hystories
Hydrogen Storage in European Subsurface

SYNTHESIS OF THE BACTERIA REACTIONS AND DEFINITION OF MOST FAVOURABLE ENVIRONMENTS FOR H2 STORAGE

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Revision History

Revision	Revision date	Summary of changes
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1. Introduction

The objective of the WP3 of the Hystories project was to investigate the potential effects of hydrogen-stimulated development of microorganisms in various porous media reservoirs used as underground gas storages.

Hydrogen is an important electron donor for microbial respiration in subsurface environments with limited electron donors. It is noticed that subsurface storages would harbour a diversity of microorganisms, including hydrogen-consuming microorganisms. Many different groups of subsurface microorganisms can use hydrogen in their metabolisms such as sulphate-reducing prokaryotes, methanogens, acetogens, iron-reducing microorganisms (Gregory, Barnett, Field, & Milodowski, 2019). These microbial metabolic processes, eventually, have undesired effects for hydrogen storage e.g., decrease of H_2 concentration, CH_4 production, H_2S production, corrosion of metal infrastructure, formation of organic acids and biomass generation. As a result, it is necessary to understand microbial risks for assuring the success of the implementation of this storage technology.

Several laboratory tests were conducted to determine the risk of hydrogen consumption by bacteria and the risk to produce traces of other gases such as methane or hydrogen sulphide.

This last deliverable summarizes the different results that were obtained at laboratory scale to highlight the influence of external parameters as temperature, salinity or pH. Kinetics modelling that was developed up to reservoir scale also point out the necessity to upscale the results from laboratory to the on-field observations that could be expected.

Last, microbial risk assessment was carried out to define the most favourable environments for underground hydrogen storage.

2. Microbiological characterization of formation water samples from underground storages

To assess the potential risks associated to microbial activity in future underground hydrogen storages, the formation waters present in eleven storage sites in porous formations in Europe currently exploited for gas storage have been sampled. Downhole samplings were performed with a specific procedure in order limit as much as possible bacteria disturbance. Protocol that was followed during sampling is available in Appendix 1. Microorganisms present in water were then characterized. The following qualitative and quantitative analyses were performed on each formation water sample:

- Chemical analyses (pH, salinity, anions, organic acids)
- Microscopic examination
- Enrichment and enumeration of different groups of microorganisms with focus on hydrogenotrophic microorganisms
- Molecular biological analyses using specific primers for most relevant physiological microbial groups such as methanogenic archaea, sulphate-reducing prokaryotes.

Results of microbiological characterization are summarized in Table 1, where the detection and activity of hydrogenotrophic microorganisms are expressed as a microbial risk for hydrogen storage. Chemical and temperature conditions of the different sampled underground storages are also reported. For some of these conditions, only poor (green) or medium level (orange) of hydrogen-consuming groups of bacteria were detected. Microbial risk in these environments is not considered as high.

Table 1: Summary of the microbial activity of hydrogen consuming microorganisms identified in the different formation water sampled in underground gas storage sites. Microbial risk is assessed based on the concentrations of hydrogenotrophic bacteria that were detected

Sample number	Storage Site	Salinity (equiv. to % NaCl (w/v))	Temperature (°C)	pH	Microbial risks (hydrogen-consuming groups)
1	1	1.5	49	6.8	High (SRB, methanogens, acetogens)
2	2	4.8	60	7.4	±
3		1.7	60	5.8	High (SRB, acetogens)
4	3	0.1	66	6.2	High (SRB, acetogens)
5	4	1.4	91	10.2	Low, no MO detected
6	5	0.1	34	7.5	High (SRB, methanogens, acetogens)
7	6	3.6	41	6.5	±
8		3.7	41	6.5	
9		5.2	48	6.45	±
10		6	48	7.01	
11		3.6	48	6.8	
12	7	10	64	5.9	±
13		0.6	64	6	±
14	8	2.8	40	6.54	High (SRB, methanogens)
15	9	16.3	88.3	5.7	±

3. Investigation of Hydrogen consumption by underground storage formation water by laboratory tests

Reactivity tests were conducted in environments where microbial risk was evaluated as high (identified in red in Table 1).

Low pressure tests were carried out just above the atmospheric pressure (maximum 2 bar). For each site, one test was performed with carbonate ions addition as carbon source and another one with introduction of cores from the same site as carbon source.

High pressure tests were also conducted at the minimum pressure of the considered storage, that was considered as the worst case for bacteria development and with cores introduction. This last test can be considered as the most representative of the underground storage conditions.

The tables below summarize the results that were obtained from the different tests at low pressure (Table 2) and at high pressure (Table 3). For more details the deliverable D3.2 can be consulted.

Table 2: Summary of the results of hydrogen reactivity tests at low pressure

			low pressure tests carbonate source			low pressure tests cores		
Site	pH for experiment	Duration of the test (day)	Initial Sulphate (mg/l)	Maximum H2 Consumption rate (mole/m^3/day)	H2 loss	Initial Sulphate (mg/l)	Maximum H2 Consumption rate (mole/m^3/day)	H2 loss
1	8,2	44	27,02	4,7	47 %	178,3	2,5	35 %
3	5,4	52	92	0,26	15 %	94	0,25	15 %
4	6,5	58	0	4,5	29 %	64	2	29 %
6	7,2	40	40	3	50 %	100	1,7	35 %
8	7	47	499	5,15	76 %	294,5	4,95	70 %

Table 3: Summary of the results of hydrogen reactivity tests at high pressure

			high pressure			
Site	pH for experiment	Duration of the test (day)	Initial sulphate (mg/l)	Pressure for HP (bar)	Maximum H2 Consumption rate (mole/m^3/day)	H2 loss
1	8,2	45	180	30	26	3 %
3	5,4	52	128	70	4,4	9 %
4	6,5	58	93	100	6,5	10 %
6	7,2	41	157	45	0,6	7 %
8	7	47	700	35	7,6	48 %

From the above values, it is observed that a significant percentage of hydrogen was consumed during the low-pressure tests (between 15 and 76 %), or the high-pressure tests (between 3 and 48 %) in only few weeks (about 50 days).

Maximum hydrogen consumption rate is most of the time observed during the first days of the experiment, as the living conditions for the microorganisms changed adversely during the batch experiments (e.g. pH higher than 9, limitation of carbon source). The kinetics is then progressively slowed down until the stop of the reaction.

During these tests, methane was progressively released in the gas phase which confirms the methanogenesis reactivity of the environment. H_2S was not detected in the gas phase, but a decrease of sulphate concentration was noticed over time in some tests, which confirmed the potential of sulphate reduction too, to a lesser extent.

Based on the above data, reactivity at low pressure was compared between carbonate and core sources. Results are represented in Figure 1.

