may progressively dry out the reservoir, altering its mechanical properties over time. These changes could lead to reduced fluid-rock reactions, potentially affecting reservoir integrity and the sealing properties of fractures, potentially reopening leakage pathways.

### **1.3 Description of the work**

The goal of the experiments described in this report is twofold: (1) To assess the effect of hydrogen-rock reactions and cyclic pressure loading on the mechanical and flow properties of porous reservoir rocks and caprocks, and (2) to provide a preliminary overview of the geomechanical integrity of potential candidate reservoir for UHS. In this report, we will also detail the rationale behind the sample selections. The adopted experimental protocol allows us to answer the research questions and discuss the results in terms of UHS operations.

The experiments consist first of reaction tests where samples are exposed to hydrogen at reservoir pressure and temperature conditions for about two months. Some brine and part of the samples were analyzed to evaluate potential geochemical reactions. We then performed the mechanical and flow tests at reservoir conditions on the reacted samples to assess any effect from the hydrogen exposure. We then simulate seasonal injection withdrawal by cycling the pressure in the sample and measuring changes in mechanical and flow parameters after each cycle. The results of hydrogen-exposed samples are compared to non-exposed and nitrogen-exposed samples.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:11 of 66



# 2 Materials and Methods

### 2.1 Sample selection

In this section, we outline the criteria and rationale behind selecting rock samples for our study. The criteria aim to assess the impact of  $H_2$  exposure on their mechanical and flow properties in two types of reservoirs (and caprock) that more or less represent two end members of potential hydrogen storage sites in Europe. Our sample selection process was constrained by time considerations and aimed to represent specific geological conditions. We prioritized reservoirs where both caprocks and reservoir rocks were readily available, and the composition of the formation fluid was well-documented. Additionally, we sought samples characteristic of the clusters of potential hydrogen storage reservoirs, as defined by Cavanagh et al., 2022, 2023 (HyUSPRe deliverable D1.3 and D1.5).

### **Cluster Definitions:**

Cavanagh et al. (2022, 2023) classified potential hydrogen storage reservoirs into four distinct clusters based on key geological parameters:

- Northwestern Europe Cluster: These reservoirs are characterized by their significant depth (up to 3300 meters), elevated temperatures (70-115 °C), and high initial gas pressure (up to 28 MPa).
- Central Europe Cluster: Reservoirs in this cluster are situated at intermediate depths (400-1550 meters) with temperatures below 60 °C and initial gas pressure lower than 20 MPa.
- Eastern Europe Cluster: Similar to the Central Europe Cluster, these reservoirs are characterized by intermediate depths (400-1550 meters) and lower temperatures below 60 °C.
- Southern Europe Cluster: Reservoirs in this cluster also exhibit intermediate depths (400-1550 meters) and lower temperatures below 60 °C.

### Selected Samples:

From the available materials, we identified two reservoirs that met our specified criteria:

- Northwestern European Cluster Sample: We obtained rocks and caprocks from an anonymized gas field provided by the Nederlandse Aardolie Maatschappij (NAM). These samples closely resemble the deepest reservoirs, with depths of 3300 meters and formation temperatures of 115°C, as considered representative of the Northwestern European Cluster.
- Central, Eastern, and Southern European Cluster Sample: Rocks and caprocks from an anonymous gas field provided by SNAM. These samples represent reservoirs at intermediate depths of 1500 meters and temperatures of 50°C. These conditions align with the criteria outlined for the Central, Eastern, and Southern European Clusters.

It is worth noting that we were unable to locate materials representative of the shallowest and coldest candidates meeting our criteria during our sample selection process.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:12 of 66



### 2.2 Sample description

In this section, we provide a comprehensive description of the samples obtained from both NAM's anonymous reservoir (well Z) and the SNAM anonymous gas field. These samples serve as the foundation for our study's subsequent analyses.

### Samples from NAM's Anonymous Reservoir (Well Z):

The samples extracted from well Z consist of three caprocks (denoted as Z\_1) and six sandstone plugs (denoted as Z\_2 and Z\_3), as illustrated in Figure 2.1. To complement our geological analysis, we obtained formation brine from the Y well, also situated within the same reservoir. Although the rock and fluid samples originate from different wells, we assume a uniform composition of the formation fluid within the reservoir.



Figure 2-1: Rock and Formation water samples as received from NAM.

The selected sandstones, Z-2 and Z-3, exhibit a composition comprising approximately 82% silicate minerals, primarily quartz, with ~8% carbonates represented by dolomite and nearly ~9% clay minerals. These sandstone samples are considered representative of the average composition of sandstones within well Z for this particular reservoir. Notably, optical observations reveal grain size variations at the scale of individual plugs.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:13 of 66





Figure 2-2: Mineralogical composition of the studied sample as a function of the studied reservoirs and the sample depth. The mineral composition of each sample is available in Appendix A.

In contrast, the caprock samples (Z-1) are claystones composed of roughly 55% clay minerals and 42% silicates, primarily quartz, with trace amounts of carbonates and oxides. It is worth mentioning that the caprock Z-1 exhibits a relatively high clay content, as depicted in Figure 2.2. Visual inspections indicate a homogeneous texture in the caprock samples.



Doc.nr: HyUSPre-D5.3 Version: Final 2023.11.29 Classification: Public Page: 14 of 66



#### Table 2-1: Chemical composition of the formation waters used for the exposure tests.

	NAM	SNAM			
	Y unit	Reservoir	Synthetic unit		
Na	63979 mg/kg	18179.14	18318 mg/L		
к	1546 mg/kg	530	530 mg/L		
Ca	21422 mg/kg	4	4.9 mg/L		
Mg	2171 mg/kg	1000	961 mg/L		
Sr	820 mg/kg	171.865	- mg/L		
Ba	18 mg/kg	-	-		
Mn	32 mg/kg	3.66	- mg/L		
Fe	260 mg/kg	147	26 mg/L		
Cu	<0.2 ma/kg	-	-		
Zn	139 ma/ka	-	-		
AI	<0.05 ma/ka	-	-		
Si	<20 ma/ka	-	-		
Li	40 ma/ka	2.554	- ma/L		
Ni		0.045	- ma/L		
Pb	57 ma/ka	_	-		
в	31 ma/ka		-		
NH4+	155 ma/ka	-	-		
CI	155668 mg/kg	34540	30892 mg/l		
F	<100 mg/kg	-	-		
l.	<25 mg/kg	_	-		
Br	366 mg/kg	244	- ma/l		
SO4=	153 mg/kg	<50	- mg/L		
HCO3-	183 mg/kg	772.8	773 mg/L		
CO3=					
S=					
PO4(-3)		<8	- ma/L		
NO3-	<100 ma/ka	<50	- ma/L		
NO2-					
Amoniacal Nitrogen		68.5	- ma/L		
Glycolic acid	30 mg/kg	-			
Formic acid	101 mg/kg	-			
Acetic acid	40 mg/kg	_			
Propionic acid	<1 mg/kg	-			
Butyric acid	<1 mg/kg				
Density @ 20 °C	1192 kg/m3	-			
pH (as received)	5.0	5.99	6 -		
Conductivity	210600 uS/cm	82625	- uS/cm		
TDS	239000 mg/kg	-			
Total alkalinity as HCO3-	281 mg/L	-			
Total organic acids as	02 mm/				
acetic acid	92 mg/L				
Total organic carbon		2556	426 mg/L		
Total inorganic carbon		60	- mg/L		
Total carbon		2616	- mg/L		

The composition of the formation fluid is detailed in Table 2.1, providing information about its pH (5) and salinity (TDS) at 239,000 ppm.

#### Samples from SNAM's anonymous reservoir:

SNAM contributed preserved (waxed) core sections from an anonymous gas field (Fig. 2.3). The sandstone core measures 50 cm in length and 5 cm in diameter and is characterized by



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:15 of 66



a coarse-grained, loosely consolidated structure prone to disaggregation during plug coring. Conversely, the caprock core boasts a larger dimension, measuring 1 meter in length and 10 cm in diameter, and exhibits a more cohesive nature, facilitating plug drilling.



Figure 2-3: Extraction of the caprock and sandstone samples from SNAM preserved cores.

While direct measurement of the mineral composition for these SNAM samples was unavailable, we have inferred their composition by averaging the values from the nearest analyzed samples above and below the chosen depth intervals along the well. Figure 2.2 illustrates that the sandstones and caprocks used in our study tend to exhibit relatively high silicate mineral contents, approximately 40% and 20%, respectively, and reduced carbonate content, estimated at 40-45%, comprising equal parts calcite and dolomite, compared to the other samples from the same well.

Complete recovery of the formation fluid was unattainable for the exposure and triaxial tests. Consequently, we have used a synthetic brine closely resembling the composition measured by SNAM for the studied reservoir, as outlined in Table 2.1. This synthetic brine includes major components such as calcium, sodium, magnesium, potassium, chloride, and bicarbonate, with the organic carbon content simulated by the addition of ethanol. pH adjustment was achieved using HCI.

### 2.3 Exposure tests

### 2.3.1 At TNO

In our experimental setup, the reaction tests were conducted at the laboratory of TNO's Material Solutions Department in Eindhoven. The samples were categorized into three groups: those not exposed to gas, those exposed to  $H_2$ , and those exposed to  $N_2$ , as detailed in Table



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:16 of 66



2.2. In each of these groups, each rock type is represented. The samples that were exposed to gas are placed either in plastic centrifugal tubes or glass vials submerged in their formation fluid, and a small hole was made in the cap of the vial's seal to allow contact between the gas and the formation fluid (Fig. 2.4a and b). To ensure the integrity of the caprock samples during decompression and temperature fluctuations, we encased them in PTFE tubes. These PTFE sleeves provided mechanical support and minimized the risk of failures along clay cleavage planes. We also introduced perforations in the sleeves to enhance contact and potential reactions along the outer surfaces of the samples. The samples were then positioned within autoclaves, and the working gases, either N<sub>2</sub> or H<sub>2</sub> (with a purity of 99.999 %), were introduced at a rate of 0.1 MPa/min until the desired target pressures were achieved (corresponding to the mean effective stress of the reservoir before depletion, i.e. 20.6 MPa and 13.4 MPa for the NAM and SNAM samples, respectively, see Table 2.3). The actual applied gas pressures were 20 MPa and 14 MPa during the reaction tests. Once pressure is achieved, temperature is increased. Due to limitations associated with the autoclave, the NAM samples were exposed to a temperature of 100°C, while the SNAM samples were maintained at the reservoir's temperature of 50°C (Table 2.2).

