hystories
Hydrogen Storage in European Subsurface

Modelling of microbial effect on H2 reactivity in porous media at laboratory and reservoir scales

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1. Introduction

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

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. Based on the kinetic reactions observed during those laboratory tests, the goals were first to develop a model in 0D with PHREEQC software, and then to apply that model at the reservoir scale by creating a 3D model with CMG STARS software in order to observe the various impacts of the microbial reactions.

This report presents first the modelling works already available in the literature, then specifies the results from laboratory tests that were used to develop a new model. In a third part, works performed to build 0D and 3D models are detailed. At last, conclusions from these models are drawn.

2. Previous Modelling from Literature

As Hydrogen is an electron donor, it is a very attractive source of energy for numerous microorganisms, under both aerobic and anaerobic conditions.

However, in abiotic environment (without bacteria), the abiotic hydrogen redox reactivity is kinetically restricted, and many of the potential hydrogen-induced redox reactions tend to stay negligible at low temperatures. This result was for example observed on the chemical modelling carried out in the pilot project "Underground Sun Storage" (Hassannayebi, 2019). The exception for H_2-induced redox reactions is pyrite reduction into pyrrhotite, which can be significant at low temperature conditions.

Same conclusions were driven in Hystories project WP2 in which abiotic models were tested in 0D with the software PHREEQC[1].

On the contrary, in biotic conditions, several reactions are anticipated. As a matter of fact, in contrast to methane, which cannot be microbially converted in significant amounts in underground storage facilities without oxygen, feeding hydrogen into underground storage facilities will induce or accelerate microbial metabolic processes. As a result, this can lead to considerable technical damages and economic disadvantages, if it is not controlled and inhibited, particularly in combination with sulphate or thiosulphate reduction.

The main bacteria reactions will be the following:

- Bacterial sulphate reduction (BSR): $SO_4^{2-} + 4H_2 \rightarrow H_2S + 2H_2O + 2HO^-$
- Methanogenesis: $HCO_3^- + 4H_2 + H^+ \rightarrow CH_4 + 3H_2O$ or $CO + 3H_2 \rightarrow CH_4 + H_2$
- Acetogenesis: $2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O$
- Ferric bacterial reduction: $Fe_2O_3 + H_2 \rightarrow 2FeO + H_2O$

The two last reactions are less visible and have less impact on gas quality. Therefore, most of the studies are focused on the first two.

The importance of microbial activity on the catalysis of these reactions in the presence of hydrogen is recognized but only few studies use a model that consider a kinetic control on these redox reactions in solution (Hemme and Van Berk, 2018; Hassannayebi et al., 2019; Veshareh et al., 2022). For example, Hemme & van Berk created a hydrogeochemical model to identify the risk of hydrogen loss in depleted gas fields (Hemme & Berk, 2018). In their model, the authors assumed conditions specific to a North Sea reservoir and modelled storage periods of 30 and 300 years. The model uses a reservoir temperature of 40 °C, which is on the low side for a depleted gas field. The loss of hydrogen was carried out by bacterial conversion to CH_4 and H_2S. The authors found that after 30 years of hydrogen storage, changes in the mineralogy of the reservoir were minimal, with dissolution and precipitation accounting for a combined porosity loss of 0.05 - 0.21 % (decrease of porosity from 10 % to 9.79 % - 9.95 %). They concluded that when selecting a depleted gas reservoir for hydrogen storage, it should have low levels of carbonate- and sulphate-containing minerals, and low concentrations of residual CO_2.

[1] Deliverable D2.4, that will be published in 2023.

Hassannayebi et al. (2019) simulated the injection of H_2 of the Underground Sun Storage project in Austria in a batch model. In this model, a kinetic control is considered on the dissolution of H_2 in water rather than on the aqueous redox reactions. Only sulphate reduction and pyrite to pyrrhotite reduction are considered, while the reaction of methanogenesis and acetogenesis were decoupled and, then, were not occurring. Despite these simplifications and a large uncertainty on the kinetic rates, Hassannayebi et al. (2019) concluded that the reactions of H_2 with minerals can only be relevant over time scales longer than the storage operations.

Veshareh et al. (2022) simulated the reactivity of H_2 if stored in Danish North Sea chalk reservoirs. A Monod-type equation considering a constant bacteria concentration was used to model a microbial kinetic control on the methanogenesis, sulphate-reduction and acetogenesis reactions. Their simulations indicate that methanogenesis is the main mechanism able to consume H_2, but it is difficult to conclude on the extent of this consumption because of the range of uncertainty on the methanogenesis kinetic rate. Formation of H_2S appeared as secondary in these simulations, with a little effect on H_2 loss but H_2S could reach concentrations that can be a concern for corrosion or safety. Under abiotic conditions, calcite dissolution was discarded. When triggered by methanogenesis and acetogenesis, little amounts of calcite were dissolved.

The loss of hydrogen by bacterial conversion to CH_4 via methanogenesis is limited mainly by the amount of CO_2 which is co-injected, the reaction kinetics and the maximum storage time. Less CO_2 co-injected will reduce the loss of H_2 but will not prevent the conversion to CH_4 if other sources of HCO_3^- are available in the form of residual gases and carbonate minerals. The generation of CH_4 by methanogenesis where HCO_3^- is only delivered by the dissolution of carbonate minerals is slower and limited by this dissolution.

In a salt cavern storage context, the loss of hydrogen by bacterial conversion to H_2S via sulphate reduction is limited mainly by the amount of sulphate available in the salt rocks. Laban developed a model for salt caverns (Laban, 2020). In this model, the author indicates that the sulphate that are used for bacteria catalysed reactions are available due to anhydrite ($CaSO_4$) dissolution, available in the sump and cavern wall (Laban, 2020).

The kinetic rate of the reaction between sulphate, hydrogen and the bacteria can be modelled through a multi-Monod equation (Laban, 2020):

$$Rate = k \times kgw \times \frac{SO_4^{2-}}{0.001 + SO_4^{2-}} \times \frac{H_2}{0.001 + H_2}$$

Where k is the kinematic rate and kgw is the mass of available brine. In Laban thesis, a kinetic rate of 9.10^{-10} mol.kgw^{-1}s^{-1} was assumed.

However, if the bacteria are taken into account in the model developed by Laban, the growth rate of bacteria and the impact of their mortality was not included. To do so, it is necessary to add a microbial growth rate, as proposed by Jin et al. (Jin, Roden, & Griska, 2013):

$$\frac{d\,X}{d\,t} = Yr - D\,[x]$$

Where $\frac{d\,X}{d\,t}$ is the rate of microbial growth, r is the kinetic rate defined by the multi-Monod equation, Y is a ratio that defines the increase in bacteria compared to the consumed substrates, called also “Growth yield” and D is another ratio associated to the mortality of the bacteria, called also “maintenance rate”. As an example, for a specific type of methanogenic bacteria, growth yield (Y) was estimated at 2.9 g/mol and maintenance rate was estimated at 1.8 10^{-4} h^{-1} (Shapiro, Hoehler, & Jin, 2018).

The review of the available literature did not enable us to find a kinetic model for porous media that takes into account in a same model the kinetic rate of the hydrogen consumption and the kinetic rate of the bacteria development. The developed of an original model in the frame of Hystories was needed.

3. Summary of laboratory tests results

During the first period of the project, ten formation water samples were provided from Advisory Board members. These samples were collected from different storage facilities (aquifers or depleted fields) and showed a wide range of different conditions such as temperature (35 °C to 90 °C), pressure (30 bar to 190 bar), salinity (<0.1 % to 10 %), and pH (5.8 to 10). This covers most of the relevant conditions for the growth and activity of microorganisms in European underground gas reservoirs. For details on these tests can be found in MicroPro's Hystories reports D3.2 and D3.4.

These waters have been analysed to characterize the microorganism's population, which can be highly diversified depending on the site. Hydrogen utilizing microorganisms, namely sulphate reducing archaea, sulphate reducing bacteria, methanogens and acetogens were detected in formation water samples.