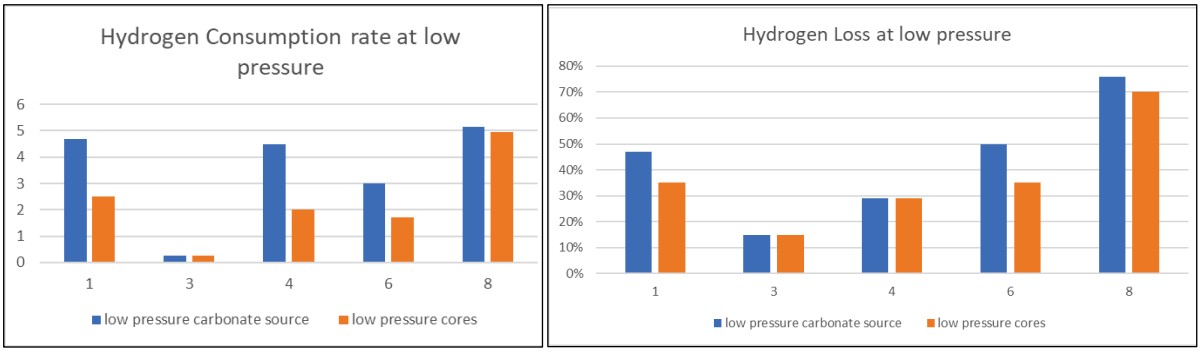

Figure 1: Maximum hydrogen consumption rate (left side) and Hydrogen loss (right side) at low pressure from tests with carbonate or cores as carbon source

It is noticed that for all the experiments maximum hydrogen consumption rate and percentage of hydrogen loss were higher for carbonate experiments than for cores. It can be concluded that all the tests performed in laboratory with carbonate ions as carbon source are conservative compared to the one carried out with cores samples, and thus conservative compared to the real underground conditions. As a matter of fact, during experiments with cores, reactivity is limited by the dissolution rate of the minerals. Furthermore, the fluid / rock ratio in reality is significantly lower than the one used in laboratory (fluid rock ratio of about 20 / 80 in porous media, whereas a ratio of about 90 / 10 was used for laboratory experiments). It was necessary to add more fluids to get enough samples for the analyses.

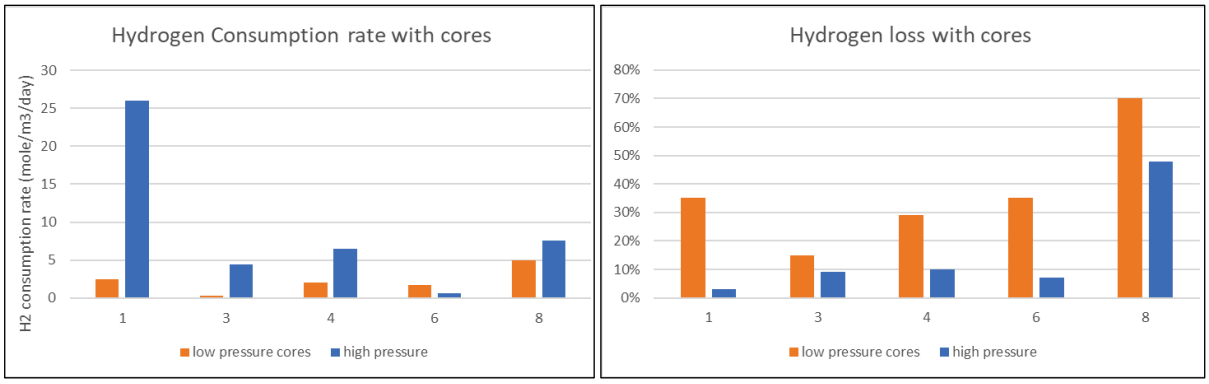

Figure 2: Maximum hydrogen consumption rate (left side) and Hydrogen loss (right side) with cores as carbon source at low and high pressures

With the same conditions in term of pH, temperature and water sample, it is noted that reactivity is not equivalent between low and high pressures. At high pressure, maximum hydrogen consumption rate is globally higher, which indicates that the reaction will be faster, especially at the beginning, just after the introduction of hydrogen. However, the percentage of hydrogen loss is lower at high pressure, as if parameters that stopped the reactions were achieved faster at high pressure. There is globally a factor of 2.5 between hydrogen loss at low pressure (average at 37 %) and hydrogen loss at high pressure (average at 15 %).

Looking in details into the results, it was wondered whether some specific parameters could be responsible for the microbial reactivity. As an example, hydrogen loss as a function of temperature is shown in Figure 3, where only tests at low pressure were taken into account.

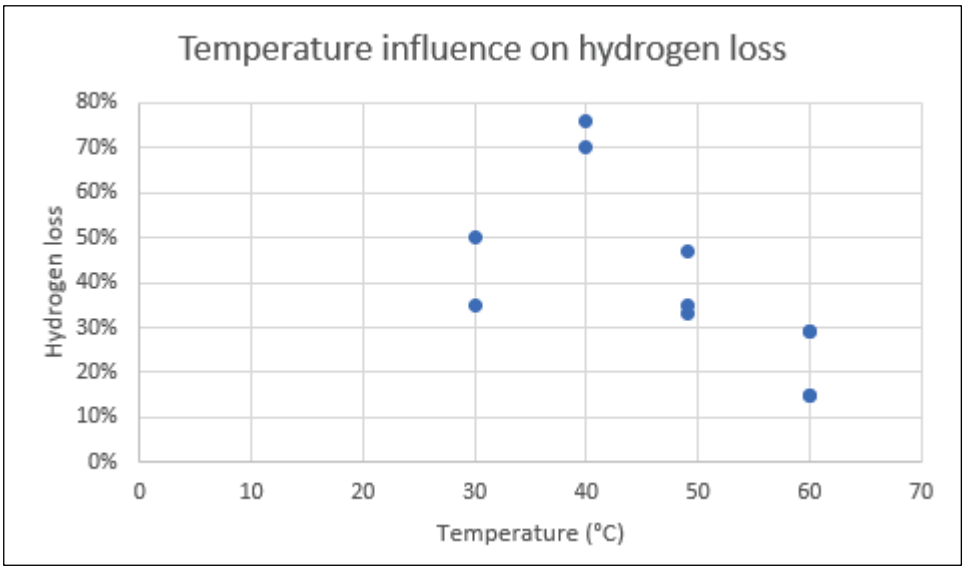

Figure 3: Correlation between hydrogen loss and temperature in the tests at low pressure

In Figure 3, it is observed that highest hydrogen loss (> 70 %) is observed with a temperature of 40 °C, which could be assimilated as the optimal temperature for microbial reactivity based on these experiments. At 30 and 50 °C, hydrogen loss was less significant (below 50 %) and with a temperature of 60 °C, hydrogen was the lowest (below 30 %).