	Samples	Gas	Time [days]	P <sub>gas</sub> [Mpa]	Temp. [°C]	Vial
	Z-3-2	-	-	-	-	-
	Z-2-2a	-	-	-	-	-
	Z-2-2b	-	-	-	-	-
	Z-1-2	-	-	-	-	-
_	Z-3-1	H2	60	20	100	Centri Tube
Ş	Z-2-1-CG	H2	60	20	100	Centri Tube
Ž	Z-2-1	H2	60	20	100	Glass
	Z-1-1	H2	60	20	100	Glass
	Z-3-3	N2	60	20	100	Centri Tube
	Z-2-3-CG	N2	60	20	100	Centri Tube
	Z-2-3	N2	60	20	100	Glass
	Z-1-3	N2	60	20	100	Glass
	CR_B2	-	-	-	-	-
	CR_M1	-	-	-	-	-
	SS_T1	-	-	-	-	-
	SS_T2	-	-	-	-	-
-	CR_B3	H2	60	14	50	Glass
1	CR_M2	H2	60	14	50	Glass
Z	SS_B1	H2	60	14	50	Glass
5	SS_B2	H2	60	14	50	Glass
	CR_B1	N2	60	14	50	Glass
	CR_M3	N2	60	14	50	Glass
	SS_M1	N2	60	14	50	Glass
	SS_M2	N2	60	14	50	Glass

Table 2-2: Conditions of the reaction (exposure) tests.

The reaction tests spanned approximately two months, after which temperature was reduced to room temperature and pressure was released with 0,1 MPa/min. The rock samples were carefully retrieved for subsequent mechanical testing (see Fig. 2.4). Additionally, when feasible, we collected formation fluid samples to investigate potential fluid-rock reactions. For this purpose, we obtained two fluid samples ranging from 5 to 10 ml per vial. One sample was used to measure anions, while the other was to quantify cations, necessitating acidification with 1 vol. % of HNO<sub>3</sub>. It is worth noting that during this study, only the fluid samples from NAM's



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:17 of 66



reservoir were subjected to analysis. Analyses performed on brine samples by NAM at the Energy Transition Campus Amsterdam (ETCA) using IC (ion chromoatography) for major cations, IC for anions and ICP-OES (Inductively coupled plasma optical emission spectroscopy) for minor cations and metals. Alkalinity was derived by titration according to the RICE method.

Table 2-3: Parameters of the reservoir for the studied samples	s (based on info from operators).
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	NAM	SNAM
Temp. [°C]	115	50
P <sub>initial</sub> [MPa]	39.3	18.31
P <sub>depleted</sub> [MPa]	18	7
S <sub>v</sub> [MPa]	71.5	33
S <sub>н</sub> [MPa]	55.27	-
S <sub>h</sub> [MPa]	52.63	31



NAM

SNAM



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:18 of 66



### 2.3.2 At the Energy Transition Campus Amsterdam

At the Energy Transition Campus Amsterdam (ETCA) similar exposure tests were performed on similar material also from Well Z. Three sample sets (Z\_4, Z\_5, and Z\_6) all consisting of three plugs from the same depth were made. The three sample sets were similar to the once described above provided to TNO. Z\_4A, Z\_5A, and Z\_6A were placed for two months in an autoclave filled with brine (from well Y, plugs were saturated before they were put in the autoclaves and in the autoclaves the plugs were submerged in brine) with a Nitrogen gas overpressure of 100 bar and a temperature of 100 degrees C. Samples Z\_4B, Z\_5B, and Z\_6B were saturated and placed for two months in a different autoclave submerged in brine from well Y. This autoclave had a hydrogen gas overpressure of 100 bar and was also at a temperature of 100 degrees C. All three samples in the one autoclave were not individually packed as in the TNO tests (see description above). The plugs Z\_4C, Z\_5C and Z\_6C were kept as is. After two months in the autoclaves plugs Z\_4A, Z\_5A, Z\_6A, Z\_4B, Z\_5B, and Z\_6B were retrieved and water samples were taken from the two autoclaves to be subjected to ICP-MS analysis at ETCA to investigate elemental changes due to chemical reactions between the brine, the different gasses and the plugs.

### 2.4 Triaxial tests at TNO

### 2.4.1 Experimental setup

All experiments and measurements were conducted at TNO's geomechanical laboratory of the Applied Geosciences Department (iM4RockLab), utilizing a High-Pressure Environmental Triaxial Automated System manufactured by GDS Instruments Ltd (GDS–HPETAS), as depicted in Figure 2.5.



Doc.nr: HyUSPre-D5.3 Version: Final 2023.11.29 Classification: Public Page: 19 of 66







# Figure 2-5: Pictures of the GDS HPETAS (a) and the inner cell experimental set up (b) used at the iM4RockLab at TNO in Utrecht.

The GDS–HPETAS apparatus offers the capability to operate under the following conditions:

- Maximum confining and pore pressures of 65 MPa.
- Applied axial load of up to 250 kN.
- Temperature control up to 100°C.

Our assemblies are designed to work with samples of 50 mm in length and 25 mm in diameter. These dimensions have been respected as much as possible during sample preparation according to the quality and initial dimensions of the rock samples. Samples starting dimensions are recorded in Table 2.4., and pictures in Figure 2.6.

For the measurement of axial and radial deformation of the samples during experiments, local linear variable differential transformers (LVDTs) were employed. This included:

- Two axial LVDTs to measure axial strain.
- Two radial LVDTs to measure radial strain.

The radial LVDTs were fixed to a stage and secured onto the sample using springs to ensure stability (Fig. 2.5b). In these experiments, we employed a double-jacket sample (FEP and PTFE sleeve) to mitigate the risk of jacket rupture, common with large-grain, poorly consolidated sandstones.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:20 of 66



Before commencing the experiments, the local LVDTs were meticulously calibrated to the specific temperature and pressure conditions relevant to our study. All experimental parameters were recorded at a sampling rate of 1 Hz.

Acoustic velocity measurements were performed using embedded transducers in the top cap and the pedestal holding the top and bottom pistons, as shown in Figure 2.5b. These transducers consist of three piezo-electric plates: one for generating and receiving P-wave signals and two others, oriented 90° apart, for generating and receiving S-wave signals.

In our experimental setup, the transducers from the pedestal and the top cap were employed for generating and receiving wave signals. Waves were pulse-generated at a frequency of 1 MHz, and the resulting acoustic signals were recorded and processed using the GDS\_AV software from GDS Instruments Ltd.

Table 2-4: Physic	al description and mechanical	parameters. The i and	d R superscripts denote
initial and reserve	oir conditions, respectively.		

	Sample description				ion	Densities Porosities			Acoustic Velocities			Young's Modulus			Poisson's Ratio					
s	amples	Gas	Rock Type	Length (mm)	Diameter (mm)	d <sub>sat</sub>	d <sub>s</sub> <sup>lab</sup>	d <sub>s</sub> <sup>XRD</sup>	Φ <sub>lab</sub>	$\Phi_{\rm xrd}$	Vp <sup>i</sup> (m/s)	Vs <sup>i</sup> (m/s)	Vp <sup>R</sup> (m/s)	Vs <sup>R</sup> (m/s)	E <sup>i</sup> <sub>dyn</sub> (GPa)	E <sup>R</sup> <sub>dyn</sub> (GPa)	E <sup>R</sup> stat (GPa)	ν <sup>i</sup> <sub>dyn</sub>	v <sup>R</sup> <sub>dyn</sub>	σ <sub>d</sub> max (MPa)
	Z-1-2	-	CR	49.870	25.787	2.626	-	2.810	-	0.102	3480.05	1824.76	3775.11	1795.21	22.91	22.92	-	0.31	0.35	-
	Z-1-1	H2	CR	49.900	25.775	2.641	-	2.810	-	0.104	3759.73	1878.03	-	-	24.85	-	-	0.33	-	-
	Z-1-3	N2	CR	50.543	25.727	2.638	-	2.810	-	0.106	3735.68	1877.15	4035.60	1926.67	24.75	26.49	15.00	0.33	0.35	73.10
Σ	Z-2-2a	-	SS	47.367	25.565	2.458	2.569	2.670	0.080	0.143	4276.89	2618.79	4548.15	2565.60	40.46	47.89	10.33	0.20	0.27	-
A	Z-2-1	H2	SS	46.965	25.770	2.419	2.535	2.670	0.087	0.170	3964.61	2398.47	4699.52	2554.79	33.55	40.73	17.92	0.21	0.29	80.58
-	Z-2-3	N2	SS	47.452	25.577	2.430	2.494	2.670	0.049	0.162	4208.08	2564.76	4367.69	2379.10	38.51	35.46	19.80	0.20	0.29	89.33
	Z-3-2		SS	51.507	25.503	2.275	2.350	2.690	0.065	0.277	-	-	-	-	-	-	-	-	-	
	Z-3-1	H2	SS	40.237	25.737	2.323	2.457	2.690	0.106	0.245	3539.72	2029.00	3935.64	2006.90	24.01	24.78	12.18	0.25	0.32	71.55
	Z-3-3	N2	SS	39.702	25.513	2.386	2.661	2.690	0.151	0.203	3871.09	2313.13	3825.97	2103.10	31.21	27.09	11.74	0.22	0.26	-
	CR_B2	-	CR	50.674	24.215	2.246	-	2.769	-	0.304	3112.37	1691.91	3077.98	1602.38	16.74	15.16	-	0.30	0.31	-
	CR_B3	H2	CR	44.642	25.377	2.300	-	2.769	-	0.272	2823.26	1843.46	3013.61	1550.89	19.83	14.60	-	0.27	0.32	-
Ρ	CR_B1	N2	CR	47.383	24.428	2.267	-	2.769	-	0.292	3081.84	1408.18	3002.46	1541.96	12.19	14.24	-	0.35	0.32	-
SN	SS_T1	-	SS	35.900	23.620	2.129	2.511	2.729	0.257	0.312	2742.03	1358.97	-	-	10.51	-	-	0.34	-	-
1	SS_B1	H2	SS	45.403	23.660	2.165	2.555	2.729	0.251	0.298	3054.99	1656.37	3119.00	1635.20	15.35	15.17	-	0.29	0.31	-
	SS_M1	N2	SS	42.576	23.347	2.173	2.554	2.729	0.245	0.294	2991.69	1591.98	3129.84	1643.87	14.34	15.38	-	0.30	0.31	-

### 2.4.2 Experimental protocol

Triaxial tests were conducted to study the effects of H<sub>2</sub>-rock reactions and cyclic loading on the mechanical behavior and flow properties of reservoir and caprock. These tests were designed to measure dynamic and static elastic moduli and flow properties at reservoir stress, pressure and temperature conditions and allow for pressure cycles and post-cycle measurements. All mentioned parameters are measured during one single destructive test as we obtain the sample's compressive strength at reservoir condition by bringing it to failure (Fig. 2.6).