In order to quantify the potential consumption of hydrogen by microorganisms, the formation water, enriched with nutrients, was put in contact with hydrogen in tight anaerobic reactors. First tests were carried out close to atmospheric pressure. In each reactor, a carbon source was introduced as core materials or as carbonate ions (See Deliverable D3.2).

On specific samples, active consumption of hydrogen and therefore changes in gas composition were observed over time. Figure 1 is an example of hydrogen consumption on triplicates, left site with carbonate ions as carbon source and right side with cores as carbon source.

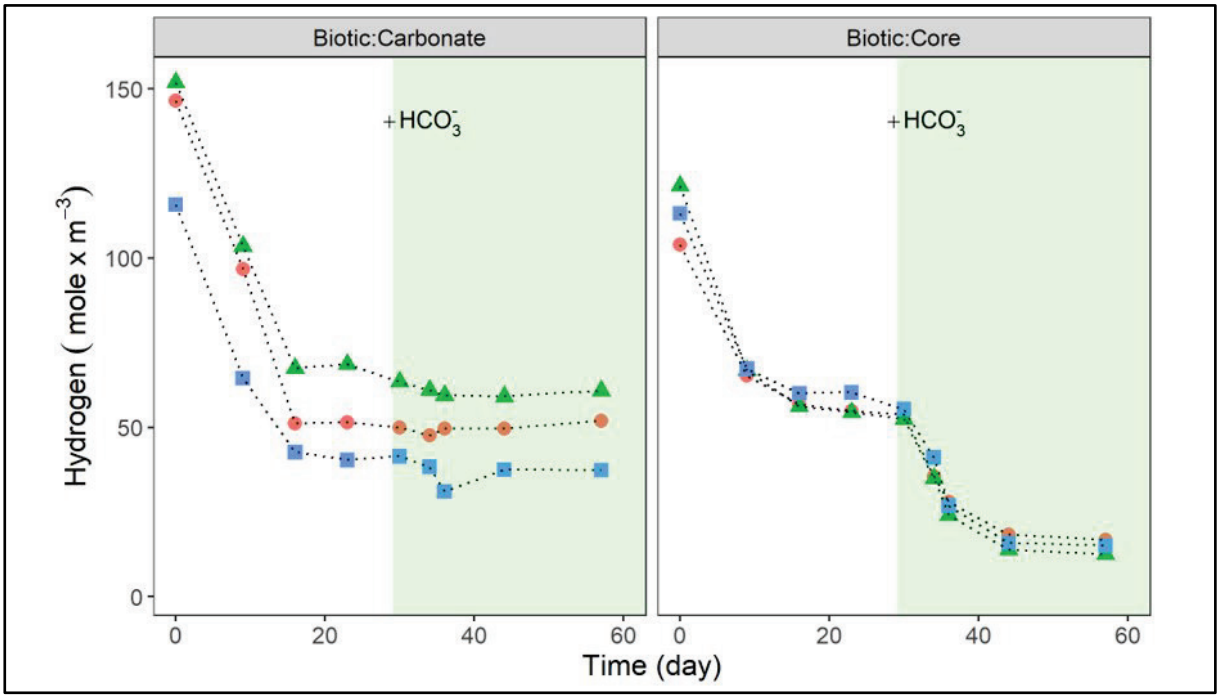


Figure 1: Evolution of hydrogen during a laboratory test in slight over pressure conditions

A rapid decrease of hydrogen in the gas phase is observed during the first 15 days, then the rate of reaction starts to decrease, and the hydrogen concentration stabilizes. After 30 days, carbonate ions are added in the reactor. A restart of the hydrogen consumption is noticed in the reactor with cores materials, whereas in the reactor with carbonate ions only, no additional reaction is observed.

This experiment highlights that the reactions mechanisms are different with and without cores.

In order to extrapolate a kinetic model from these experiments, a specific experiment plan was set up. As a matter of fact, in the regular hydrogen consumption tests, some data were missing for developing a clear model of the bacteria reactions (for example, water characteristics before and after the test or rock composition before and after the test).

4. Selection of a specific case for Modelling

To get all the necessary information, a protocol was specified for the bacteria modelling. This protocol helped defining the analyses before, during and after the tests and also some requirements during the test (for example, the volume ratio of water, gas and rock phases to be as close as possible as reservoir conditions). This protocol is available in Appendix 1.

This protocol consists in eight different tests that are summarized in Table 1.

Table 1: Summary of the conditions of the laboratory tests

Test Identification	Presence of bacteria	Temperature (°C)	Pressure (bar)	Volume of water (ml)	Cores weight (g)	Volume of Gas (ml)	Water /rock /gas volume ratio	Gas added to maintain constant pressure
A0	Sterile	50	2	175	70	1040	14 / 2 / 84	N_2
A1	Biotic	50	2	175	70	1040	14 / 2 / 84	N_2
A2	Biotic	50	2	175	70	1040	14 / 2 / 84	H_2
B0	Sterile	50	2	52	24	65	41 / 8 / 51	N_2
B1	Biotic	50	2	52	24	65	41 / 8 / 51	N_2
B2	Biotic	50	2	52	24	65	41 / 8 / 51	H_2
C0	Sterile	50	27	160	64	55	66 / 11 / 23	N_2
C1	Biotic	50	27	160	64	55	66 / 11 / 23	N_2

In the above experiments, rock/fluid ratio is between 2/98 and 11/89, where fluid is the combination of water and gas phases. It is pointed out that in real porous media, the proportion of rock is generally much higher. An average of 98/2 can be estimated for the rock/fluid ratio in real porous media. Therefore, the experiments are conservative compared to actual storages as the reactions with the rocks are enhanced in the reactors.

The formation water and the cores from a specific site were used for these hydrogen tests. Tests lasted 58 days for low pressure tests and 70 days for high pressure ones.

In this protocol, it was notably recommended to carry out ionic composition analysis before and after the test. Results of this analysis are presented in Table 2.

Table 2: Solution composition analysed before and at the end of the laboratory tests

Parameter	Unit	Start (t0)	End (t end)				
			Abiotic-low pressure A0	Biotic-low pressure A1	Biotic-low pressure A2	Abiotic-high pressure C0	Biotic-high pressure C1
Ca^{2+}	mg/L	374 ± 50	264	241	251	177	263
Fe (total)	mg/L	52.1 ± 16	4.63	0.11	0.11	< 0.06	< 0.06
K^{+}	mg/L	137.5 ± 19	93.3	79.3	85.6	85.9	85.2
Mg^{2+}	mg/L	119.45 ± 22	93.1	9.81	26	55.3	46
Na^{+}	mg/L	5415 ± 420	6 023	5 719	5 802	5 842	5 791
Cl^{-}	mg/L	8 714 ± 317	8 972	9 038	9 048	9 203	9 314
SO_4^{2-}	mg/L	678.6 ± 180	714	294	507	644.1	304.6
HCO_3^{-}	mg/L	723.05 ± 94	246.51	202.58	153.76	281.90	165.97
Acetate	mg/L	86.5 ±	81.0	112.5	75.1	83.2	89.0

From the abiotic results in this Table, it is observed that an equilibrium is settled when the rock is put in contact with water. Calcium (Ca^{2+}), iron (total Fe), potassium (K^{+}), magnesium (Mg^{2+}) and bicarbonate (HCO_3^{-}) ions concentrations decreased, which indicates some precipitations. Sodium (Na^{+}) and chloride (Cl^{-}) concentrations slightly increased, which testifies some halite dissolution.

In the biotic tests, the decrease in iron (total Fe), sulphate (SO_4^{2-}) and bicarbonate (HCO_3^{-}) ions is higher than in abiotic tests, which highlights additional reactions due to bacteria presence. With bacteria, an increase of acetate could be expected but it was not observed in these experiments.

pH evolution was monitored during the low pressure tests (not possible to sample water during the high pressure tests). Their evolutions are shown in Figure 2.