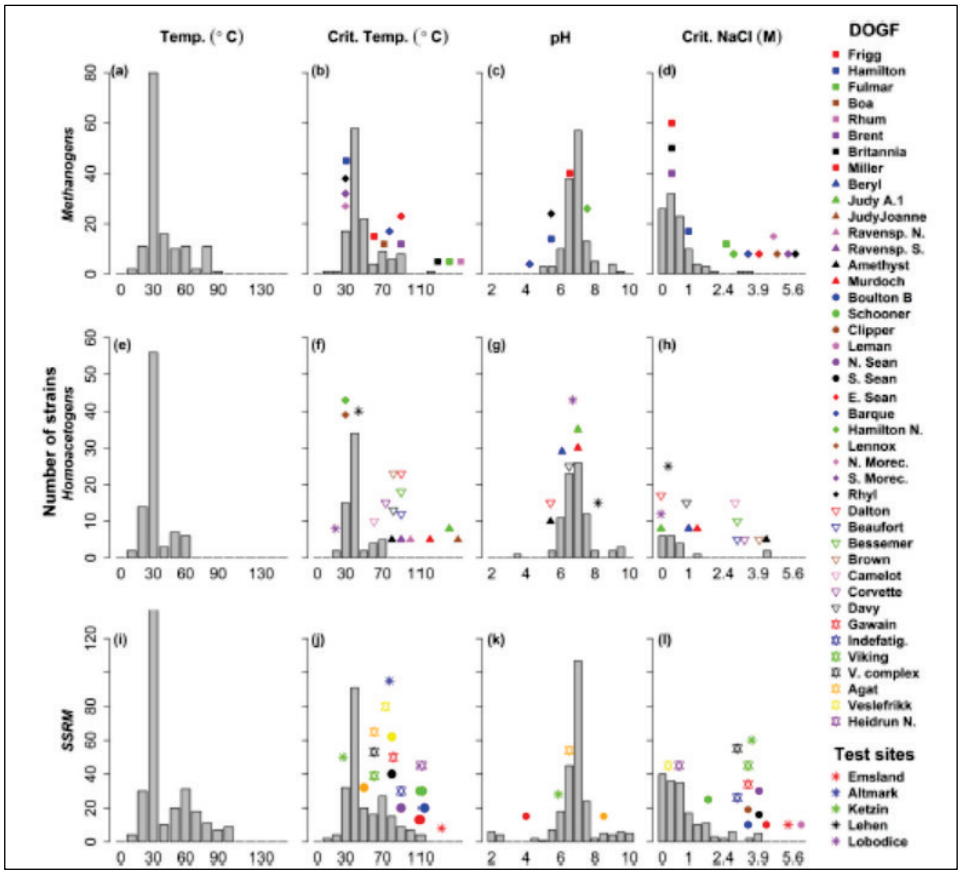

Figure 4: Distribution of optimum growth temperature, critical growth temperature, optimum pH values and critical salinity for 101–143 methanogens (a–d), 19–88 homoacetogens (e–h) and 165–277 sulphur species reducing microorganisms (SSRM) (Thaysen & al, 2021)

Our results are slightly different from the one observed by Thaysen et al (Thaysen & al, 2021). in which the optimal temperature for bacteria growth was determined around 30 °C. It is pointed out that in Thaysen's experiments, it is the bacteria growth that was directly measured, whereas in Hystories experiments, it is the consumption of hydrogen that was monitored.

Other correlations were investigated with salinity, pH or initial cell count, but no consistency could be found.

For the water sample from site 1, it was tested to add sulphate ions (from 180 to 750 mg/l) in the bioreactor to determine if sulphate concentration could influence hydrogen consumption (Figure 5).

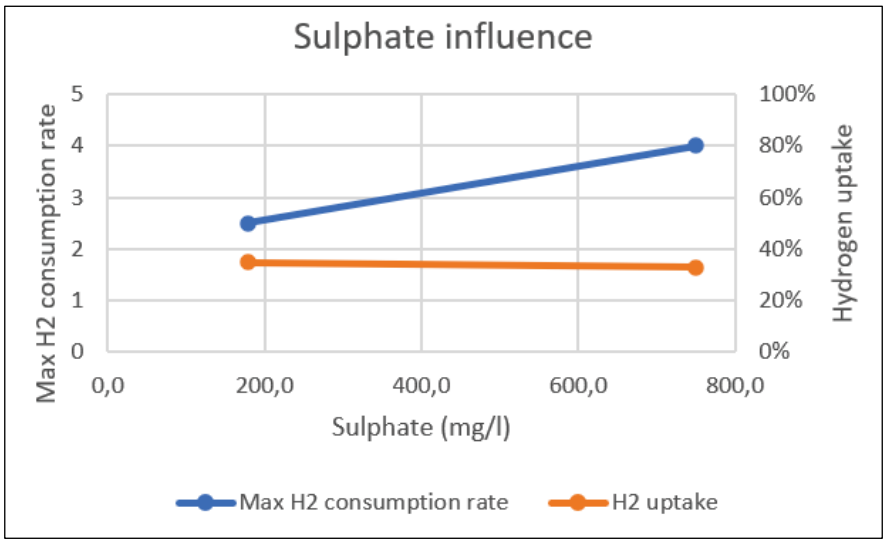

Figure 5: Sulphate concentration influence on Maximum hydrogen consumption rate and hydrogen loss on one specified test (conditions 1)

It was observed that maximum hydrogen consumption rate was multiplied by 1.6 when the sulphate concentration was multiplied by 4. However, the percentage of hydrogen loss remained stable between the two experiments.

4. Impacts of bacteria reactivity at reservoir scale

In Deliverable D3.3, a microbial reactivity model was established using PHREEQC to simulate the microbial reactions observed in the laboratory tests.

It is underlined that modelling was carried out for only one condition (site 1) that have a specific salinity of 16 300 mg/l. Bacteria development and reactivity are highly dependent on salinity. Therefore, the model and kinetics that were developed are valid only for this range of salinity.

Laboratory trend over 60 days at low and high pressures were well reproduced by the 0D model (Figure 6). Especially, at laboratory scale, the model predicts a consumption of 35 % and 5 % of hydrogen at the end of the experiment respectively at low and high pressures, which is very close to the 35 and 3 % loss that were observed by the laboratory tests. A production of methane and H_2S (up to 5300 ppm) in the gas phase was also modelled. This predicted concentration is overestimated, compared to laboratory results.

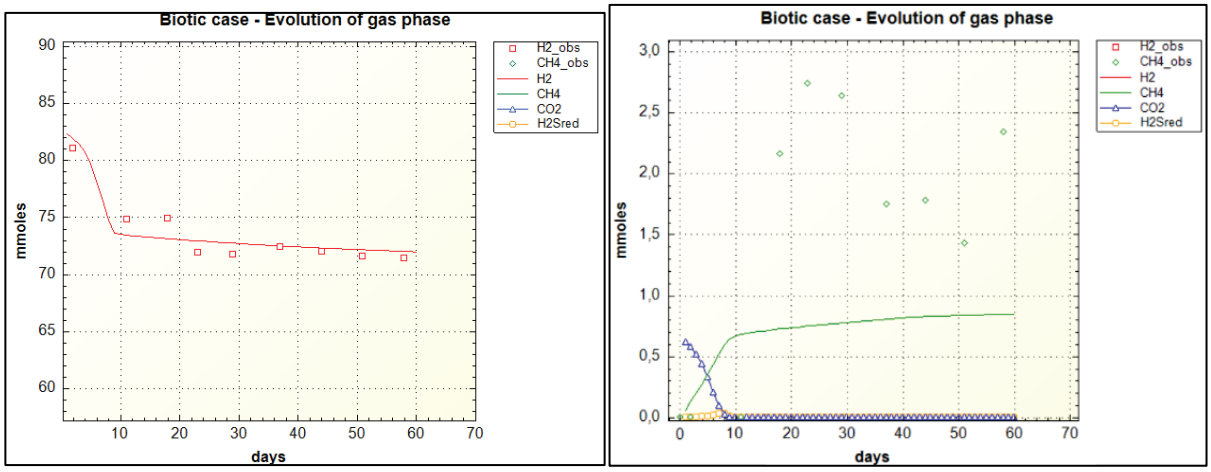

Figure 6: Biotic case at low pressure: evolution of the gas phase, comparison of laboratory results and simulation performed with PHREEQC software

Regarding the ions in water, a quick decrease of calcium, magnesium and carbonates is predicted at the beginning of the experiment because of precipitation reactions (calcite and dolomite precipitation) and carbon outgassing as CO_2. Once all the carbonates in water have been depleted, precipitation stops, and dolomite starts to dissolve, providing more carbonates to bacteria. Sulphate is not involved in precipitation reactions, but it is reduced quickly by bacteria. These last reactions are significantly slowed down when pH becomes higher than 8.