Before the triaxial tests, sandstone samples are dried for at least 48h at 80 °C before being saturated with their respective formation fluids. Our saturation method is illustrated in Figure 2.7. The pore space is first evacuated for at least 12h. The valve to the vacuum pump is then closed, and the one connected to the pore fluid tank is opened. We assume the sample is saturated when the tank's weight becomes constant (with a correction for evaporation). The



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:21 of 66



weight measurement of the dry and saturated samples is used to calculate both the sample porosity and density (Table 2.4). This operation was only performed on sandstone, the permeability of the caprock being too low to allow for this method. Caprock samples are always submerged in their formation fluids, and only the wet density was measured (Table 2.4). Two porosities were calculated, one by comparing the dry and wet densities measured in the lab (referred to as  $\Phi_{lab}$  in Table 2.4) and the other one by comparing the solid matrix density measured from XRD and wet density measured in the lab (referred to as  $\Phi_{XRD}$  in Table 2.4).

In the triaxial apparatus, the samples are first held at room temperature with an effective mean stress of 1 MPa, i.e., a confining pressure of 2 MPa, a pore pressure of 1 MPa and an axial (vertical) stress of 3 MPa. Acoustic velocities are measured at these conditions, but no triaxial tests are performed to prevent altering the rock microstructures and properties already at low confinement. These conditions are referred to as the initial conditions.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:22 of 66





Figure 2-6: Experimental protocol for the (a) sandstones and (b) the caprocks.

The confining and pore pressure are then raised simultaneously at the same rate (10 MPa/h) until  $S_h$  and  $P_{max}$  are reached (Table 2.2), respectively. The sample is then heated to reservoir temperatures at 10 °C/h. However, the NAM samples were only tested to a maximum of 100 °C due to the limitation of the apparatus. Once at temperature, the axial load is increased to reach the vertical stress experienced at the top of the reservoir (Table 2.2). Once at reservoir conditions, acoustic velocities are measured, and two triaxial tests are done by lowering the



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:23 of 66



axial stress to about 2 MPa in order to obtain the rock's elastic moduli. These two tests are followed by another acoustic velocity measurement and a flow test to measure the initial permeability.

The cyclic loading steps, aiming to simulate H<sub>2</sub> seasonal injection and withdrawal, were done by decreasing the pore pressure from P<sub>max</sub> to P<sub>min</sub> and raising it again to P<sub>max</sub>, followed by two triaxial tests and the acoustic velocities measurements described above. The last step was to measure the sample permeability at reservoir temperature, stress and P<sub>max</sub> conditions. This cycle (Fig. 2.6a) is repeated ten times. It is important to note that the pressure cycle applied to the sandstone cannot be applied to the caprock samples within a reasonable time frame. Therefore, the pressure cycle was simulated by increasing the confining pressure to a value of S<sub>h</sub> + (P<sub>max</sub>-P<sub>min</sub>) and decreasing back to S<sub>h</sub> (Fig. 2.6b). Permeability tests on the caprocks were impossible to carry out with brine as pore fluid in our setup due to the low permeability of the samples.



Figure 2-7: Schematic representation of the sample saturation method.

This protocol has several advantages. It allows for the measurement of dynamic elastic moduli at initial conditions without damaging the sample, the measurement of static and dynamic elastic moduli and permeability at reservoir conditions and the evolutions of these parameters with the pressure cycles. Despite altering the sample's microstructure upon failure, the consistency in testing conditions ensures comparability across all samples.

The description of each experiment, i.e. the stresses, pressures and temperature curves vs. time, are shown in Appendix B.

### 2.4.3 Static elastic moduli

The static elastic moduli represent the elastic behavior of a material undergoing large deformation in drained conditions and are measured during the triaxial stages. The static elastic moduli we measured were Young's modulus  $E_{stat}$  and Poisson's ratio  $v_{stat}$ .

In a triaxial experiment, Young's modulus quantifies the elastic axial deformation of the material when a tensile or compressive axial stress is applied to it and is defined by the relationship:



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:24 of 66



$$E_{stat} = \frac{\sigma_d}{\varepsilon_a} \qquad [1]$$

Where  $\sigma_d$  is the axial differential stress, which is obtained by the ratio of the axial load of the surface area of the cylinder subtracted by the confining pressure, and  $\epsilon_a$  is the axial strain recorded by the two axial LVDTs.

The Poisson's ratio quantifies the deformation of material perpendicular to the direction of the axial load and can be calculated from the following relationship:

$$v_{stat} = -\frac{d\varepsilon_r}{d\varepsilon_a}$$
 [2]

Where  $\varepsilon_r$  is the radial strain measured from the two radial LVDTs, both E and v were calculated during loading, taking the slope between 57 and 77% of the maximum applied differential stress, which corresponds to calculating the elastic moduli at two third of the stress-strain slope where it is most linear.

### 2.4.4 Dynamic elastic moduli

The dynamic elastic moduli represent the elastic behavior of a material submitted to very small undrained deformation exerted by seismic waves, which can be derived from the velocity of acoustic waves propagating in the material.

Prior to the experiments, our acoustic velocities acquisition system needs to be calibrated at every effective pressure  $P_e$ , axial load and temperature at which we want to measure the P-wave (V<sub>p</sub>) and S-wave velocities (V<sub>s</sub>). The calibrations consist of measuring the travel time of both wave types at each relevant condition while putting the pistons directly in contact with each other (tip-to-tip calibration). This travel time calibration is then subtracted from the measured travel time during the experiment, thus removing any effect of the apparatus and piston potential deformation.

The travel times were picked using the first arrivals on the dedicated receiver transducers (P,  $S_1$ ,  $S_2$ ) with a precision of about 0.02 µs. The velocities are then obtained by dividing the sample length (corrected for the axial deformation) by the travel time.

The dynamic elastic moduli can be determined according to the following relationships: Young's modulus:

Deizeen's retie	$E_{dyn} = \frac{\rho V_s^2 (3V_p^2 - 4V_s^2)}{V_p^2 - V_s^2}$	[4]
Poisson's fallo:	$v_{dyn} = \frac{V_p^2 - 2V_s^2}{2(V_p^2 - V_s^2)}$	[5]
Bulk modulus:	$K_{dyn} = \rho (V_p^2 - \frac{4}{3}V_s^2)$	[6]
Shear modulus:	$G_{dyn} = \rho V_s^2$	[7]



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:25 of 66



Although the dynamic bulk and shear moduli were calculated, only the dynamic Young's Modulus and Poisson's ratio will be discussed in this study.

### 2.4.5 Permeability measurements

Steady-state permeabilities are measured at reservoir stresses, temperature and  $P_{max}$  conditions (Tab. 2.3) using two Teledyne ISCO 260D pumps controlling the upstream and downstream pore pressure. Once the upstream and downstream flow are constant, Darcy's law (Equation 1) is applied to calculate the sample permeability:

$$k = \frac{\mu QL}{A\Delta p} \qquad [6]$$

Where k (m<sup>2</sup>) is the permeability, Q (m<sup>3</sup>.s<sup>-1</sup>) is the volumetric flow of the pore fluid, A (m<sup>2</sup>) is the cross-sectional area of the sample perpendicular to the flow,  $\Delta p$  (Pa) is the pressure gradient between the two (upstream and downstream) ends of the sample, and  $\mu$  (Pa.s) is the pore fluid viscosity. The values of  $\mu$  vary with the fluid salinity, pressure and temperature and were obtained from (Kestin et al., 1981). In these experiments, the  $\Delta p$  ranged from 0.2 to 0.5 MPa and the calculated dynamic viscosity of the NAM's Y formation fluid was calculated to be 6x10<sup>-4</sup> Pa.s. The plot for flow and permeability as a function of time during the tests are presented in Appendix C.

### 2.5 Technical Challenges

Most sandstones in our study are characterized by coarse grains and poor consolidation; it is easy to chip grains just by rubbing a finger on their surface. As a result, these samples were challenging to polish and prone to breaking during exposure tests. It was often impossible to achieve the conventional minimum length-to-diameter ratio of 2:1 (in particular for the SNAM samples, Table 2.4).

Our experimental protocol also required constant load control for extended periods at the maximum functioning temperature of the load cell. In several instances, these conditions led to inaccurate load readings and failure of the sample and, therefore, the experiment (i.e. in load control, spiky fluctuations in load readings and control feedback that sometimes lead to stress peaks reaching sample failure). It happened for all the Z-1-1 samples. These issues caused the loss of samples before the experimental conditions could be adjusted, and the full experimental protocol (presented in section 2.4.2) could only be applied to  $Z_2_1$  (sandstone,  $H_2$  exposed),  $Z_2_3$  (sandstone  $N_2$  exposed) and  $Z_1_3$  (caprock,  $N_2$  exposed). For all other experiments, only Vp, Vs, dynamic elastic moduli and sometimes static elastic moduli were recorded.