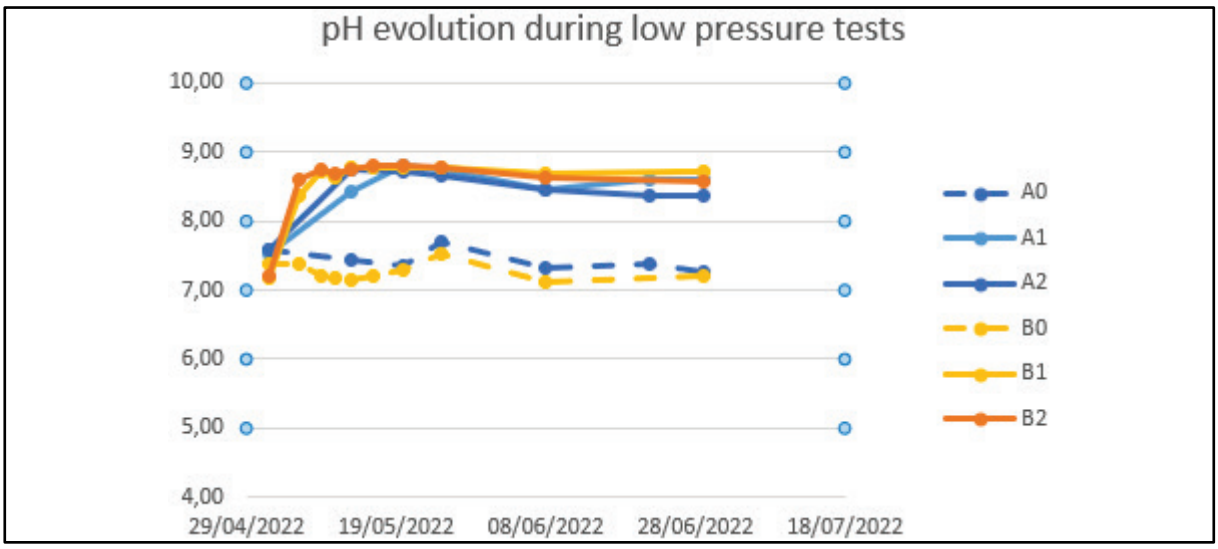


Figure 2: pH evolution during low pressure tests

An increase of pH from about 7.5 to 8.6 is visible in biotic tests (it was 8.4 in biotic high pressure tests). On the contrary, in sterile reactors, pH remained stable. This point highlights the fact that bacteria reactions with hydrogen will induce an increase of pH. This increase is quite fast as it occurs during the first week.

It was also recommended to perform XRD (X-Ray Diffraction) analysis on the rock samples before and after the tests (Table 3).

Table 3: Quantitative mineralogy composition obtained from the XRD analysis performed before and after the laboratory tests

		After the low pressure test A (%)			After the low pressure test B (%)			After high pressure test C (%)	
	Before the test (%)	Sterile control A0	Biotic 1 A1	Biotic 2 A2	Sterile control B0	Biotic 1 B1	Biotic 2 B2	Sterile control C0	Biotic C1
Quartz	37.7	32.3	33.2	35.9	37.5	35.3	37.4	32.3	28.9
Dolomite	10.7	14.0	13.0	12.7	11.7	13.1	12.4	13.0	12.3
Calcite	10.2	13.6	12.2	12.1	12.1	12.0	11.6	13.9	13.7
Plagioclase	10.0	11.6	11.0	11.6	11.4	10.9	11.1	11.3	10.3
Chlorite	14.1	10.8	11.9	10.1	10.3	11.1	9.9	12.2	16.8
Muscovite	9.1	11.3	11.5	10.3	9.8	10.2	10.2	10.5	11.2
K-Felds path	5.5	5.1	5.6	6.0	5.9	5.7	6.1	5.0	5.2
Pyrite	2.3	1.4	1.7	1.4	1.5	1.7	1.4	1.8	1.6

From this Table, it is noticed that the initial cores are composed mainly of quartz (about 38 %). Dolomite, calcite, plagioclase, chlorite and muscovite are also present in proportion of about 10 % each. Last, feldspar and pyrite are detected in lower percentage (6 % and 2 % respectively). It is underlined that this rock contains a high content in carbonate with the presence of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Therefore, a methanogenesis reaction could be expected. The presence of pyrite can also enhance reactions with sulphate reducing bacteria.

After the experiments (58 days for low pressure tests and 70 days for high pressure tests), cores were reobserved with XRD analyses. It was noted that the composition of the cores had slightly changed. Particularly, the percentages of calcite and dolomite had increased after all tests (abiotic or biotic) suggesting precipitation of these two minerals during the experiments, while pyrite proportion had decreased, suggesting dissolution of this mineral.

Concentrations of CH_4 and H_2 in the gas phase were monitored during the tests. Figure 3 shows the evolution of these gases in both low and high-pressure tests.

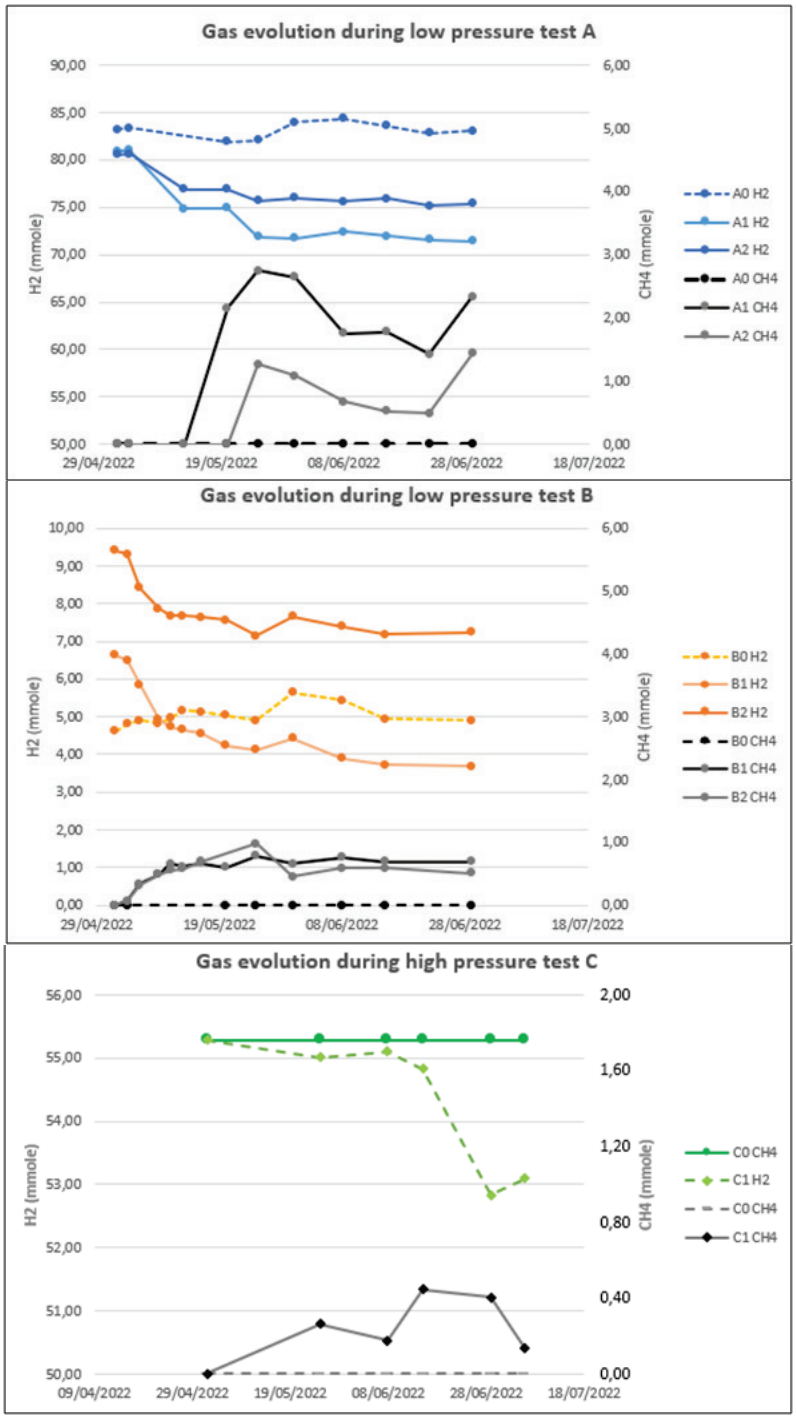


Figure 3: Gas phase evolution during laboratory tests

As displayed in Figure 3, H_2 remained stable and no CH_4 generation was observed in the abiotic tests (A0, B0, C0), showing the absence of H_2 reactivity in the absence of bacteria. On the contrary, in biotic tests (A1, A2, B1, B2 and C1), a decrease of H_2 was observed, as well as the formation of CH4.