This model accounts for the microbial catalysis of these reactions. The simulation of the experiments enabled calibrating the kinetic reaction rates.

After this 0D model, the methanogenesis and sulphate reduction reactions were modelled through approximation formula within STARS™ to describe reactions between main components.

On a synthetic carbonate saline aquifer reservoir without water influx, the model computes the expected consumption of hydrogen through these bacterial reactions. The main parameters of the reactions in the 3-D model were derived from the PHREEQC modelling. As for 0D-Modelling, the model developed in 3-D is valid only for a specific salinity of 15 100 mg/l.

One key remaining issue is the upscaling of the experimental results to the field scale as the expected behaviour would be quite different if the laboratory-derived reaction rates are implemented without care to the storage scale. Using a similar approach to the upscaling of chemical reactivity for water flooding upscaling (Islam, 1990),a dumping factor of about 10^{-4} could be foreseen compared to laboratory conditions. Consequently, two simulation conditions were investigated using the laboratory (matched by PHREEQC) or the upscaled reactivity. As expected, reaction parameters with or without upscaling strongly influence the hydrogen consumption and production of methane and/or hydrogen sulphide in the storage.

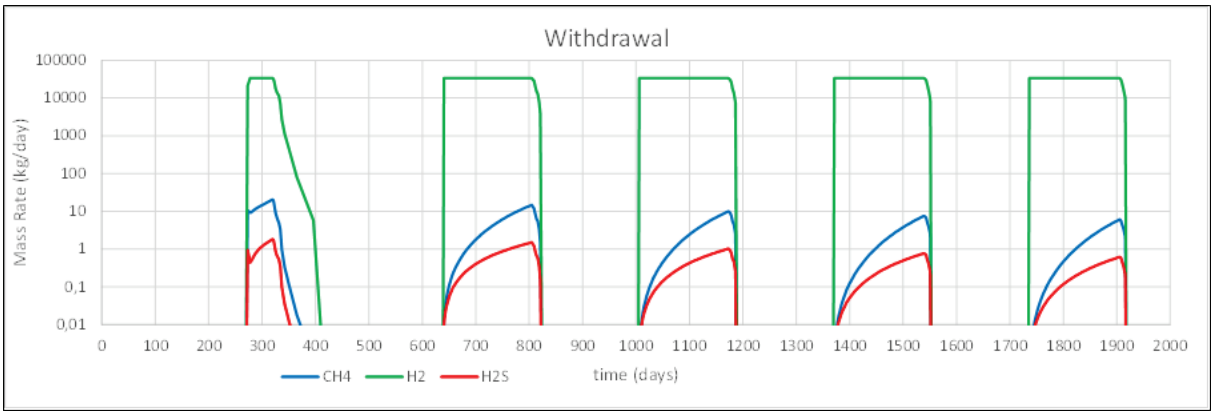

Figure 7: Evolution of withdrawal mass for the synthetic storage for laboratory-scale reaction parameters

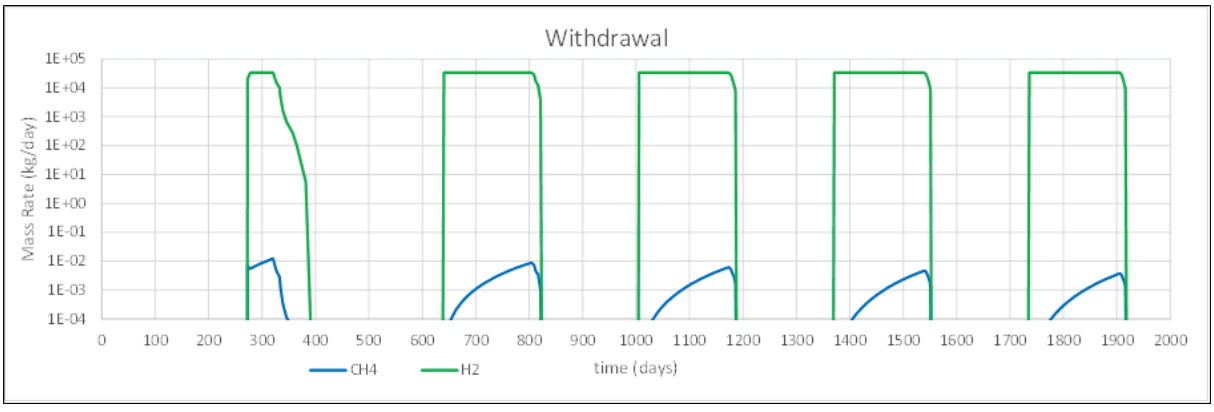

Figure 8: Evolution of withdrawal mass for the synthetic storage for upscaled reaction parameters

According to the results shown in Figure 7 and in Figure 8, most of the reactivity occurs at the start of hydrogen injection. Depending on the selected scale (laboratory scale or upscaled reactivity), the 3D model indicates a maximum number of impurities between 4.10^{-5} and 0.06 % for methane and 0 and 54 ppm for H_2S.

Based on these simulations, hydrogen loss was estimated to a maximum of 0.18 % for laboratory-scale reactions and $1{,}07.10^{-6}$ for upscaled reactions. These factors are really low compared to the 3 % measured with laboratory tests at high pressure. It is also much lower than the 1.5 % of H2 consumption that was assumed in Hystories D7.2-1 based on a review of literature and analogues and used in further economic calculations in Hystories. There is a reduced factor of 16 between laboratory results and 3D simulation without taking into account any upscaling factor.

It is pointed out that models were performed with a specific site where hydrogen loss at high pressure was quite low (only 3 %). Other sites have observed higher losses during the laboratory tests up to 48 %. Supposing that the same factor could be applied (16), at the scale of the storage, without any upscaling factor, this hydrogen loss should not be higher than 3 %, which is quite reassuring. This result is really close to the one from Thaysen et al. who estimated a hydrogen consumption due to microbial reaction between < 0.01 to 3.2 % (Thaysen & al, 2021), and to the figure of 1.5 % considered in Hystories D7.2-1 and the costs models of the project. In the Underground Sun. Storage project, a significant shift in the microbial consortium was identified and it was also concluded that 3 % of the injected hydrogen was converted to CH4 by methanogens.

This approach highlights the difference between the significant hydrogen loss that are observed during the laboratory tests and the one that would probably occur at the scale of one storage.

However, extension to field case of this modelling approach would require further validation and investigations of the current innovative approach. Field scale observations of the reactivity occurring during hydrogen injection in porous reservoirs will be necessary to set some of the parameters of the reservoir reactive transport models and provide predictions with confidence.