Part of the radial strain in the sandstone samples is absorbed by the double jacket designed to prevent leakage. Due to the relatively low range of differential stress applied during the triaxial tests, the recording of sample radial strain was often omitted because the jackets deformation absorbed all radial deformation leading erroneous radial strain measurements.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:26 of 66



Due to the difficulty of obtaining polished parallel surfaces on the sample plugs, accurately picking the first arrivals of P- and S-waves on acoustic velocity (AV) signals becomes challenging, especially for the P-waves at lower confining pressures and stresses. This issue was overcome by using the Vs measurements and recalculating Vp by averaging the relationships found in the literature that relates Vp to Vs (Han et al, 1986; Castagna et al. 1993), Vp to prorosity and clay content (Han et al., 1986) and Vp to density (Castagna et al., 1993). For sandstones,  $V_p$  at initial conditions was recalculated using the following relationship:

$$Vp = \frac{1}{4} (Vp_{Castagna93}^{Vp-Vs} + Vp_{polynom-Castagna93}^{density} + Vp_{Power-Castagna93}^{density} + Vp_{Han86}^{porosity})$$
[7]

where each of the labelled elements corresponds to the empirical relationships of Castagna et al., 1993 and Han et al., 1986.  $V_p$  and  $V_s$  can be written as follows:

 $Vs_{measured} = 0.8046V p_{Castagna93}^{Vp-Vs} + 0.856$  [8]

$$\rho_{b} = -0.0115 (V p_{polynom-Castagna93}^{density})^{2} + 0.261 (V p_{polynom-Castagna93}^{density}) + 1.515$$
[9]  
$$\rho_{b} = 1.66 (V p_{power-Castagna93}^{density})^{0.261}$$
[10]

$$V p_{Han86}^{porosity} = 5.59 - 6.93 \Phi - 2.18C$$
 [11]

With  $\rho_b$  as the bulk density,  $\Phi$  as the porosity and C as the clay content. Note that these relationships are given for AV expressed in km.s<sup>-1</sup>.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:27 of 66



### 3 Results

### 3.1 NAM samples

### 3.1.1 Chemical reactions in autoclave setup used by TNO

After the exposure tests, the first noticeable difference observed between the  $H_2$  and  $N_2$  exposed samples is the color and the turbidity of the brine in the vials (Fig. 2.4). In the samples exposed to  $H_2$ , the brine appears clear and colorless with some yellowish sediments at the bottom whereas in the sample exposed to  $N_2$ , the brine and sediments have a reddish color, which could indicate a certain degree of oxidation and precipitation of iron oxides. That observation is consistent with the strong reducing behavior of  $H_2$ . The Fe content of the formation water was analysed on an acidified aliquot, dissolving any precipitated iron oxide. In the formation water, the Fe content decreases in both  $H_2$  and  $N_2$  exposed samples relative to the original composition (Table 3.1). In samples exposed to  $H_2$ , it is higher for the caprock brine but lower for the sandstone brine. Precipitation of Fe-oxidies would have strongly reduced brine Fe-levels. Either precipitation of iron oxides occurred primarily after subsampling of the brine, or Fe floccules were also subsampled and acidified, leading to still elevated Fe levels.

Comparing ionic compositions, an error margin of 5% should be applied for major ions and and error margin of 10% is appropriate for minor cations and anions and 20% for trace metals. No significant and consistent difference is observed between the composition after the  $H_2$  or  $N_2$  exposure for Na, Ca, Mg, Sr, Mn K, Mg, Sr, Mn, Zn and SO<sub>4</sub>. An increase in K is observed for  $H_2$ -exposed samples, while  $N_2$ -exposed samples show elevated Si concentrations.

All exposed samples display a decrease in Ca, Fe, Pb and Ba, which could result from mineral precipitation as supported by sedimentation at the bottom of the vials. This decrease in content shows no relationship with the type of gas they were exposed to. Similarly, K, Mg, and  $SO4_2^-$  concentrations increase, but no clear correlation with H<sub>2</sub> or N<sub>2</sub> exposure can be made. Si increased after incubation for all samples, more significantly for N<sub>2</sub> exposed samples.

The most noticeable difference is the pH. It has a value of 5 in the original brine and decreases to 4-4.5 in the  $H_2$  exposed samples but increases to 6.2-6.4 in the  $N_2$  exposed samples. This is different compared to the observation of similar samples incubated at ETCA, see next section.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:28 of 66



Table 3-1: Chemical composition of the original formation water from NAM compared with the composition after the exposure tests executed at TNO.

Name Payzone		Y-1 Original	Z-1-1 H2 Rotliegendes I	Z-1-3 N2 Rotliegendes	Z-2-1 H2 Rotliegendes	Z-2-3 N2 Rotliegendes
ID Analyzed by			2191849 FTCA	ETCV ETCV	2191850 FTCA	2191852 FTCA
Na	mø/kø	63979	63137	62464	56949	62475
к	mg/kg	1546	1793	1669	1805	1657
Ca	mg/kg	21422	19900	19649	17561	19463
Mg	mg/kg	2171.0	2326	2153	2319	2313
Sr	mg/kg	820.0	790	800	790	810
Ba	mg/kg	18	10.6	13	5.8	7.3
Mn	mg/kg	32	30	30	37	32
Fe	mg/kg	260	152	99	56	168
Cu	mg/kg	<0.2	<0.2	0.5	<0.2	0.9
Zn	mg/kg	139	145	145	146	147
Si	mg/kg	<20	17	40	<0.5	17
Li	mg/kg	40	46	47	47	49
Pb	mg/kg	57	43	44	32	46
В	mg/kg	31	27	29	27	30
Cl	mg/kg	155668	151548	151902	152627	152012
Br	mg/kg	366	395	382	406	392
SO4=	mg/kg	153	200	196	244	225
Density @ 20	1	4400				
°C	kg/m3	1192	4.07	6.2		6.20
pH	<b>C</b> (	5	4.07	6.2	4.54	6.39
Conductivity	mS/cm	211				
IDS	mg/kg	239000				

### 3.1.2 Chemical reactions, autoclave setup used at ETCA

All plugs were exposed to the same brine- $H_2$  mix or the same brine- $N_2$  mix, and therefore we can only evaluated the bulk brine before (same as above, see Table 3-1) and after the exposure experiment. See Table 3-2 for the compositional analyses of the brines from the two autoclaves at ETCA.



Doc.nr: HyUSPre-D5.3 Version: Final 2023.11.29 Classification: Public Page: 29 of 66



Table 3-2: Chemical composition of the original formation water from NAM compared with the composition after the exposure tests executed at ETCA.

Name		Y-1 Original	STCA Brine + H2	STCA Brine + N2		
Payzone			Rotliegendes	Rotliegendes		
ID			2191842	2191844		
Analyzed by			ETCA	ETCA		
Na	mg/kg	63979	61480	58505		
К	mg/kg	1546	1611	1620		
Са	mg/kg	21422	18929	18345		
Mg	mg/kg	2171	2254	2236		
Sr	mg/kg	820	800	780		
Ва	mg/kg	18	13	13		
Mn	mg/kg	32	36	34		
Fe	mg/kg	260	81	68		
Cu	mg/kg	<0.2	<0.2	<0.2		
Zn	mg/kg	139	155	150		
Si	mg/kg	<20	<0.5	<0.5		
Li	mg/kg	40	47	46		
Pb	mg/kg	57	47	46		
В	mg/kg	31	30	29		
CI	mg/kg	155668	149512	151072		
Br	mg/kg	366	393	371		
SO4 <sup>2-</sup>	mg/kg	153	198	201		
HCO3 <sup>-</sup>	mg/kg	273	49	150		
total alkalinity		280	275	410		
Density @ 20 °C	kg/m3	1192	1188	1192		
pH (as received)		5	4.4	4.6		
Conductivity	mS/cm	211	220	219		
TDS	mg/kg	239000	240250	239500		

No significant and consistent difference is observed between the composition after the  $H_2$  exposure compared to  $N_2$  exposure for any of the elements, except possibly for Fe, which is lower compared to the original brine for both.Total alkalinity is somewhat elevated for the  $N_2$  exposed brine compared to  $H_2$  exposed sample, while the  $H_2$  exposed sample does not show an elevation compared to the original brine. Total alkalinity is difficult to measure and the associated error margin is 20-30%.

The brine samples show a reduction in pH after incubation with both  $N_2$  and  $H_2$  from 5 to 4.4 and 4.6, which is different from the samples incubated at TNO.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:30 of 66



### 3.1.3 Mechanical properties measured at TNO

The results of the densities, porosities, dynamic elastic moduli calculated from acoustic velocities, the static Young's Modulus and the differential stress at failure ( $\sigma_d$  max) are shown in Table 2.4.

Direct comparison of the acoustic velocities and elastic moduli between unexposed, H<sub>2</sub>exposed and N<sub>2</sub>-exposed NAM samples is difficult due to microstructural differences. This is particularly noticeable for the sandstones, where the porosity can vary considerably between plugs of the same core depth. For Z-2,  $\Phi_{lab}$  and  $\Phi_{XRD}$  range from 0.049 to 0.087 and 0.143 to 0.170, respectively. For Z-3 porosity ranges are from 0.065 to 0.151 and 0.203 to 0.277, respectively. The XRD porosity in the caprock Z-1 is constant at around 0.105. The SNAM samples showed limited variations.

Acoustic velocities display values consistent with what is expected at these porosities (if compared to relations of Han et al., 1986; Castagna et al., 1993). They also strongly depend on the sample porosity, as illustrated in Figure 3.1, where  $V_p$  and  $V_s$  of both NAM and SNAM samples measured at initial and reservoir conditions are plotted against  $\Phi_{lab}$  and  $\Phi_{XRD}$ . For both conditions, a negative linear correlation is defined. This correlation is stronger (larger R<sup>2</sup>) when the acoustic velocities are compared with  $\Phi_{XRD}$  than with  $\Phi_{lab}$ . It is also important to note that the correlations of acoustic velocities vs.  $\Phi_{XRD}$  are better at initial conditions (Fig. 3.1a and b) than at reservoir conditions (Fig. 3.1b and c). Several factors can explain this difference: the pressure, stress and temperature at reservoir conditions have influenced the consolidation state between the NAM and SNAM samples; the velocities are compared with the initial porosity and do not account for the porosity evolution with the variations of the thermomechanical conditions; and finally, the unexposed SNAM sandstone with the highest porosity could not be measured at reservoir conditions.

These correlations can be used to compare the acoustic velocities at different porosities. Subsequently, after applying relations [4] and [5], dynamic Young's modulus and Poisson's ratio can also be compared at different porosities. An arbitrary porosity of 0.2 was chosen to apply this normalization, meaning that all the sandstone  $V_p$  and  $V_s$  values are recalculated to a porosity of 0.2 using the linear relationship defined in Figure 3.1 for velocities vs.  $\Phi_{XRD}$  as it shows a stronger correlation. This normalization of acoustic velocities to a porosity of 0.2 is necessary to remove the effects of porosity variatons between samples and allow a direct comparison of unexposed, H<sub>2</sub>-exposed and N<sub>2</sub>-exposed samples. The normalized acoustic velocities are given in Table 3.3.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:31 of 66





Figure 3-1: Acoustic velocities as a function of  $\Phi_{lab}$  (blue) and  $\Phi_{XRD}$  (orange). The equations on each diagram were the one used to calculate the corrected AV and dynamic elastic moduli in Table 3.3.