Table 4 shows the mmoles of H_2 in the reactor at the end of the test compared to the beginning of the test. The amount of formed CH_4 is also displayed[2]:

Table 4: Decrease in H_2 in the gas phase during the test and concentration in CH_4 in the different laboratory tests.

		H_2 (mmole)	CH_4 (mmole)
Low pressure A	A0	-0.15 *(-0.2 %)*	0
	A1	-9.47 *(-12 %)*	2.12
	A2	-5.16 *(-6 %)*	0.91
Low pressure B	B0	+0.29 *(+6 %)*	0
	B1	-2.95 *(-44 %)*	0.59
	B2	-2.17 *(-23 %)*	0.53
High pressure C	C0	0 *(0 %)*	0
	C1	-2.45 *(-4.4 %)*	0.29

CO_2 contents were also measured in the gas phase during the tests. Only the abiotic tests at low pressure showed some amount of CO_2 formation (with maximal values of 0.51 mmol and 0.22 mmole in test A0 and B0 respectively). This CO_2 could come from water carbon outgassing when the sample is put in contact with a 100 % H_2 gas phase. Outgassing is also expected in biotic tests, but the formed CO_2 could be quickly converted into CH4 by methanogenic bacteria, explaining the absence of CO_2 detection in biotic tests.

Other gases like H_2S were not measured during the tests.

[2] Methane concentration shows some fluctuation during the test probably due to the accuracy of the measurement. In reality, methane formation is irreversible, and it is not expected to take part in other reactions. Therefore, the average measured CH4 during the test is displayed instead of the value at the end of the test.

Last, bacteria content was measured before and after each test in water phase (planktonic bacteria only). Total microbiology was measured by microscopic examination and specific amount of Sulphate Reducing Bacteria, Methanogens Bacteria and Acetogens Bacteria were measured by molecular analyses. Microbiological results are presented in Table 5 for low pressure tests.

Table 5: Bacteria content in water phase measured before and after the low pressure tests

	A1		A2		B1		B2	
	before	after	before	after	before	after	before	after
Total Microbiology (cfu/ml)	1.14E+7	3.73E+7	1.14E+7	3.60E+7	1.14E+7	3.60E+7	1.14E+7	2.80E+7
SRB (gen copies/ml)	3.76	44.3	3.76	68.2	3.76	7.49	3.76	78.6
Methanogens (gen copies/ml)	3.59E+3	4.17E+4	3.59E+3	6.92E+4	3.59E+3	1.43E+4	3.59E+3	7.2.E+4
Acetogens (gen copies/ml)	84.6	34.3	84.6	66.6	84.6	64.5	84.6	60.0

From these analyses, it is observed that the dominant family is the methanogens. Sulphate Reducing Bacteria and Acetogens are also quantified but their concentrations are about 1000 times lower. It is also observed that in all the biotic tests, total microorganisms concentration is growing during the experiment. In 58 days, methanogens and Sulphate Reducing Bacteria are multiplied by about 13. On the contrary, acetogens population has rather decreased.

5. 0D Modelling with PHREEQC

PHREEQC is a computer programme for simulating geochemical reactions and transport processes in natural water or laboratory experiments. The first version of the programme was developed by David L. Parkhurst and C.A.J Appelo in 1995. The version 3 of PHREEQC has been used to model the chemical reactions observed during the laboratory tests.

5.1. Microbial kinetics

Microbial cells use nutrients for growth, energy production and product formation.

Cell increase rate is defined by:

$$dX/dt = \mu X$$

where:

- μ is the specific growth rate, characteristic of a particular bacteria species.
- X is the cells concentration.

Cell growth can also be expressed as a function of substrate consumption. Rates of substrate consumption are generally proportional to the concentrations of cells capable of degrading the substrate and also depend on the substrate concentration.

$$\frac{dX}{dt} = -Y\frac{dS}{dt}$$

where:

- Y is the Yield factor (mass new cells /mass substrate) which expresses how much of substrate is converted to biomass.
- S is the substrate concentration.

Several kinetic models have been developed to describe this type of substrate-based growth.

The most widely used expression for describing microbial growth rate as a function of substrate concentration is attributed to Monod. It is:

$$\mu = \mu_{max}\frac{S}{(Ks + S)}$$

where:

- μ is the growth rate of a microorganism.
- μ_{max} is the maximum growth rate of this microorganism.
- K_s is the "half-velocity constant" i.e. the value of [S] when $\mu/\mu_{max} = 0.5$.

Combining the above equations gives:

$$\frac{dS}{dt} = -\frac{dX}{dt\,Y} = -\frac{\mu X}{Y} = -\mu_{max}\frac{S}{(Ks + S)}\frac{X}{Y}$$

If μmax/Y = Kmax (maximum substrate utilisation rate), then the rate of substrate utilization (-dS/dt) can be expressed as a function of substrate concentration and the cell concentration:

$$-\frac{dS}{dt} = K_{max}\frac{S}{(Ks+S)}X$$

And the cell growth is given by:

$$\frac{dX}{dt} = -Y\frac{dS}{dt} - DX$$

Where D is the biomass decay coefficient (also called maintenance rate).

These equations can be solved with PHREEQC.

5.2. Model set up

5.2.1. BIOCHEMICAL REACTIONS

As explained in chapter 4, the oxidation of H_2 by HCO_3 or SO_4 has been observed and measured during the laboratory tests:

$$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$$

$$4\,H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$$

These irreversible reactions, catalysed by microorganisms, are kinetically controlled in the PHREEQC model using the Monod type equation developed in previous chapter.

HCO_3^- utilization rate:

$$\frac{d\,HCO3-}{d\,t} = K_{max}\,[X]\left(\frac{[HCO3-]}{Ks_{\,HCO3-} + [HCO3-]}\right)\left(\frac{[H2]}{Ks_{H2} + [H2]}\right)$$

Methanogenic cell growth rate:

$$\frac{d\,X}{d\,t} = -Y\frac{d\,HCO3-}{d\,t} - D[X]$$

Where X is the biomass, Kmax is the maximum substrate utilization rate, and $KsHCO_3^-$ and KsH_2 are the half-saturation constants, Y is the yield rate and D is the biomass decay coefficient.

The same equations can be used to express sulphate reduction (sr) reactions:

$$\frac{d\,SO4^{2-}}{d\,t} = K_{max}\,[X_{sr}]\left(\frac{[SO4^{2-}]}{Ks_{SO4^{2-}} + [SO4^{2-}]}\right)\left(\frac{[H2]}{Ks_{H2} + [H2]}\right)$$

$$\frac{d\,Xsr}{d\,t} = -Y_{sr}\frac{d\,SO4-}{d\,t} - D_{sr}[X_{sr}]$$

The values of Kmax and Ks can be estimated from the laboratory tests results and then adjusted with PHREEQC to match the laboratory observations regarding the different substrate consumption rates. Table 6 and Table 7 report the values that have been retained in the model for methanogenesis and sulphate-reduction, respectively. It can be observed that the substrate consumption rates are higher at low pressure than at high pressure.