5. Microbial Risk Assessment

Based on the experiments carried out for the Hystories project and on previous literature, it becomes possible to define the most favourable environment for hydrogen storage and to draw a microbial risk assessment flowchart.

For this exercise, porous media and salt caverns have been considered, although salt caverns were not investigated in the frame of this project.

These two storage types differ in terms of their parameters and thus also in terms of microbiological colonization and possible metabolic processes.

5.1. Salinity

First parameter that is used to classify a microbial risk is the salinity. Even if based on our laboratory tests, the correlation between salinity and hydrogen consumption was not obvious, it is admitted that this parameter will strongly influence the microbial reactivity. For example, based on Thaysen experiments, optimal growth for methanogens is with a salinity lower than 60 g/l, whereas optimal growth for SRB is obtained below 100 g/l of NaCl (Thaysen & al, 2021).

From this first assumption, it can directly be concluded that salt caverns with higher salinity will be less prone to microbial development than porous media. Nevertheless, it is admitted that some halophilic bacteria, especially halophilic SRB, are able to develop in these extreme environments. Activity thus depends on the purity of the salt in which the cavern is situated. When the cavern is situated in a salt layer with lower halite purity, or situated within several salt layers, the chance for bacteria is increased, even if it remains negligible, this is caused by the fractional decrease of NaCl (Laban, 2020).

5.2. Temperature

Temperature will also play a role in the microbial reactivity towards hydrogen. Optimal growth rate based on Thaysen experiments is located at 30 °C (Thaysen & al, 2021). Based on our experiments, the optimal growth was more located around 40 °C. Nevertheless, bacteria are able to develop up to 120 °C. Nevertheless, underground storages with temperatures above 90 °C can be considered relatively safe with regard to technically relevant microbial processes.

While salt caverns are rarely deeper than 1,500 m and therefore usually have temperatures of 20-70 °C, temperatures of 90 °C and more can also be reached in deep geologic structures.

5.3. Availability of carbon source

Even if carbon source is not specifically detailed in the reaction of sulphate reduction or methanogenesis, they are essential for the bacterial growth. This carbon source is used by bacteria as biomass food to help their growth. The carbon source can also serve as electron donor (Thullner & Regnier, 2019).

Carbon source can be CO_2 gas, carbonate or bicarbonate ions in water, organic acids as acetate, lactate, valerate, formate, or any other organic compounds (hydrocarbons) due to past activities of the storage that could be converted into organic acids via fermenting bacteria.

In the example below the influence of acetate concentration in the growth yield for SRB is highlighted.

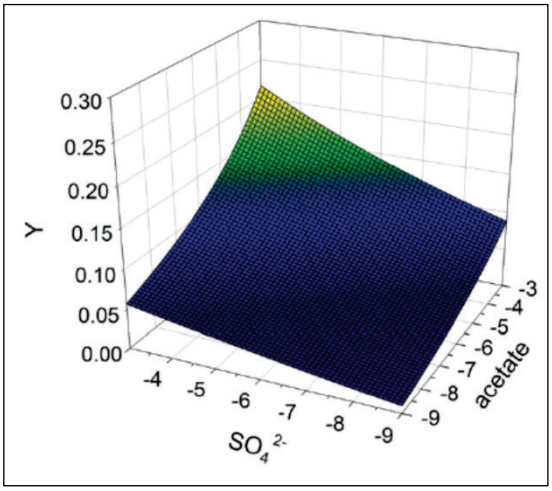

Figure 9: Predicted growth yields Y for sulphate reduction as a function of log acetate and sulphate activities (Thullner & Regnier, 2019)

From this criterion, it is deduced that depleted oil or gas reservoirs would have more risk than aquifers or salt caverns. Previous natural gas or liquid hydrocarbon storages will also have more risk due to residual hydrocarbons that could be still present in the brine or gas.

5.4. Sulphate content

Based on Hystories laboratory experiments, it was proven that increase of sulphate content had an influence on hydrogen consumption rate. This influence is also visible in the graph from Thullner and Regnier on Figure 9.

A limited value of 10 mg/l was defined to distinguish high and low risk in porous media due to sulphate reduction reaction.

5.5. Chart for the assessment of microbial risks

Based on the above parameters, it was attempted to define a simplified chart to assess the microbial risks of potential hydrogen storages.

Microbial risks are defined based on the below table:

Table 4: Table of definition of microbial risks in underground hydrogen storage

Risk assessment
Low risk (almost no microbial activity or extremely limited)
Moderate risk (though there is inhibition for some microbial groups, there are development of some microorganisms)
High risk (conditions are optimum for many microorganisms in UGS)

The following chart is then proposed:

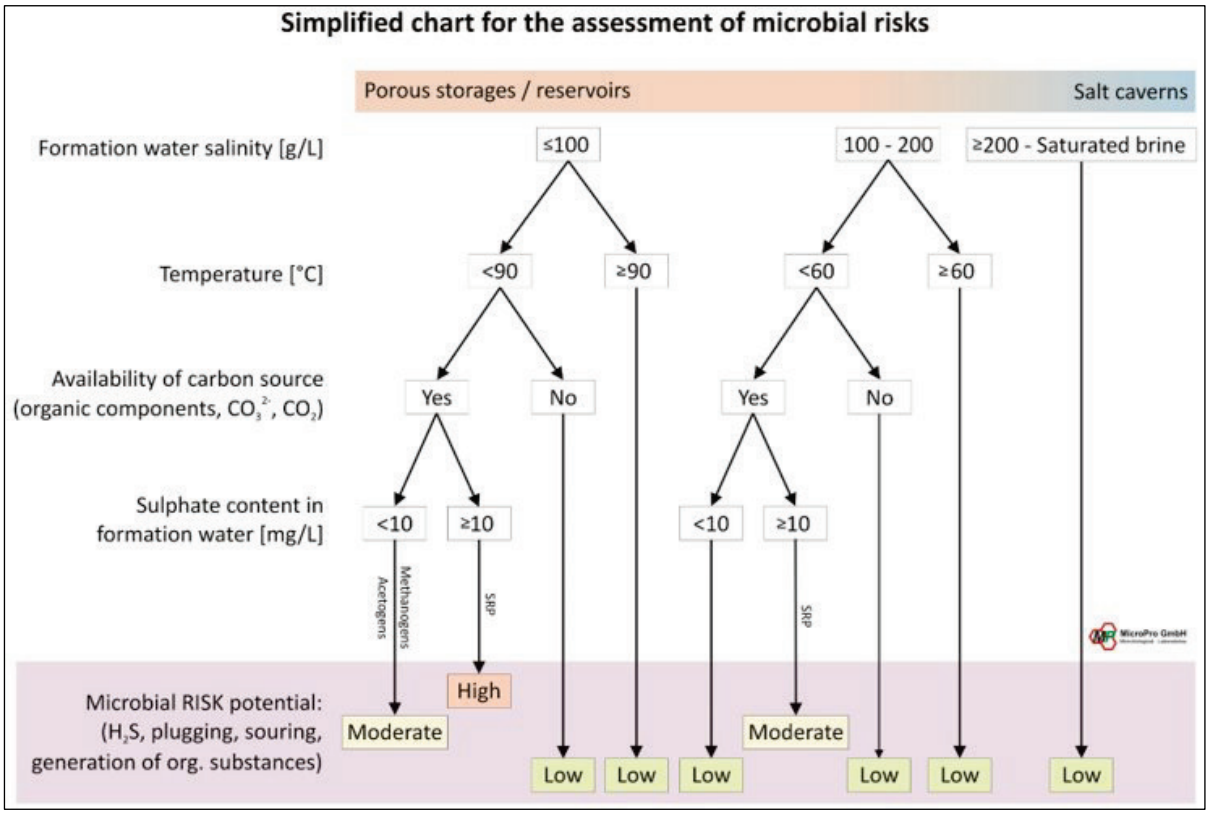

Figure 10: Simplified chart for the assessment of microbial risks

Although a case-by-case assessment of underground storages is necessary from a microbiological point of view, based on this assessment it is noticed that salt caverns are classified in low risk. This general conclusion is based on the following characteristics:

- Saturated brine in the cavern sump
- Low mass transfer between gas phase and brine
- Closed fluid system (no exchange with external formation waters).