Figure 3.2 illustrates the variation of the dynamic elastic moduli for NAM unexposed, H<sub>2</sub>exposed and N<sub>2</sub>-exposed sandstones normalized to 20% porosity and caprocks (no normalization) at initial and reservoir conditions. Normalized Young's dynamic modulus for the sandstones at initial conditions is around 30 GPa. Slight variations are observed depending on the gas the samples were exposed to; it is higher for N2-exposed samples and lower for H2exposed samples, although these variations are under 10%. At reservoir conditions, the opposite trend is observed with lower normalized Young's modulus for unexposed and N<sub>2</sub>exposed samples compared to H<sub>2</sub>-exposed samples. The difference is more significant than at initial conditions and can reach 14% for sample Z-2. The normalized Poisson's ratio at initial conditions varies between 0.22 and 0.24 with lower but near identical values for exposed samples. At reservoir conditions, normalized Poisson's ratio is higher, 0.28-0.31, and shows the opposite behavior compared to initial conditions, with higher values for exposed samples than for unexposed samples. Overall, the range of variations observed for both initial and reservoir conditions is, at most, ~10%. The opposite behavior between the initial and reservoir conditions could result from structural modifications occurring during the loading and thermal stages of the exposure tests. Newly formed microcracks could impact the mechanical properties of the exposed samples, and their closure at high pressure would bring them closer to the unexposed samples at high stresses.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:32 of 66



Table 3-3: Acoustic velocities and dynamic elastic moduli for sandstones normalized to 20% porosity.

	Samples	Gas	Vp <sup>i</sup> (m/s)	Vs <sup>i</sup> (m/s)	Vp <sup>R</sup> (m/s)	Vs <sup>R</sup> (m/s)	E <sup>i</sup> <sub>dyn</sub> (GPa)	E <sup>R</sup> <sub>dyn</sub> (GPa)	v <sup>i</sup> <sub>dyn</sub>	V <sup>R</sup> <sub>dyn</sub>	ERstat (GPa)
	Z-2-2a	-	3787.92	2220.91	4034.39	2241.85	30.02	31.54	0.24	0.28	-
	Z-2-1	H2	3707.22	2180.02	4429.07	2384.36	28.40	35.64	0.24	0.30	15.13
NAM	Z-2-3	N2	3882.68	2299.97	4025.72	2163.64	31.60	29.51	0.23	0.30	16.26
	Z-3-2	-	-	-	-	-	-	-	-	-	-
	Z-3-1	H2	3924.52	2342.11	4339.95	2261.68	31.18	31.22	0.22	0.31	16.37
	Z-3-3	N2	3896.05	2333.45	3852.20	2119.62	31.71	27.51	0.22	0.28	12.02
5	SS_T1	-	3706.17	2143.52	-	-	24.43	-	0.25	-	-
A	SS_B1	H2	3898.62	2342.84	3580.29	2193.79	28.93	24.99	0.22	0.20	-
S	SS_M1	N2	3800.88	2250.44	3536.86	2179.68	27.07	24.64	0.23	0.19	-



Figure 3-2: Comparison of the dynamic elastic moduli for NAM's samples at initial (blue) and reservoir conditions (orange) according to their exposure.

Due to experimental failure at reservoir conditions for the caprock Z-3 exposed to  $H_2$  (cf. section 2.5), only the results at initial conditions can be compared. Normalization (porosity corrections) were not applied to the caprock Young's modulus and Poisson's ratio. The same pattern is observed for Young's modulus and Poisson's ratio; it is characterized by lower values for the unexposed samples and higher but nearly equal values for N<sub>2</sub>- and H<sub>2</sub>-exposed samples. That observation suggest that structural or mineralogical effects occur due to the gas exposure but effects due to reactions between H<sub>2</sub> and caprock are not apparent.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:33 of 66



Static Young's modulus was measured at reservoir conditions for a number of samples. The dependence between porosity and Young's modulus is also observed in these data (Table 2.4, Fig. 3.3). A linear negative correlation is observed and consistent with both the theory (Wang, 1984) and experiments (e.g., Heap et al., 2019; Hol et al., 2018). The only exception is Young's modulus measured for sample Z-2-2a, which shows a relatively low value (10.33 GPa). This sample has been removed from the regression to establish the relationship with porosity as it is one of the samples that suffered from the load cell reading issue at high temperature (cf. Appendix A). Although goodness of fit is less than for  $\Phi_{lab}$ , the relationship with  $\Phi_{XRD}$  was chosen to maintain consistency with the analysis of dynamic modulus. The recalculated (normalized) Young's Modulus shows similar values of 15-16 GPa for Z-2 and Z-3-1 but a lower value for Z-3-3 (Table 3.3). For Z-3, it is higher for the H<sub>2</sub>-exposed (16 GPa) than for the N<sub>2</sub>-exposed sample (12 GPa). The main difference between Z-2 and Z-3 is the porosity: higher in Z-2 (0.16-0.17) than in Z-3 (0.20-0.23). The static Young's modulus for the unexposed samples of the two sandstones could not be properly measured for comparison.



Figure 3-3: Static Young's modulus as a function of  $\Phi_{lab}$  (blue) and  $\Phi_{XRD}$  (orange).

### 3.1.4 Cyclic loading tests

Cycling loading tests have been successful for two samples of the same sandstone samples: Z-2-1 ( $H_2$ -exposed) and Z-2-3 ( $N_2$ -exposed). At reservoir conditions and after each cycle, two triaxial tests were performed, and acoustic velocities measured before and after were followed up by a permeability test.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:34 of 66





Figure 3-4: Inelastic axial strain, acoustic velocities and dynamic elastic moduli as a function of the cycle. The "before" and "after" notation stand for AV measurements done before and after the two triaxial tests.

Inelastic axial strain is maximum after the first cycle and then slowly decreases (Fig. 3.4). It is higher for the  $H_2$ - than for the  $N_2$ -exposed sample before each cycle. Consequently, the cumulated inelastic strain increases with the number of cycles but seems to stabilize after ten cycles for the  $N_2$ -exposed sample, whereas it is still increasing for the  $H_2$ -exposed sample.

Figure 3.5 presents the results for the static Young's Modulus measured during the triaxial tests during unloading and loading. For each cycle, two values are given, corresponding to the two triaxial tests done at each cycle. The first triaxial test constantly yields the lower values, showing that at each first triaxial text, even under such low differential stresses, the sample is reconditioned and permanently deformed with grain readjustment, microcrack closure and overall porosity reduction. The values recorded during unloading are also lower than those in loading, which contradicts traditional triaxial tests where the unloading path shows a steeper stress-strain slope due to hardening occurring during loading. A possible explanation is that during the initial axial stress increase (Fig. 2.6a), to reach and simulate the reservoir vertical stress, the sample was preconditioned to the reservoir stress state, inducing plastic deformation such as grain re-arrangement or microcracking. It is supported by the relatively low Young's Modulus recorded through this stage: 9.38 and 13.68 GPa for Z-2-1 and Z-2-3, respectively. Then, during the triaxial tests and the unloading (decreasing axial stress), the mean effective stress is decreasing (vice-versa during loading). The Young's Modulus is dependent on the mean effective stress (e.g., Pijnenburg et al., 2019), so it decreases and increases during the unloading and the loading, respectively.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:35 of 66





Figure 3-5: Static Young's modulus as a function of the cycle for the loading and unloading paths. The line represent the average between the first and the second triaxial tests.

Z-2-3 and Z-2-1 display static Young's modulus values ranging from 20.5 to 22 GPa and 16 to 18 GPa, respectively (loading, Fig. 3.5). This difference is explained by Z-2-3 having a lower porosity than Z-2-1 (cf. section 3.1.2). More interesting is the evolution of the Young's Modulus with the cycles. The N<sub>2</sub>-exposed sample shows an increase of the Young's Modulus due to progressive compaction and porosity reduction (e.g., Corina et al., 2023; Schimmel et al., 2021; Soustelle et al., 2023). Conversely, the H<sub>2</sub>-exposed sample displays the opposite trend and shows weakening. The same behavior is observed for V<sub>p</sub>, V<sub>s</sub>, the dynamic Young's Modulus, and, to a lesser extent, the dynamic Poisson's ratio (Fig. 3.4). The overal magnitude of the variations observed after cyclic loading for the static Young's Modulus is less than 5% and less than 1% for the dynamic Young's modulus.

The flow tests give brine permeabilities at reservoir conditions of 0.016 mD ( $N_2$ -exposed) and 0.078 mD ( $H_2$ -exposed) (Fig. 3.6), reflecting the porosity variations between these samples. These permeabilities are relatively low for geological reservoirs. However, permeability measurements from a wide range of Permian Rotliegend quarry sandstones show that for He porosities between 10 to 25%, the permeability ranges between 0.01 and 1000 mD (Monsees et al., 2020). These were gas permeability corrected from the Klinkerberg effect (Klinkenberg,



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:36 of 66



1941), assuming a confining pressure of 1.2 MPa. The study of Tanikawa and Shimamoto (2009) has demonstrated several points that could explain our low permeabilities:

- 1. The permeability decreases with the effective pressure by almost a factor 4 between 0.1 and 40 MPa.
- 2. The Klinkenberg factor is negatively correlated with water permeability, which could lead to an overestimation.
- 3. The gas-water permeability ratio depends on the rock permeability and the pressure gradient.

At the measured permeabilities and for a pressure gradient of 0.2 to 0.5 MPa, the gas permeability corrected from the Klinkenberg effect is 5 to 10 times higher than the water permeability. All these factors have to be taken into consideration when comparing our data with those from the literature. In addition, another factor that could influence our permeability measurement is that porous discs at the contact between the pistons and the sample were not used to prevent the attenuation of the acoustic waves. As these two samples were tested at exactly the same conditions, using the same equipment, this report will focus more on the trend and evolution of the permeability with respect to exposure and cyclic loading rather than on the absolute values.

After the first cycle, a sharp decrease in permeability is observed, consistent with the strong inelastic axial strain (Fig. 3.5) occurring at this stage. As expected from inelastic strain measurements, the permeability decreases slowly for the N<sub>2</sub>-exposed sample. Permeability slowly increases after initial reduction for the H<sub>2</sub>-exposed sample. This behavior is inconsistent with the strong cumulated inelastic strain observed for this sample during subsequent cycles.



Figure 3-6: Evolution of the formation water permeability with the cycles.

### 3.2 SNAM samples

The dynamic elastic moduli were calculated at initial and reservoir conditions for three caprock samples and three sandstones samples. For both reservoir sandstone and caprock, one



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:37 of 66



unexposed, one  $N_2$ -exposed and one  $H_2$ -exposed sample was tested. The results are described in Table 2.4. The values for the sandstones normalized to a porosity of 20% are indicated in Table 3.3.