Table 6: Values of Kmax, Y and Ks for methanogenesis estimated from the laboratory tests

	Low pressure	High pressure
Kmax (mol/l/s)	7.5×10^{-6}	3.2×10^{-7}
KsH_2 (mol/l)	1.5×10^{-4}	2.5×10^{-3}
$KsHCO_3$ (mol/l)	1.5×10^{-4}	0.01
Y	4×10^{-6}	2.5×10^{-5}

Table 7: Values of Kmax, Ysr and Ks for sulphate-reduction estimated from the laboratory tests

	Low pressure	High pressure
Kmax (mol/l/s)	4×10^{-3}	4.7×10^{-5}
KsH_2 (mol/l)	2.5×10^{-3}	2.5×10^{-3}
$KsSO_4$ (mol/l)	0.01	4.5×10^{-3}
Ysr	2.5×10^{-7}	4×10^{-7}

Effects of pH on bacteria growth

Besides substrate availability, bacteria growth is also affected by environmental factors such as temperature, salinity, pressure and pH. While the first three factors are kept relatively constant throughout the tests, the pH value varies significantly.

Most methanogens and sulphate reducing bacteria are adapted to a pH of 6.5 to 7.5 and cannot grow outside a pH range of 4 - 9.5 (Thaysen, 2021). Thus, it is expected that as the pH grows in the experience, the microbial activity will decrease.

The pH effect on bacteria has been studied in the frame of Work Package 3. In a parallel test using the core and formation water of the same underground storage site, the effect of different pH values in H_2 consumption by microorganisms was tested (Figure 4). The most important consumption was observed at pH 7, and then it decreased, with very small activity detected when the pH was higher than 10.

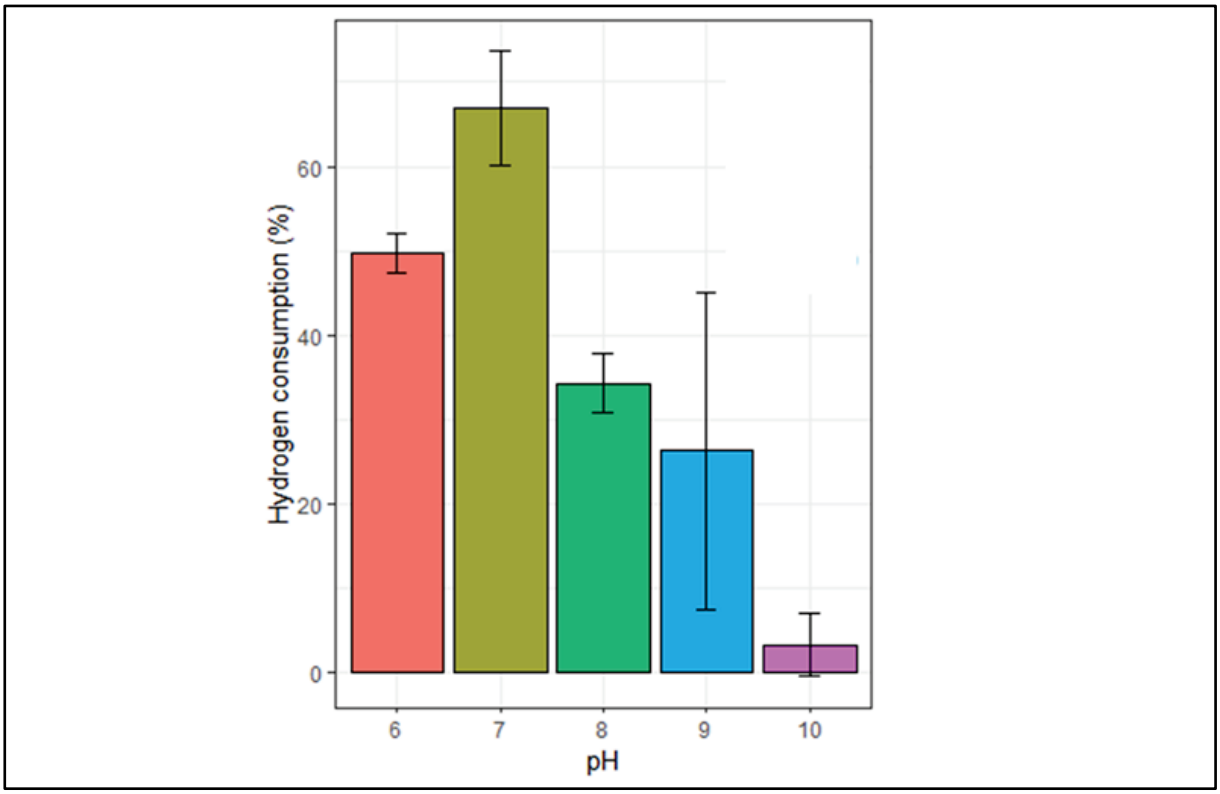


Figure 4: Hydrogen consumption at different pH values, based on MICROPRO laboratory experiments

This observed pH effect has been considered in the model: the substrate utilization rate is maximal when pH is 7, but it is lowered when the pH is higher or smaller than 7 (proportionally to the measurements in the laboratory).

What is more, regarding sulphate reduction, it can be observed in the different tests that if the pH becomes higher than 8.7, sulphate concentrations do not decrease anymore, suggesting that sulphate reduction reaction is inhibited or significantly slowed down. This pH condition has also been considered in the PHREEQC model.

Biomass measurement

Biomass has been measured in the laboratory in cells/ml. To use the equations described previously, biomass must be converted into mol/l. For this conversion, it has been assumed that a simple bacterial cell (CH_2O) contains 10^{-14} mol carbon (Appelo and Postma, 2005). Therefore, the number of cells/ml can be easily converted into mols C/l ≈ mols cells/l.

Another difficulty for the model is the accuracy of the measurement of cell number in the laboratory. The total cells in measured at the beginning and at the end of the tests (and at each gas sampling step in the low-pressure tests) by microscopic counting with Thoma chamber. This method does not allow the distinction between death cells and alive cells. It is also not possible to know whether all living cells are metabolically active cells (under unfavourable environmental conditions, cells might not die but have reduced metabolisms). Finally, only planktonic cells are counted in the laboratory (cells present in the liquid phase). Sessile cells (which form biofilm and are also metabolically active) were not measured. However, biofilm formation though the experiment cannot be excluded, meaning that the total number of cells could be underestimated specially at the end of the tests.

One last consideration for the modelling is the cells mortality. As explained previously, the cell growth is expressed as:

$$\frac{d\,X}{d\,t} = -Y\frac{d\,HCO3-}{d\,t} - D[X]$$

Where D is the biomass decay coefficient, which relates to cell mortality. In the model, D is considered to be equal to 0, which is conservative (cells do not to die, even in the case of substrate depletion).

After the first reactions with methanogens and sulphate reduction bacteria, it is possible to observe secondary reactions with other types of bacteria, especially when the first generation of bacteria has achieved its mortality. These secondary reactions were not taken into account in the models.

PHREEQC Database

To simulate a microbial kinetics on the sulphate-reduction and methanogenesis terminal electron accepting reactions in solution it is necessary to use an uncoupled thermodynamic database. In this database, the species that can present various redox states are duplicated to oxidized and reduced species. Dealing now with different species, PHREEQC can consider a reaction between these species and include a kinetic control. The thermodynamic database established in WP2 was used for these calculations (Hystories D2.4).

5.2.2. GEOCHEMICAL REACTIONS

As explained in chapter 4, the core used in the tests contains carbonate minerals namely dolomite and calcite. These minerals are expected to react with the formation water in precipitation/dissolution reactions, eventually providing a source of carbon to microorganisms and maintaining the methanogenesis reaction over time.

The geochemical reactions involving calcite, dolomite and pyrite have been considered in the model and are kinetically controlled. Thanks to the XRD analysis, the initial amount of minerals that can react is available. The kinetics are taken from the research work carried out in WP2 and are described in the report D2.4.