Porous media can also be considered as favourable environments for hydrogen storage with low microbial risk, provided that their availability of carbon source is low (low calcite or dolomite content) or that their temperature is high enough (> 90 °C for salinity between 100 and 200 g/l and > 60 °C for salinity below 100 g/l).

On the contrary, worst case for hydrogen storage is a porous media, with salinity below 100 g/l, temperature below 60 °C, significant amount of carbon source and sulphate content above 10 mg/l.

5.6. Additional parameters

In order to get a more precise assessment, other parameters need to be considered.

For example, pH between 6 and 7.5 is most of the time optimal for bacterial growth based on Thaysen classification (Thaysen & al, 2021). Below or above this range, growth yield will be decreased. Influence on pH on hydrogen consumption was demonstrated in Hystories where the same bacterial culture was tested with different pH between 6 and 10.

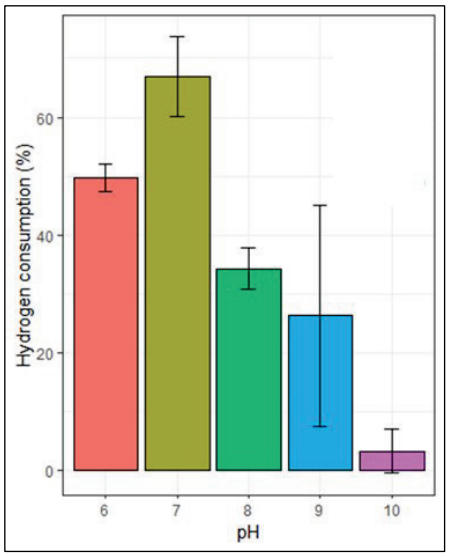

Figure 11: Hydrogen consumption depending on pH for low pressure tests

It is visible that pH of 7 was the optimal condition for hydrogen consumption. This consumption decreases progressively with higher pH and is almost non-existing at pH 10.

Additionally, only planktonic bacteria were taken into consideration in this study. Sessile bacteria also have a very strong influence on hydrogen consumption. Their activity should be studied in more details to understand their impacts in the global phenomenon. Especially, in porous storages, the pore space, in particular the surfaces of the rock particles, represents the habitat of the microorganisms. Porous structures offer biofilm-forming microorganisms gigantic areas for settlement and intensive contact with the rock matrix. Due to the operation of a pore storage facility, the reservoir water is displaced from the top of the structure during the gas injection and pushed into the edge zones. During gas withdrawal, this process is reversed. This operating regime leads to a cyclical change between water-saturated storage gas and reservoir water in the upper working range of the storage facility. Through the transport processes thus set in motion, the microorganisms are constantly supplied with substrates.

Other elements could inhibit the bacterial development as presence of metal ions, or additives as drilling fluids, biocides, inhibitors, etc. It is necessary to know the background of the well to take it into account in the microbial risk assessment.

Last, some of the sites that were tested gathered all the conditions to offer microbial development: low salinity, low temperature, presence of carbon source, neutral pH, etc. but there was no microorganisms detected or in very low concentrations. This last point highlights that microbial risk is very site specific. To clarify the risks on a specified site, it is highly recommended to sample the formation water or brine to quantify the microorganisms that are effectively present and active in the environment.

6. Conclusion

In the WP3 of Hystories project, the goal was to analyse in more detail microbial processes associated with hydrogen in different potential porous underground storages at European level based on formation water and rock samples from various storage formations.

This exercise was carried out on 15 different formation waters. At first, it was observed that depending on the sites, concentrations of microorganisms and their activities could be quantified as in poor, medium or high.

Based on these observations, hydrogen reactivity tests were conducted at low and high pressures with the sites containing the highest concentrations in bacteria.

Results of these laboratory tests highlighted a clear hydrogen consumption that was recorded between 15 and 76 % for low pressure tests and between 3 and 48 % for high pressure tests. H_2 consumption was directly related to microbial reactivity and mainly due to methanogenesis reaction, and to sulphate reduction to a lesser extent.

0D and 3D models were developed on one specific case to predict the kinetics of the reaction at the scale of one storage and during several cycles of hydrogen injection and withdrawal. It was highlighted that hydrogen consumption that was quantified at 3 % based on laboratory experiments in this specific case, could be reduced between $1.07.10^{-6}$ and 0.18 % at the scale of the entire storage, depending on the upscaling factor that is selected.

The second objective of the WP3 was to assess and classify underground storage technologies in respect to the microbial risk. It was found from literature and from laboratory experiments that several parameters will highly influence the microbial reactivity. Higher salinity (> 200 g/l) or higher temperature (> 90 °C) will tend to inhibit bacterial growth. On the contrary, presence of carbon source or sulphate content will act as a catalyser for microorganisms development. Based on this observation, a simplified chart for microbial assessment risk was created.

This approach is of course general, and a case-by-case assessment is highly recommended to consider an underground as potential candidate for hydrogen storage. No matter what parameters are observed on a specific environment, the first task would be to characterize if microorganisms are effectively present and active in it.

The models that were developed in 3D considered the chemical reactivity and the catalytic effect of microbial activity on reactions consuming hydrogen in a reservoir model. Results obtained from these models are, for the moment, tainted with a high uncertainty, due to the kinetics of the bacteria that are site-specific, but also due to the upscaling factor to scale from laboratory results to field estimations. Field data extracted from a hydrogen pilot are necessary to calibrate and get better confidence in models.

7. References

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APPENDIX 1

Sampling Procedure for Microbiology Analyses

TECHNICAL NOTE

OBJET / SUBJECT : Sampling Procedure for Microbiology Analyses

DATE PUBLICATION / DELIVERY DATE	08/03/2021
RÉDACTEUR / WRITER	C. FOURNIER

1. CONTEXT

In the context of Hystories project, it is planned to carry out formation water sampling from different reservoirs (depleted field and aquifers). The aim of this sampling is to collect representative water at downhole conditions to analyze the bacteriological characteristics of each water and to determine their potential reactions with pure hydrogen atmosphere. **4 liters are necessary** per sample to carry out the analyses and launch simulation tests.

The aim of this note is to specify the guidelines for sampling in order to collect water as representative as possible of downhole conditions without disturbing its bacteria population.

2. SAMPLINGS POSSIBILITIES

Several different methods can be considered to sample formation water. The aim is to collect water that could be in contact with hydrogen in case of underground storage in porous reservoirs.