At initial conditions, the dynamic Young's modulus of the caprocks ranges between 12 to 20 GPa. Dynamic Young's modulus is 17 GPa for the unexposed sample, and 12 GPa and 19 GPa for  $N_2$  and  $H_2$ -exposed samples, respectively (Fig. 3.7). At reservoir conditions, the dynamic Young's modulus is about 15 GPa, and does not vary significantly with  $N_2$  or  $H_2$  exposure. A similar pattern is observed for the Poisson's ratio. Dynamic Poisson's ratio is 0.3 for the unexposed sample, and 0.35 and 0.27 for the  $N_2$  and  $H_2$  exposed samples, respectively. As for the Young's modulus, the Poisson's ratio at reservoir conditions is nearly identical across the samples. These results show that the  $N_2$  or  $H_2$  exposure has no or limited effect on the caprock samples at reservoir conditions. The results for the sandstones show a similar behavior as for the caprock in the sense that both the normalized dynamic Young's Modulus and Poisson's ratio vary as a function of the exposure at initial conditions but are near identical at reservoir conditions (Fig. 3.7).

For both caprock and sandstone, the different trends observed at initial and reservoir conditions could have different causes. It can be an actual effect of sample variation and exposure effects, but it can also be caused by effects of sample preparation, pre- and post-exposure tests or preconditioning during the exposure tests (pressure and temperature changes).



Figure 3-7: Comparison of the dynamic elastic moduli for SNAM's samples at initial (blue) and reservoir conditions (orange) according to their exposure.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:38 of 66



# 4 Discussion

### 4.1 Effect of H<sub>2</sub>Exposure on Flow and Mechanical Properties

### 4.1.1 Deep hot reservoirs (NAM Samples)

The impact of hydrogen (H<sub>2</sub>) exposure on the mechanical and flow properties of deep hot reservoir rocks (as represented by NAM samples) displayed notable findings. One key observation was the difference in brine properties, particularly pH, of H<sub>2</sub> exposed samples compared to the N<sub>2</sub> exposed samples for the rock and brine tested at TNO. This difference was not observed for the samples tested at ETCA.

The samples tested at ETCA showed a drop from pH 5 to 4.4-4.6 for both H<sub>2</sub> and N<sub>2</sub> exposed samples, while the samples at TNO showed a drop from pH 5 to 4-4.6 for the H<sub>2</sub>-exposed samples and an increase from pH 5 to 6.2-6.4 for the N2-exposed samples. A decrease in pH would induce the dissolution of carbonates, resulting in an increase of Ca, Mg, Ba, SO4<sub>2</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup> in the brine. An increase in Ca and Ba is not observed in the brines (rather a decrease). An increase in Mg and SO<sub>4</sub><sup>2-</sup> is observed, but also for one of the N<sub>2</sub>-exposed samples where the pH increased. In addition, variations in the mineralogy of original (unexposed) samples may also play a role. In the samples tested at ETCA, no significant and consistent change in the brine properties between H<sub>2</sub> versus N<sub>2</sub> exposed samples were observed. Accordingly, the exact chemical reactions underpinning changes in ion concentrations and pH are not clear.

Previously other researchers have suggested that a pH drop could be the direct effect of  $H_2$  on the brine, see several numerical and laboratory experiments described in the literature (Bo et al., 2021; Flesch et al., 2018; Henkel et al., 2014). In principle, the dissolution of  $H_2$  itself should not lead to a reduction of the pH as it does not protonate into solution under reservoir conditions. This reaction is kinetically inhibited due to the strong H-H bond (Truche et al. 2013). In fact, many of the geochemical reactions described in geochemical databases are kinetically limited. In geochemical simulations,  $H_2$  should therefore be treated as an uncoupled species (Tremosa et al. 2023). The reactions with known kinetic rates can be defined separately for example for microbial reactions. Bo et al. 2021 did not uncouple  $H_2$  in the geochemical database, and the numerical results should therefore be considered with caution.

A decrease in pH would induce the dissolution of carbonates, resulting in an increase of Ca, Mg, Ba,  $SO_4^{2-}$  and  $HCO_3^{-}$  in the brine. Flesh et al., 2018 and Henkel et al., 2014 observed carbonate and anhydrite dissolution and attributed that to the pH reduction caused by H<sub>2</sub> exposure. However, oxidized sulfur cannot be reduced by H<sub>2</sub> without the interaction with microbes at reservoir conditions (Truche et al. 2009; Tremosa et al. 2023). In the study of Flesch et al., 2018 it is not fully clear whether the described anhydrite dissolution is H<sub>2</sub>-driven, or possibly driven by undersaturation of the synthetic brine with sulfate, which is not defined in the paper. The same applies to the CO<sub>2</sub> and H<sub>2</sub> induced carbonate and anhydrite dissolution observed in the study by Henkel et al .2014; the synthetic brine composition is not described.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:39 of 66



The question remains what the cause is of the pH change and observed differences. It is possible that microbial activity affected the brine leading to acifidification, during incubation or after the tests at lower temperature. Sulfate levels do not show a decrease, which does not indicate sulfate reduction. However, acidofiles could have been active, despite the rather high salinity. Still, no consistent drop in bicarbonate levels is observed and this therefore cannot be confirmed. It can also not be excluded that the brine had acidified prior to the tests, as there was a time lag of about 6-12 months between analyses and start of the test.

Possibly some level of  $CO_2$  was present in the injection gas leading to acidification, however the H<sub>2</sub> and N<sub>2</sub> bottles denote a 99.999 % purity. Other processes that could have led to acidification are oxidation reactions, as the formation water was not fully O<sub>2</sub> free when added to the sample. Oxidation of sulfides like pyrite would lead to sulfuric acid formation and a pH reduction. The increase in sulfate would be consistent with this, however the level of increase is relatively high and the amount of pyrite in the reservoir is actually below detection limit. The increase in sulfate is more likely caused by dissolution of some anhydrite due to slight undersaturation of the formation water. The reduction of hematite to magnetite could also lead to some acid formation. Precipitation of hematite would however increase the pH, for example for the N<sub>2</sub> exposed samples at TNO. Alternatively, the elevated Si levels in especially the N<sub>2</sub> – exposed samples and to a lower extent the H<sub>2</sub> exposed samples at TNO (Table 3.1) could indicate silicate dissolution of the glass-liner. No glass liner was used at ETCA. Glass dissolution would lead to an increase of the pH. Since the highest increase in Si is observed in the most alkaline samples, this would be in line with observed pH values.

The cause of the acidification and pH differences cannot be fully clarified, and since the brine properties of the various tests are not consistent, it cannot be concluded that the  $H_2$  exposure leads to a drop in pH of the brine. It can however also not be excluded that the difference in pH affected the geomechanical rock properties.

Mechanical properties, including static and dynamic Young's Modulus, were assessed in NAM samples in the TNO labs at both initial and reservoir conditions. It was challenging to directly compare these properties due to the natural heterogeneity within the same samples most clearly shown in the porosity measurements. However, for H<sub>2</sub>-exposed samples, Young's Modulus (normalized to 20% porosity) decreased compared to unexposed or N<sub>2</sub>-exposed samples tested at initial conditions while it increased when tested at reservoir conditions. The change in behaviour with triaxial testing conditions is potentially resulting from microstructural modifications during exposure tests (Table 3.3, Fig. 2.4). Poisson's ratio (normalized to 20% porosity) of both N<sub>2</sub>- and H<sub>2</sub>-exposed samples show a small decrease compared to unexposed samples when tested at initial conditions and an increase when tested at reservoir conditions.

Furthermore, cyclic loading tests under H<sub>2</sub> exposure unveiled that static and dynamic Young's modulus are increasing for a N<sub>2</sub>-exposed sandstone sample and decreasing for a H<sub>2</sub>-exposed sample (Fig. 3.5). An increase in Young's Modulus can be expected due to progressive compaction and porosity reduction as observed in N<sub>2</sub>-exposed samples. The decrease in the dynamic Young's Modulus and Poisson's ratio suggest that cyclic loading on H<sub>2</sub>-exposed



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:40 of 66



sandstones had an impact on the mechanical integrity of the NAM samples that were exposed to  $H_2$  and mechanically tested at TNO. Although the magnitude of changes are low (~ 1% after 10 cycles), if continuing for a larger number of pressure cycles, decreasing stiffness during  $H_2$  injection/extraction affect stress distribution in the near-wellbore area and may have implications for the long term mechanical integrity of the reservoir.

Overall, the effects of cyclic loading and  $H_2$  exposure on mechanical properties of NAM samples are modest under investigated conditions. Larger effects would likely be needed to result in critical effects on reservoir integrity or fault stability. Experiments over a larger range of conditions and number of cycles on samples covering more of the observed variation in (for example) porosity are needed to assess if effects can become critical for reservoir and seal integrity.

### 4.1.2 Intermediate depth reservoirs (SNAM Samples)

The mechanical properties of the SNAM samples demonstrated complex behaviors. At initial conditions, the dynamic Young's Modulus and Poisson's ratio exhibited variations attributed to exposure. However, at reservoir conditions, these properties converged for both exposed and unexposed samples and variations are negligible (Fig. 3.7). The similarity in properties at reservoir conditions could result from factors such as exposure type, structural differences introduced during sample preparation, or preconditioning during exposure tests. This implies that the impact of  $H_2$  exposure on the mechanical integrity of intermediate reservoir rocks is limited and is likely related to the lower temperature of exposure limiting further the kinetics of  $H_2$ -brine-rock reactions.

As for the deep reservoirs, similar conclusions can be drawn. For the conditions of our experiments and after two months of  $H_2$  exposure, effects on dynamic elastic properties of the reservoirs and caprocks are negligible. Again, these observations need to be confirmed in experiments over a longer time of exposure, larger range of conditions and number of cycles.

### 4.2 Effect of H<sub>2</sub> Cyclic Loading on Flow and Mechanical Properties

The results of cyclic loading tests under  $H_2$  exposure revealed significant insights into the effect of repeated depletion-injection cycles on the mechanical and flow properties of the samples.

Cumulative inelastic axial strain, representing permanent deformation, was more pronounced in the H<sub>2</sub>-exposed samples after the first cycle, which continued to increase with additional cycles. The cumulated inelastic strain increases much slower for the N<sub>2</sub>-exposed samples than for the H<sub>2</sub>-exposed samples (Fig. 3.4). However, as the samples have different initial porosities that could explain this trend, the effect of H<sub>2</sub>-exposure cannot be assessed by this parameter only.

The impact of cyclic loading was also evident in the changes in the static and dynamic Young's Modulus, which decreased during subsequent cycles for H<sub>2</sub>-exposed samples (i.e. samples become less stiff) and increased for N<sub>2</sub>-exposed samples (i.e. samples become stiffer). These



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:41 of 66



trends suggest different effects on elastic moduli of the reservoir in N<sub>2</sub>- and H<sub>2</sub>-exposed samples (Fig. 3.5). The changes observed after 10 cycles where limited :~1% and < 10% for dynamic and static elastic moduli, respectively. This suggests limited impact on the stress redistribution and mechanical integrity of the reservoirs for our experimental conditions and limited N<sub>2</sub> and H<sub>2</sub> exposure of two months. The cause of the limited measured geomechanical effect is possibly related to the difference in pH measured in the brine. However, this pH effect can in turn not be attributed to H<sub>2</sub> or N<sub>2</sub> as it was not confirmed in comparable tests. The effect could be related to the experimental procedures used (material, autoclave, glass liners etc).