The initial solution composition corresponds to the composition measured at the beginning of the laboratory experiments (Table 2). It is underlined that these laboratory tests and modelling were carried out at a specific salinity: 16 300 mg/l. Bacteria development and reactivity are highly dependent on salinity. Therefore, the model and kinetics presented below are valid only for this range of salinity.

Below 15 g/l, most of the time, methanogenesis is the dominant reaction. Above 15 g/l, methanogens bacteria have more difficulty to develop, and sulphate reduction becomes more active. In our selected case, methanogens and sulphate reduction bacteria are still in competition.

5.3. Model results

5.3.1. HIGH PRESSURE TEST

High pressure tests (“tests C”) were carried out at 27 bar and lasted 65 days. During the tests, H_2 and CH_4 concentrations in gas phase were measured regularly. The high-pressure reactors do not allow for water sampling during the experience, therefore, pH, ions concentrations and bacteria concentration in water are only available at the beginning and at the end of the tests.

Abiotic Test

In the abiotic test, sterilised formation water was put in contact in the reactor with the core and a hydrogen gas phase.

During this test, no hydrogen consumption was observed, nor methane generation (Figure 5). The model also predicts the absence of hydrogen reactivity, and no CH_4 or H_2S generation. Only some CO_2 appears in the gas phase, because of water sample carbonates outgassing when the sample is put in contact with a 100 % hydrogen atmosphere.

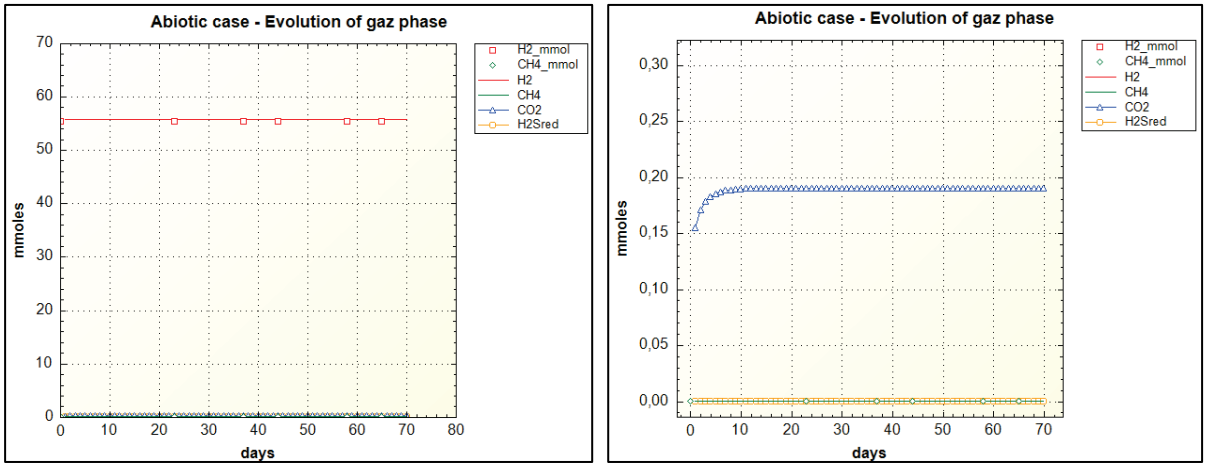


Figure 5: Abiotic test at high pressure. Evolution of the gas phase

As explained in chapter 4, the XRD analyses showed some precipitation of calcite and dolomite. This precipitation is also predicted by the model (Figure 6).

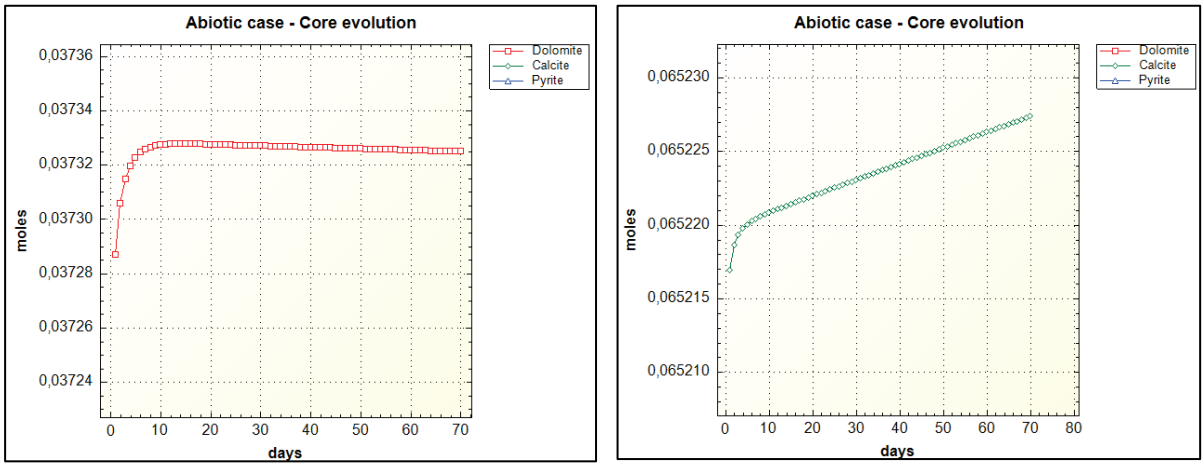


Figure 6: Abiotic test at high pressure - Evolution of the solid phase

According to the model, calcite precipitates all along the test, forming 1 x 10^{-5} moles of new calcite. Dolomite precipitates during the first 10 days of the test. Afterwards, the tendency is reversed and dolomite dissolution starts, but overall, the formation of 3.8 x 10^{-5} moles of dolomite during the test is predicted by the model.

Unlike calcite and dolomite, the model does not predict any pyrite precipitation or dissolution during the test.

Biotic Test

In biotic test, the formation water is enriched in methanogenic bacteria, then put in contact with the core and H_2 gas phase in the high-pressure reactor.

The evolution of the gas phase predicted by the model is displayed in the Figure 7, together with the values measured in the laboratory during the tests.

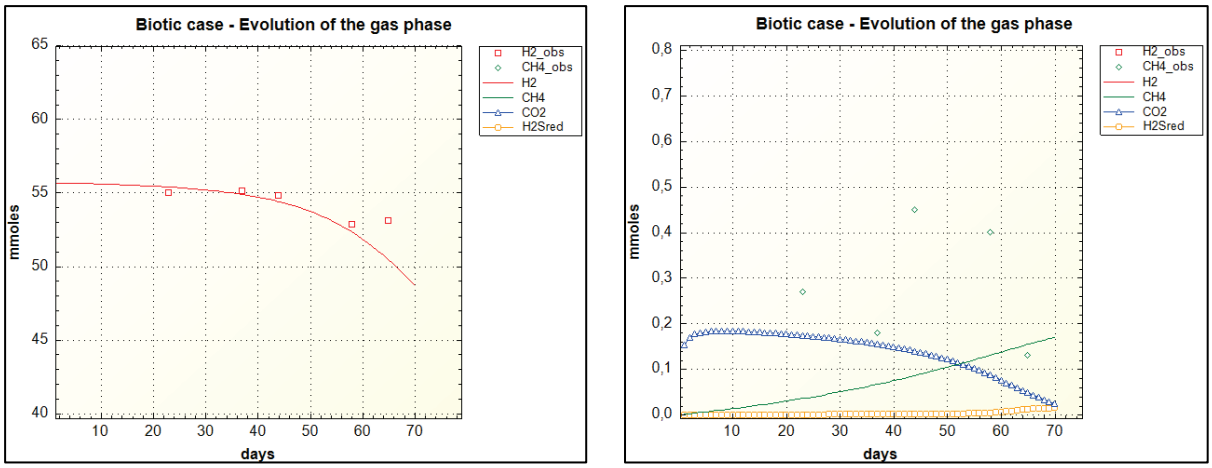


Figure 7: Biotic test at high pressure: Evolution of the gas phase

During the experiment, a H_2 consumption of about 5 % in total was observed, with an acceleration of consumption after day 47. This trend is reproduced by the model, with a relatively low consumption of H_2 during the first half of the test, then an acceleration of H_2 decrease until the end. Between day 58 and day 65, the model predicts though a higher H_2 consumption than observed in the laboratory measurement.