2.1. Downhole sampling from interface or peripheral wells

This method is the most reliable to collect a representative sample. To do so, it is necessary to identify a well that is located in the storage bubble and in contact with water (interface well) or a well that is at the periphery of the storage and at the same depth (peripheral well).

Formation water shall be collected with a specific sampler. This sampler should be able to open at the desired depth to collect water, then to close automatically to preserve the sample before going up. For this purpose, sampler with mechanical clock or pneumatic downhole sampler are to be used.

A slickline unit is necessary to lower the sampler at the desired depth. Furthermore, if an interface well is selected, a pressure control equipment would be necessary to handle the pressure in the well.

2.2. Surface sampling from artesian wells connected to the water at the level of the storage

Some wells depending on the seasons can become artesian. In these specific wells, downhole pressure is so high that formation water flows to the surface naturally. Thanks to this phenomenon, water can be collected more easily.

However, if water collected at surface would have the same salinity as in downhole conditions, bacteria could have been disturbed by the rapid decrease of pressure during its rising. For this reason, this method is less recommended than the first one, but could be taken as an opportunity to complement downhole sampling.

Specific Wellhead sampling kit should be used to connect the wellhead to the sterile bottles. Contact with air must be prohibited.

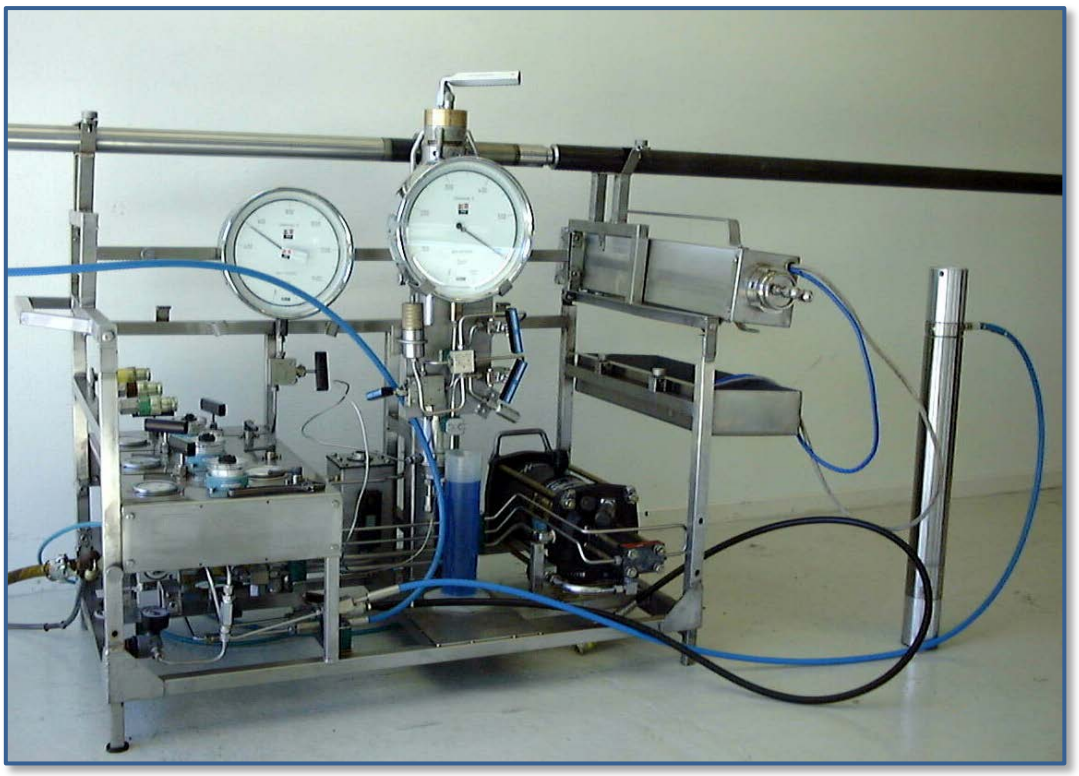


Figure 1 : Example of Expro Wellhead sampling kit

2.3. Surface sampling from water separator

This last method can be practiced as complement or as an alternative of the two latter ones if they cannot be considered. It consists in sampling water from the water separator.

Water separator is used to separate condensed water or free water from natural gas. This condensed water or free water can then be easily collected from the sump of the water separator.

It has to be understood that condensed water and free water are not representative of downhole formation water, it will be less saline. Furthermore, the bacteria that are collected in this water could have been developed in the water separator and not in the underground environment. Interpretation will need to be very careful with this sample.

As for latter methods of sampling, contact with air must be prohibited.

3. PREPARATION BEFORE SAMPLING

This preparation consists in checking the correct functioning of the downhole or surface sampler, programming their mechanical clock (if any) to guarantee that the sampler will open at the correct depth, and finally sterilizing it.

To sterilize the sampling kits or the transfer bottles if they do not have been sterilized by MicroPro, the following methodology can be applied :

- The sampler can be heated during a specific time. Time required for the sterilization of the objects under different temperatures according to BP 1988 is summarized in the following table:

Temperature	Time*
180 °C	30 min
170 °C	1 hour
160 °C	2 hours
121 °C	16 hours

If sterilization is too complicate to set up, the samplers should at least be decontaminated using an antimicrobial solution[1] (ethanol or similar) that will kill most types of bacteria. For example, a solution composed of 30 % of water and 70 % of ethanol can be prepared. Then, internal and external parts of the sampler including valves and pipes with direct contact to water sample will be entirely rinsed with this solution. Then, the sampler will be naturally dried in the configuration with the valve at the bottom to avoid any liquid retention inside the sampler. In addition, the sampler can be rinsed with sterile, distilled water afterwards to rinse out any remaining alcohol.

During the sterilization process, valves of the sampler need to remain open. When the sampler is dried, the valve will be closed and remain closed until the sampling operation.

After sterilization, sampler and transfer bottles will be filled with a neutral gas (Argon or Nitrogen) to avoid any oxygen (air) contact with water. As a matter of fact, some anaerobic bacteria are very sensitive to oxygen presence and can dye quickly in case of contact. The sampler can also be under vacuum.

If the sampling is carried out in downhole conditions with slickline unit, it is also recommended to pass a dummy run with a tool of the same diameter as the sampler to be sure that it is possible to go down at the desired depth without any trouble.

[1] As per information, the usual solvent used by EXPRO (Ensolv) is not appropriate for this application, as it is used as a degreaser only and not as a sterilization agent.

4. METHODOLOGY DURING SAMPLING

4.1. Downhole sampling

After connecting the sampler to the slickline unit, the tool will be run down into the well until the desired depth. The opening and closing of the sampler will be waited with a safety margin. Then, the tool will be pulled up with the slickline.

During the way up, it is not recommended to maintain downhole pressure with the introduction of a pressurized fluid (ex : glycol). As a matter of fact, this fluid could have an interaction with the bacteria and may disturb their development. It is preferred to let the pressure slowly decrease during the way up that should not be too fast (max 50 meters/min).

4.2. Surface sampling

Before connecting the surface kit sampling to the tapping on the wellhead or on the water separator, it is recommended to let the water flow during at least 1 minute to guarantee that the collected water was not static.