The permeability tests further reflected the complex response of the samples to cyclic loading. After the first cycle, both H<sub>2</sub>-exposed and N<sub>2</sub>-exposed samples showed a sharp decrease in permeability, consistent with the significant inelastic strain occurring at this stage. However, in subsequent cycles, the permeability in H<sub>2</sub>-exposed samples increased again, diverging from the expected behavior that inelastic deformation leads to continuous sample compaction. It should be noted that only two tests were performed, and further experiments are needed to confirm this behaviour for a larger range of conditions and sample variation. However, the observation highlights the need for detailed assessments of the impact of cyclic loading on the flow properties of the reservoir rocks, especially under H<sub>2</sub> exposure and pressure variations (Fig. 3.6).

In general, it should be emphasized that reactions and mechanical tests are performed subsequently in this study, while at UHS sites stress changes and interaction of H<sub>2</sub> with the reservoir occurs simultaneously during cyclic injection/extraction of H<sub>2</sub>. Also, mechanical tests were done with brine rather than hydrogen as injected fluid. Whether similar effects will be observed for hydrogen injected into a brine-filled reservoir (with different levels of saturation) remains an open question. Microphysical processes such as stress corrosion cracking may be affected by fluid composition (in particular pH), and aid inelastic compaction or dilation of sandstone reservoirs (Schimmel et al., 2021).



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:42 of 66



# 5 Conclusions

This report presents the outcomes of an extensive investigation into the effect of hydrogen ( $H_2$ ) exposure and cyclic loading on the mechanical and flow properties of deep hot reservoir rocks (as represented by NAM samples) and intermediate depth reservoir rocks (as represented by SNAM samples).

In the deep hot reservoirs represented by NAM samples, no significant and consistent difference was observed between the brine composition after the  $H_2$  or  $N_2$  exposure for most of the brine properties, except for pH, K and Si for exposure at the TNO labs. These differences were not observed for related samples that underwent similar tests at Shell's ETCA labs. The difference in pH cannot be fully clarified, however, since the results of the various tests are not consistent, it cannot be concluded that the  $H_2$  exposure leads to a drop in pH of the brine. It can however not be excluded hat the change in pH affected the geomechanical rock properties.

The mechanical properties of the NAM samples exhibited complex behavior, with  $H_2$ -exposed samples showing that Young's Modulus (normalized to 20% porosity) decreased compared to unexposed or  $N_2$ -exposed samples tested at initial conditions while it increased when tested at reservoir conditions. However, these changes are below 10%, suggesting a limited impact on the mechanical integrity of deep hot reservoirs for the investigated experimental conditions, exposure of two months, and limited number of samples (i.e. sample variation and experimental repeatability may affect the results).

For the intermediate depth reservoirs represented by SNAM samples, the impact of  $H_2$  exposure was less pronounced, with similar trends in chemical reactions between  $H_2$ - and  $N_2$ -exposed samples. The mechanical properties at initial conditions exhibited some variation attributed to exposure but properties converged at reservoir conditions. This behaviour may be influenced by factors such as the type of exposure, structural differences introduced during sample preparation, or preconditioning during exposure tests. The findings imply that  $H_2$  exposure may have a limited impact on the mechanical integrity of intermediate reservoir rocks. It remains an open question whether significant changes in mechanical properties will occur for longer exposure to hydrogen.

The cyclic loading tests under  $H_2$  exposure provided valuable insights into the mechanical and flow properties of the samples. Inelastic axial strain increased in  $H_2$ -exposed samples with each cycle, suggesting that cyclic loading of  $H_2$  had a notable impact on the mechanical behavior. However, the changes observed after ten cycles, under 1%, are expected to have little to no impact on the mechanical integrity of the reservoirs. Again, given the experimental conditions, the two-month exposure period, and the effect of the experimental procedure used for the exposure of the samples.

The analysis of permeability revealed different behavior during both  $H_2$  and  $N_2$  exposure. After the first cycle of cyclic loading, both  $H_2$ -exposed and  $N_2$ -exposed samples displayed a sharp decrease in permeability, which was consistent with the substantial inelastic strain experienced



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:43 of 66



during this stage. However, in the subsequent cycles, the  $H_2$ -exposed samples exhibited an increase in permeability that is unexpected for the case that inelastic deformation lead to continuous sample compaction. This observation highlights the complex response of these samples to cyclic loading, particularly under  $H_2$  exposure. This finding emphasizes the importance of conducting more comprehensive assessments of the impact of cyclic loading on the flow properties of reservoir rocks, particularly in the presence of hydrogen.

Overall, the results indicate that the impact of  $H_2$  exposure and cyclic loading on the mechanical and flow properties of porous reservoir rocks is limited under the conditions and exposure duration tested in this study. Although the findings suggest limited effects of  $H_2$  exposure and cyclic loading on reservoir and caprock, they also emphasize the need for further research to understand the long-term effects of  $H_2$  exposure and cyclic loading in different geological settings and under extended exposure durations. Such research can include experimentally-validated model forecasts to extrapolate experimental results to longer timescales and spatial scales relevant for UHS sites. It can provide valuable additional insights into the feasibility of renewable hydrogen storage in porous reservoirs, in particular related to long term reservoir injectivity and productivity, and integrity of geological seals.



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:44 of 66



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Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:47 of 66



# **Appendix A: Mineral compositions**

Table Appendix A-1: XRD mineral composition of NAM's Well-Z samples including the studied samples Z-1, Z-2 and Z-3.