According to the model, methane formation by methanogenic bacteria is lower than the average amount measured during the test (0.29 mmol) but remains within the range of observed values.

The generation of some CO_2 is predicted at the beginning of the test, because of carbon outgassing from the water sample when the sample is put in contact with the H_2 gas phase. However, this CO_2 generation was not observed during the experiment.

The generation of some H_2S is also expected by the model, because of sulphate reduction reactions. At the end of the test, 1.5 $x10^{-5}$ moles of H_2S would be created. Considering the moles of H_2 in the reactor at the end of the test (4.87 x 10^{-2} moles), the concentration of H_2S would be around 5300 ppm. During the laboratory test, the concentrations of H_2S were not measured.

This concentration of H_2S predicted by the model is high, but it is reminded that the sulphate consumption in the water phase during the test was very important (concentrations went down from 860 mg/l to 304.6 mg/l in the biotic test, which is equal to a consumption of 9.2 x 10^{-4} moles of SO_4). In the model, the sulphur mass balance is equilibrated as shown in Table 8.

Table 8: Consumed moles of sulphate and produced moles of sulphide and gaseous H_2S in the model at high pressure

	Moles
Sulphate consumption	7.72 x 10^{-4} mol
Sulphide generation (liquid phase)[3]	7.56 x 10^{-4} mol
H_2S generation (gas phase)	1.53 x 10^{-5} mol

However, the model does not take into account other reactions where the generated HS^-/H_2S could take part. These reactions such as bacterial or chemical sulphur oxidation to elemental sulphur or SO_4^{-2} are supposed negligible as they require oxygen, which is in very low quantity in the underground storage. Furthermore, the reduction of sulphates to thiosulphates or elemental sulphur has not been considered in the simulation. Therefore, the final generation of H_2S could be overestimated.

Figure 8 displays the evolution of ions concentration in water and pH evolution:

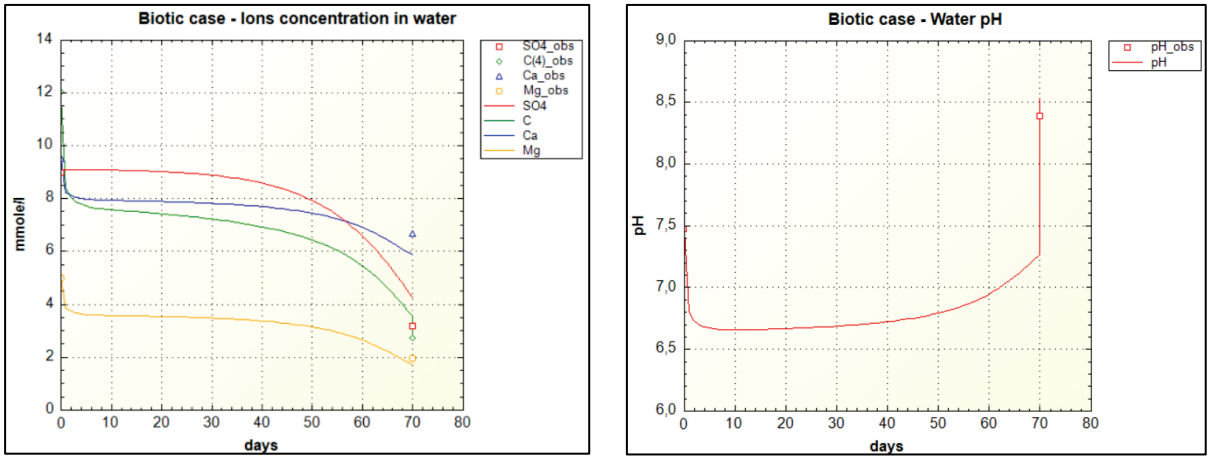


Figure 8: Biotic test at high pressure: evolution of water phase

The model predicts an important decrease of calcium, magnesium and carbonates at the beginning of the test. As mentioned before, carbonates decrease can be explained by water sample outgassing, but also by precipitation reactions along with Ca^{2+} and Mg^{2+} to form calcite and dolomite respectively. [4] It is reminded that precipitation reactions are also observed in abiotic tests.

[3] Mainly HS-, but also other compounds bearing Sulphur (-2)

[4] It is reminded that formation water was not in equilibrium with the core, as water was sampled many years after the core drilling. This explain the quick precipitation of ions when the water sample is put in contact with the core.

After day 4, the reduction of Ca^{2+}, Mg^{2+} and carbonates keeps going but slows down, as the precipitation reactions take place at a lower rate. In addition, as methanogenic bacteria grow, they also consume carbonates and H_2 to generate CH_4.

Regarding SO_4, the observed concentration decrease is explained by bacteriological sulphate reduction. As these bacteria grow, the rate of sulphate depletion increases, to reach a maximum rate at the end of the test.

Because of the precipitation reactions at the beginning of the test, the model predicts an initial decrease of pH value from 7.5 to 6.6. As the bacteria grow and the methanogenesis and sulphate-reduction reactions become predominant, the pH starts to increase, and reaches a value of 7.2 at the end of the test.

However, the measured value at the end of the test was 8.4, far from the predicted value of 7.2. A hypothesis to explain the difference between these two values could be the pH measurement conditions in the laboratory. During the pH measurement, water sample could have been put in contact with the atmosphere, and therefore, the CO_2 partial pressure of the sample would equilibrate with atmospheric CO_2. Since the partial pressure of CO_2 at the end of the test (1.37×10^{-2} atm) is higher than atmospheric CO_2 partial pressure ($\approx 3 \times 10^{-4}$ atm), an outgassing of CO_2 can be expected during the measurement, which would increase the pH value of the water sample. This eventual outgassing has been simulated with PHREEQC: when the water sample is equilibrated with atmospheric CO_2, the model predicts an increase of pH up to 8.5, very close to the observed value (8.4). Likewise, the carbonate concentration in water decreases from 3.5 mmol/l to 2.71 mmol/l (the measured value at the end of the test being 2.72 mmol/l).

Regarding bacteria, the model predicts an increase of active methanogenic bacteria from 1.2×10^{-4} mol/l (i.e. 1.2×10^{7} cells/ml) to 5.2×10^{-4} mol/l (5.2×10^{7} cells/ml). Sulphate reducing bacteria also grow. from 1.2×10^{-7} mol/l (1.2×10^{4}cells/ml) to 2.7×10^{-5} mol/l (2.7×10^{6} cells/ml). In the laboratory, the total number of cells of the sample were measured at the beginning of the test (1.25×10^{7} cells/ml) and at the end (1.73×10^{7} cells/ml). Comparison is made in Figure 9. This total number of cells includes both methanogenic and sulphate reducing bacteria. However, as the water sample was enriched only in methanogenic bacteria, it can be assumed that most of these measured cells would be methanogenic.

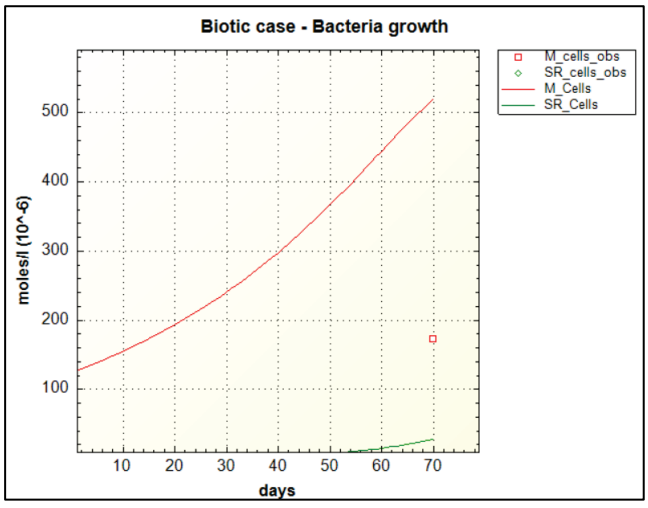


Figure 9: Biotic case at high pressure: active bacteria development

The laboratory also analysed the sulphate reducing bacteria and methanogenic bacteria gen copies at the beginning and at the end of the tests. While gene copies cannot be directly translated into cell numbers, they allow to estimate the proportion of one type of bacteria related to the other. According to gene copies analyses, methanogenic bacteria were about 1000 times more important than sulphate reducing bacteria both at the beginning and at the end of the test.