Then, the surface kit sampling, that has been sterilized (or at least decontaminated) before, is connected from one side to the transfer bottles and from the other to the wellhead or water separator. If possible, nitrogen or argon is introduced inside the whole system to remove the air. The kit can also be under vacuum.

The tapping can then be open to start completely filling the bottle until its top without leaving any gas space. The bottle must be hermetically sealed to avoid exposing the sample to air contact. Close the tapping before disconnecting the surface kit sampling.

5. METHODOLOGY AFTER SAMPLING

5.1. Downhole sampling

After sampling in downhole conditions, water will need to be transferred from the sampler to the transfer bottles that will be sent to the laboratory, except if the sampling chamber can be disconnected and used for transport purposes as shown in the picture below.

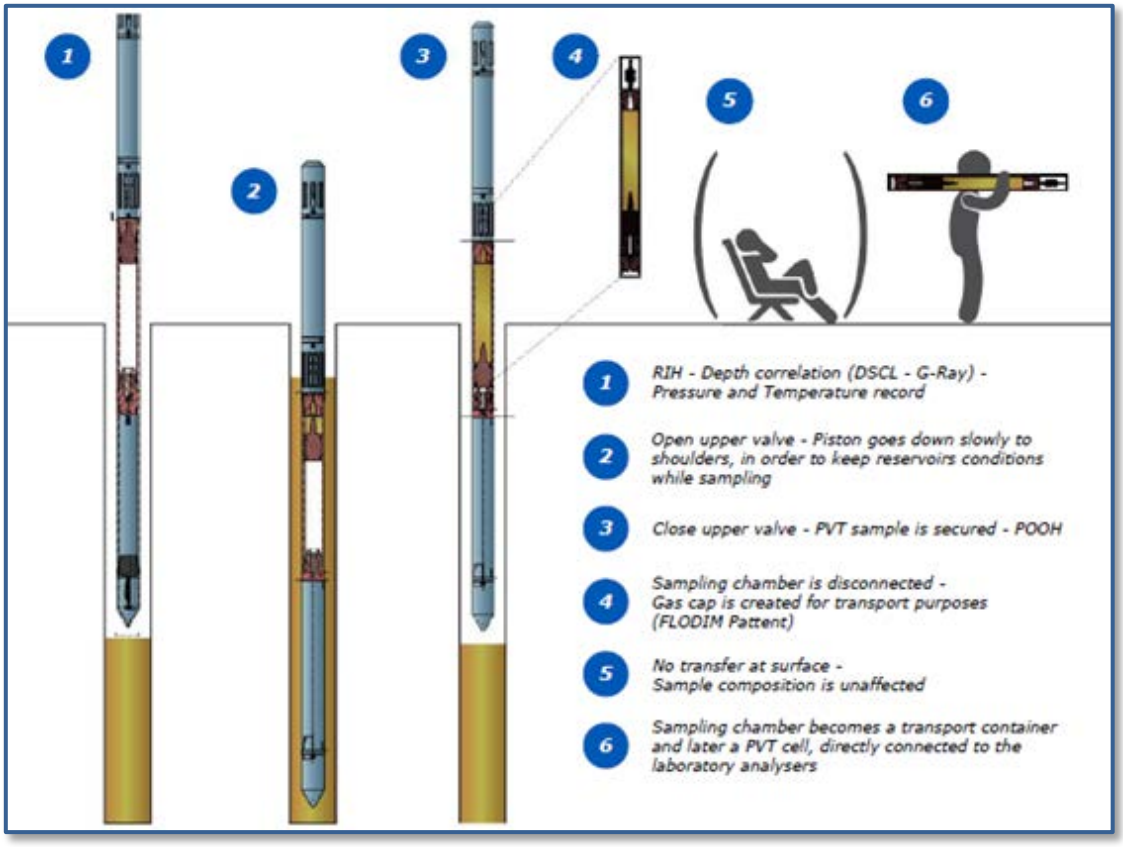


Figure 2 : Example of sampling chamber from FLODIM that can be used for shipment

If the sampling chamber cannot be used for shipment, water will be transferred from the sampler to the transfer bottles without any contact with air.

MicroPro can depressurize the transfer bottes at its laboratory, so the transfer bottles can be sent under pressure. However, if the transfer bottles cannot handle pressurized sample, it will be necessary to depressurize the sampler on field. This operation needs to be performed very carefully as bacteria are sensitive to pressure variation. No more than 4 bar/min has to be respected.

5.2. Surface sampling

For surface sampling, as water is already in the transfer bottle at the end of the operation, there is no specific requirement. If necessary, additional analyses can be carried out on site with a separate portion of the water sample. (e.g. pH-value, electrical conductivity, ATP-test)

6. SHIPPING

Each sample should be properly tagged in order to be identified easily by MicroPro laboratory. The following information should be written on the tag :

- Sampling Date and Time
- Nature of the sample : Formation water (preferably with a chemical analysis if available)
- Location of the sampling (ex : Well ABB, 1700 meters)
- Name of the storage
- Name of the company

It is also recommended to ask to the sampling contractor to write a small report about the sampling conditions, with some pictures and observations during the sampling (example : smell, color, etc.).

It is not necessary to maintain the bacteria in cold chamber during shipping. Optimum temperatures are between 8°C to 12°C. It should never be below 4°C. A data logger can be provided by MicroPro to continuously record the temperature during transportation. Sample bottles should be carefully packed in insulated transport boxes for shipment. However, the shipping from the field to MicroPro laboratory needs to be immediate and fast (within 48 hours). The best way is to send the water samples by DHL Express. The tracking number of shipment should be forwarded to MicroPro.

Delivery address for the shipping will be :

Martin Wagner
MicroPro GmbH
Magdeburger Straße 26 b
D-39245 Gommern
GERMANY
Tel: +49 39200 703-10
Fax: +49 39200 703-12

7. EXAMPLE OF COMPANIES SPECIALIZED IN BACTERIA SAMPLING

- FLODIM https://www.flodim.fr/what-we-do/well-logging/bottom-hole-sampling/
- SCHLUMBERGER https://www.slb.com/reservoir-characterization/reservoir-testing/reservoir-sampling
- MODIS https://www.modisfrance.fr/
- EXPRO https://www.exprogroup.com/products-services/fluids/well-site/samplings

8. CORES SPECIFICATIONS

As cores are usually quite old samples and not always kept in good conditions, they will not be used for direct microbiology analyses. Nevertheless, they can be used for simulation tests under hydrogen atmosphere.

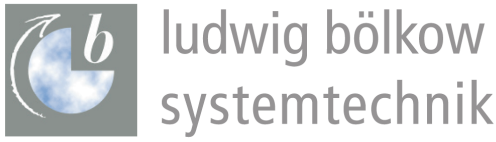
To do so, small pieces of cores of about 7 cm diameter and 15 cm height or cuttings will be introduced in the reactor with formation water and hydrogen gas.

The cores or cuttings that need to be sent are elements that are representative of the porous layer of the reservoir. If several samples are available, samples with pyrite elements would be preferred as their interactions with hydrogen could be more critical.

Three or four pieces of cores or cuttings of the approximate above dimensions or more if smaller would be enough for the tests.

Mineralogy samples can be sent together with the water samples.

Hystories project consortium



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