			Silicates		Carbonates			Oxi	Oxides Sulphate			Sul phi de	Halides	des Clay minerals and phyllosilica			ites	
Sample	Depth	Quartz	K-feldspar	Plagioclase	Calcite	Dolomite	Ankerite	Siderite	Hematite	Anatase	Anhydrite	Barite	Pyrite	Halite	I+I/S-ML	Muscovite	Chlorite(Tri)	Kaolinite
Z-1	3262.31 - 3262.38m	36.9	1.1	6.1	2.8	4.7	0.0	0.1	2.0	0.3	0.0	0.0	0.0	0.4	35.8	6.4	3.4	0.0
Z-2	3323.98 - 3324.10m	70.8	5.4	6.2	0.0	7.2	0.0	0.1	0.1	0.0	0.7	0.2	0.0	0.5	3.8	0.0	0.0	5.0
Z-3	3341.55 - 3341.63m	67.4	7.4	8.4	0.0	6.0	0.0	1.5	0.2	0.0	0.1	0.0	0.0	0.2	6.2	0.0	0.0	2.5
	3260.1	41.8	2.7	8.4	3.4	1.4	4.0	0.8	1.4	0.0	2.0	0.0	0.0	0.5	24.3	4.6	3.9	0.9
	3276.6	54.8	1.8	7.9	0.1	4.5	6.5	0.8	0.0	0.0	0.1	0.0	0.3	0.0	15.7	3.5	3.2	0.7
	3291.5	53.4	4.8	7.1	0.1	8.8	4.5	1.3	0.6	0.0	0.0	0.0	0.0	0.3	14.7	1.7	2.3	0.4
	3296.9	49.9	3.3	6.3	0.0	2.2	2.3	0.6	1.2	0.0	0.0	0.0	0.0	0.3	24.8	4.4	3.6	1.0
	3303.5	33.0	2.2	5.3	0.0	1.9	1.9	0.7	2.1	0.0	0.0	0.0	0.0	0.5	38.6	7.0	5.7	1.2
	3316.1	65.3	5.6	10.5	0.0	5.4	3.8	0.4	0.0	0.0	0.0	0.0	0.2	0.1	4.5	0.0	1.1	3.1
	3320.6	46.1	2.6	6.7	0.0	8.9	0.0	1.1	1.3	0.0	0.0	0.0	0.0	0.3	23.3	4.3	4.7	0.9
	3321.5	63.0	5.3	8.9	0.0	6.9	4.3	0.5	0.0	0.0	0.0	0.0	0.2	0.0	5.5	0.0	0.9	4.6
	3322.4	69.2	6.1	8.6	0.0	1.2	1.4	0.6	0.0	0.0	0.3	0.9	0.1	0.1	4.7	0.0	0.4	6.4
	3326.9	68.2	7.0	10.7	0.0	0.5	1.4	0.7	0.0	0.0	0.0	0.0	0.2	0.6	4.9	0.0	0.4	5.5
	3330.2	68.0	6.3	8.2	0.0	4.5	2.0	0.8	0.0	0.0	0.0	0.0	0.2	0.1	4.7	0.3	0.3	4.7
	3332.3	71.5	7.7	9.1	0.0	0.0	0.1	1.0	0.0	0.0	0.0	0.0	0.2	0.6	3.2	0.0	0.4	6.2
	3335.9	67.0	7.4	8.1	0.0	3.8	4.1	1.0	0.0	0.0	0.0	0.0	0.1	0.2	3.1	0.0	0.4	4.9
	3338.9	72.1	8.4	9.0	0.0	0.0	0.3	0.6	0.0	0.0	0.0	0.0	0.2	0.5	3.5	0.0	0.5	5.0
	3341.5	64.5	6.6	8.8	0.1	5.0	3.1	0.9	0.0	0.0	0.0	0.0	0.2	0.1	5.8	0.0	0.6	4.3
	3343.6	70.2	8.4	10.6	0.0	0.0	0.3	0.6	0.0	0.0	0.0	0.0	0.2	0.4	4.7	0.0	0.3	4.5
	3348.7	68.5	7.3	7.9	0.0	0.0	1.7	2.6	0.0	0.0	0.0	0.1	0.3	0.5	5.8	0.0	0.5	4.8
	3351.4	71.0	7.4	9.4	0.0	0.0	0.9	1.2	0.0	0.0	0.0	0.0	0.2	0.7	5.1	0.0	0.4	3.6
	3356.85	66.8	6.2	10.1	0.0	1.3	1.0	2.2	0.1	0.0	0.0	0.0	0.1	1.0	7.1	0.0	0.5	3.5
	3361.3	74.4	7.4	7.6	0.0	0.0	0.2	0.5	0.0	0.0	0.0	0.0	0.1	0.9	4.8	0.0	0.4	3.8
	3364.9	64.7	5.9	8.7	0.0	5.6	2.0	0.8	0.0	0.0	0.0	0.0	0.2	0.5	7.5	0.2	1.0	3.0
	3369.6	69.0	5.7	9.1	0.0	1.4	1.4	1.2	0.0	0.0	0.0	0.0	0.2	0.5	7.4	0.0	1.1	3.0
	3374.1	75.9	6.7	5.1	0.0	0.0	0.1	1.0	0.0	0.0	1.8	0.0	0.2	0.5	4.8	0.0	0.9	3.2
S	3374.4	61.8	6.2	6.8	0.0	9.1	4.2	0.3	0.0	0.0	0.0	0.0	0.2	0.4	6.5	0.0	0.6	3.9
<u>–</u>	3384.3	70.7	6.3	8.6	0.1	0.0	0.9	0.7	0.0	0.0	0.0	0.0	0.2	0.9	8.2	0.0	2.1	1.3
d d	3388.5	72.7	6.2	7.8	0.0	0.0	0.2	0.8	0.0	0.0	0.0	0.0	0.2	1.1	7.6	0.0	1.2	2.2
6	3393	75.0	5.9	6.9	0.0	0.0	0.3	0.5	0.0	0.0	0.0	0.0	0.2	0.9	6.7	0.0	1.5	2.1
ŝ	3399.3	73.2	5.6	6.4	0.0	1.8	1.5	0.6	0.0	0.0	0.3	0.0	0.2	1.0	6.6	0.0	0.7	2.1
Ņ	3402.3	68.2	5.7	5.8	0.0	5.0	4.8	0.6	0.0	0.0	0.0	0.0	0.2	0.5	5.8	0.0	0.8	2.6
=	3408.9	71.9	4.2	7.1	0.0	1.2	1.6	0.6	0.0	0.0	0.6	0.0	0.2	0.7	8.8	0.0	2.4	0.6
ž	3409.2	70.9	3.9	7.0	0.0	0.5	1.6	0.6	0.0	0.0	3.5	0.0	0.2	0.5	8.7	0.0	1.7	0.8
-	3417.9	56.2	3.7	5.5	0.1	1.1	0.1	0.6	1.3	0.0	0.0	0.0	0.0	0.5	24.2	3.5	2.0	1.2
	3419.4	56.9	3.5	8.4	0.0	7.7	0.3	1.8	1.1	0.0	0.0	0.0	0.0	0.5	15.5	0.9	2.0	1.4
	3420.3	55.9	3.9	7.9	0.0	6.1	0.3	0.9	1.2	0.0	0.0	0.0	0.0	0.1	18.6	2.1	1.7	1.1
	3424.5	68.1	4.3	6.1	0.0	3.6	1.9	0.6	0.5	0.0	0.9	0.0	0.0	0.5	11.0	0.3	1.3	1.0
	3429	71.9	2.2	4.7	0.0	4.9	3.0	0.5	0.5	0.0	2.0	0.0	0.0	0.5	8.5	0.1	1.2	0.0
	3432	72.0	4.1	6.4	0.0	3.3	2.1	0.4	0.2	0.0	0.5	0.0	0.1	1.0	8.4	0.1	0.9	0.5
	3435.9	75.3	4.7	7.2	0.0	0.0	0.1	0.6	0.2	0.0	0.0	0.0	0.1	0.7	10.1	0.0	1.1	0.0
	3439.2	86.9	2.9	2.7	0.0	0.0	0.2	0.9	0.0	0.0	0.0	0.0	0.2	1.4	4.2	0.0	0.6	0.0
	3441.7	77.4	3.5	3.4	0.1	2.5	3.5	0.8	0.3	0.0	0.1	0.0	0.0	0.5	6.8	0.0	1.3	0.0
	3448.25	64.2	4.8	3.8	0.0	13.5	0.6	0.4	0.3	0.0	0.1	0.0	0.0	0.2	10.1	0.1	1.4	0.5
	3448.9	58.1	4.2	4.0	0.0	26.3	1.6	0.7	0.3	0.0	0.0	0.0	0.0	0.3	3.7	0.0	0.9	0.0
	3451	76.9	5.3	5.7	0.0	0.0	0.2	0.8	0.0	0.0	0.0	0.0	0.2	1.0	8.5	0.2	1.1	0.2
	3452.8	65.3	5.0	5.1	0.0	12.3	2.1	0.8	0.0	0.0	0.5	0.0	0.3	0.5	6.8	0.0	1.0	0.3
	3454.9	65.2	4.6	5.1	0.0	10.8	4.3	0.8	0.0	0.0	0.1	0.0	0.3	0.8	6.5	0.0	1.2	0.4
	3455.2	76.4	6.2	5.7	0.0	0.0	0.1	0.7	0.0	0.0	0.0	0.0	0.2	1.4	7.8	0.0	1.1	0.6
	3455.8	79.6	5.6	4.0	0.0	0.0	0.3	1.0	0.0	0.0	0.0	0.0	0.3	1.0	7.1	0.0	1.2	0.0
	3480.9	73.8	4.6	7.1	0.0	0.2	0.8	0.6	0.5	0.0	0.4	0.0	0.0	1.0	8.7	0.2	1.4	0.7
	3469	//.3	6.4	5.3	0.0	0.0	0.7	0.6	0.3	0.0	0.0	0.0	0.0	1.5	6.3	0.0	1.7	0.0
	34/1.4	/2.0	4.0	7.4	0.0	0.1	0.1	0.6	0.7	0.0	0.1	0.0	0.0	1.2	10.0	0.9	2.2	0.5
	3480.8	80.6	5.1	5.3	0.0	0.0	0.3	0.6	0.0	0.0	0.0	0.0	0.2	1.1	5.6	0.0	1.2	0.0
	3485.9	/8.3	4.8	6.1	0.0	0.1	0.3	0.7	0.3	0.0	0.0	0.0	0.0	1.1	7.0	0.0	1.3	0.0
	3489.5	/8.5	4.9	5.2	0.0	0.0	0.7	0.6	0.2	0.0	0.4	0.0	0.0	1.2	6.5	0.0	1.3	0.4
	3496.1	/8.0	4.8	5.1	0.0	1.0	1.2	0.6	0.4	0.0	0.2	0.0	0.0	1.6	5.4	0.0	1.8	0.0
	3502.15	67.1	4.3	4.9	0.0	7.4	2.1	0.6	0.5	0.0	1.0	0.0	0.0	0.7	8.8	0.0	1.9	0.6



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:48 of 66



Table Appendix A-2: XRD mineral composition of SNAM's samples. The composition of the studied caprock and sandstones were calculated by averaging the composition of analyzed samples that corresponds to the depths of the sections of core we received.

	Sample	TECTOSILICATES				CARBONATES	5	PHYLLOSILICATES (CLAY GROUP MINERALS)				ADDITIONA	L MINERALS	TOTAL				
	Depth (m)	Quartz	K-spar	Plag.	Calcite <sup>^</sup>	Dolomite <sup>‡</sup>	Siderite	Chlorite	Kaolinite	Illite/Mica	Mx I/S*	Pyrite	Barite	TECTOSILICATES	CARBONATES	PHYLLOSILICATES	ADDITIONAL	
Caprock	1419.92	12.3	2.8	4.8	21.3	18.8	0.8	4.3	3.7	16.2	13.9	1.1	0	19.9	40.9	38.1	1.1	
(This study)	1424.02	13.9	2.7	5.1	24	16.7	Tr	4.5	3.4	14.8	14.2	0.7	0	21.7	40.7	36.9	0.7	
	1502.12	17.2	Tr	2.2	25.1	47.3	0	1.3	0	6.9	Tr	Tr	0	19.4	72.4	8.2	Tr	
	1503.67	15.9	0.7	2.4	26.1	35.9	0	2.7	1	10.6	4.7	Tr	0	19	62	19	Tr	
	1507.01	11.9	0.6	2.3	29.3	28.7	1.1	2.6	1	16.3	6.2	Tr	0	14.8	59.1	26.1	Tr	
	1553.57	28.9	0.7	3.3	35.4	19.1	0	1.3	Tr	10.4	0.9	Tr	0	32.9	54.5	12.6	Tr	
	1554.4	10.6	0.8	2.9	33.8	17.7	0	5.8	2.2	17.4	8.8	Tr	0	14.3	51.5	34.2	Tr	
Sandstone	1560.12	32.6	1.4	5.4	26.8	19.3	0	1.8	Tr	12.2	0.5	Tr	0	39.4	46.1	14.5	Tr	
(This study)	1563.23	32.8	0.8	5.5	26.4	19	0	1.4	Tr	13.6	0.5	Tr	0	39.1	45.4	15.5	Tr	

\* Randomly interstratified mixed-layer illite/smectite; approximately 50-65% expandable layers.

<sup>^</sup> Calcite species based upon d(104); %Mg reported in Calcite column of Carbonates tab <sup>‡</sup> Dolomite species based upon d(104); %Fe reported in Dolomite column of Carbonates tab



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:49 of 66





# **Appendix B: Experimental data**

In this appendix, we show the time series records for all experiments.

#### Caption:

- Pc : Confining pressure
- q : differential stress = Axial stress Confining Pressure
- Pf : pore pressure
- T: Temperature
- A: Average Axial strain
- A1: Axial strain from Axial LVDT 1
- A2: Axial strain from Axial LVDT 2
- R: Average Radial strain
- R1: Radial strain from Radial LVDT 1
- R2: Radial strain from Radial LVDT 2
- B: Volumetric (Bulk) strain



Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:50 of 66





Z-1-1





Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:51 of 66





Z-1-2





Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:52 of 66





Z-1-3





Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:53 of 66





Z-2-1





Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:54 of 66





Z-2-2a





Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:55 of 66





Z-2-3





Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:56 of 66



Z-3-1





Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:57 of 66





Z-3-2





Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:58 of 66





Z-3-3





Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:59 of 66



CR-B1





Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:60 of 66





### CR-B2





Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:61 of 66





# CR-B3





Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:62 of 66



SS-B1





Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:63 of 66



\* \* \* \* \* Co-funded by the European Union

SS-M1





Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:64 of 66



SS-T1





Doc.nr: HyUSPre-D5.3 Version: Final 2023.11.29 Classification: Public Page: 65 of 66





# **Appendix C: Flow tests**



Z-2-1: Permeability vs. Time at each cycle





Doc.nr:HyUSPre-D5.3Version:Final 2023.11.29Classification:PublicPage:66 of 66





#### Z-2-3: Flows vs. Time at each cycle



#### Z-2-3: Permeability vs. Time at each cycle