The PHREEQC model results keep constant this ratio between methanogenic and sulphate reducing bacteria. The bacteria count at the end of the tests seems a little too high compared to the measured value but remains in the observed range. As explained in chapter 5.2.1, the cells count in the laboratory includes only planktonic cells and no sessile cells (cells forming the biofilm, which are also active and consume H_2). Therefore, the measured value in the laboratory could be underestimated, explaining the difference between the model values and the observed values.

5.3.2. LOW PRESSURE TEST

Low pressure experience was performed at 2 bar pressure and lasted 58 days. As mentioned in chapter 4, two different type of tests were carried out (tests A and tests B) in two different size reactors. However, only the tests performed in the high size reactor (test A0 and A1) have been modelled with PHREEQC, since ions concentration in water are only available for these tests.

Abiotic Test

In abiotic test, hydrogen remained stable, and no methane generation was observed in the laboratory. As shown in Figure 10, the PHREEQC model reproduces these results.

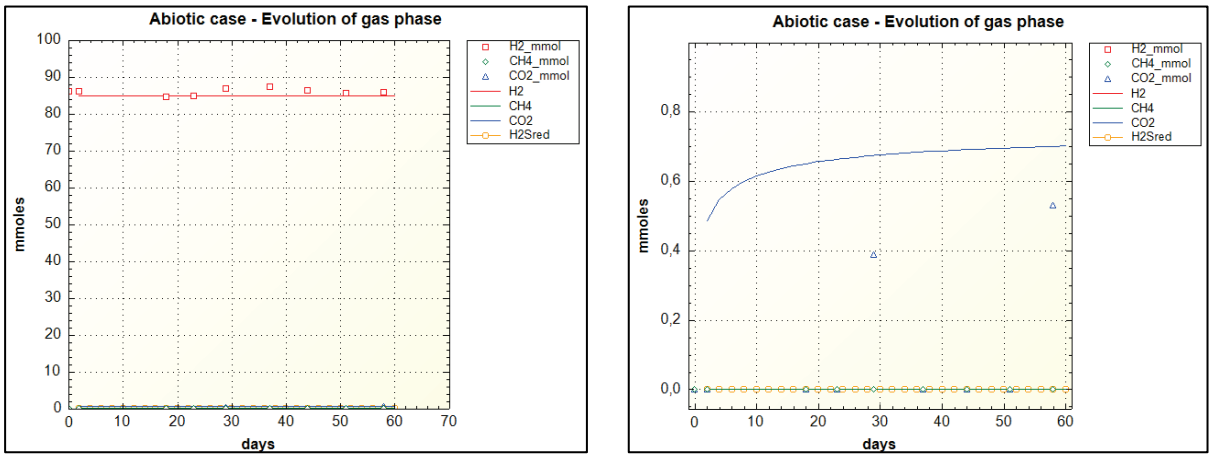


Figure 10: Abiotic test at low pressure: evolution of gas phase

The formation of CO_2 is predicted by the model, and unlike other tests, this CO_2 was also observed in the laboratory. The model does not predict the creation of any methane or H_2S.

Like in high pressure tests, dolomite and calcite precipitate during the test (Figure 11):

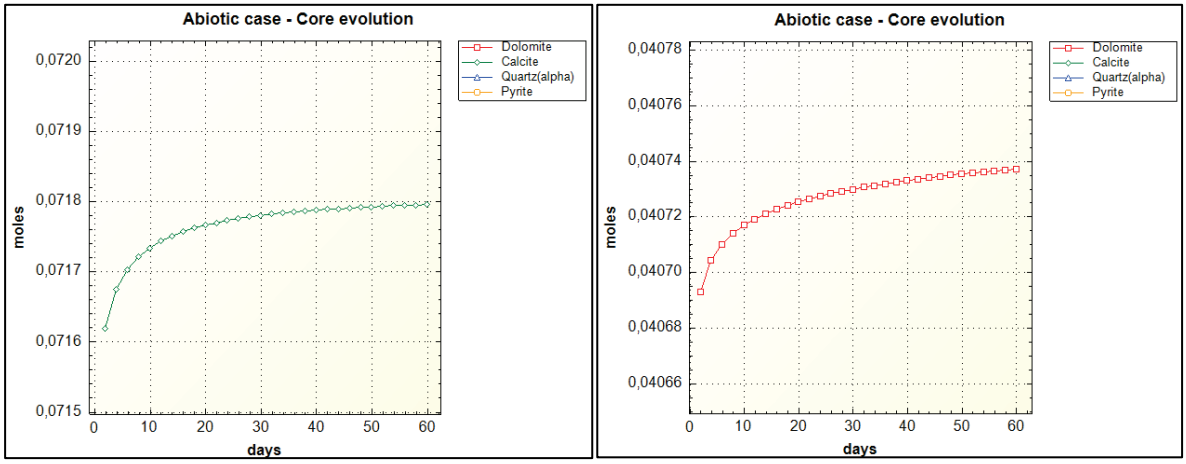


Figure 11: Abiotic test at low pressure: evolution of the solid phase

According to the model, 2.4 x 10^{-4} moles of calcite and 5.7 x 10^{-5} moles of dolomite would precipitate (higher amounts than in high pressure tests).

It is reminded that in the laboratory, precipitation was also observed through the core XRD analyses.

Biotic Test

In biotic test, formation water was enriched in methanogenic bacteria and then put in contact in the low pressure reactor with the core and the H_2 gas phase.

The gas phase evolution during the test is displayed in Figure 12:

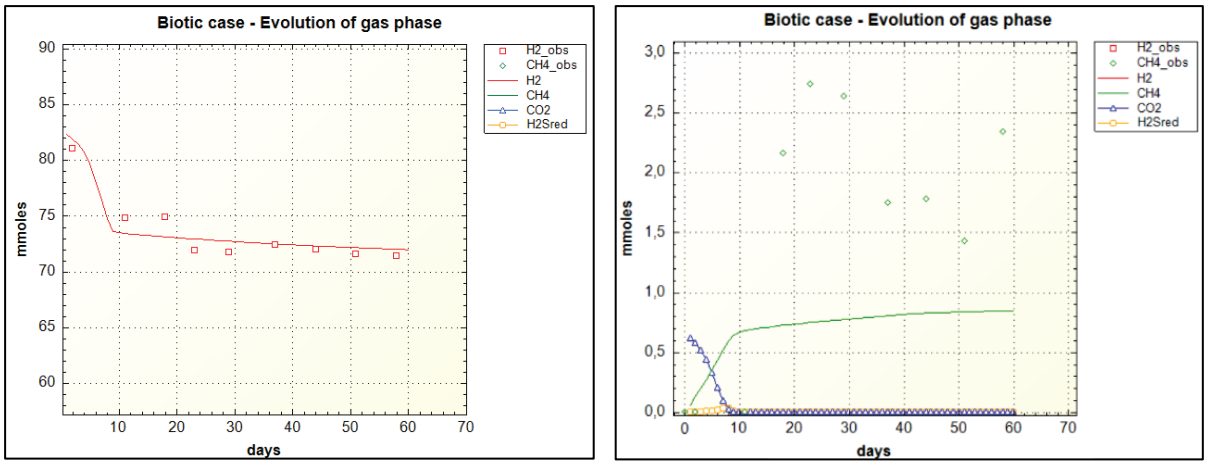


Figure 12: Biotic case at low pressure: evolution of the gas phase

At low pressure, H_2 consumption is more important than at high pressure, with a fast decrease observed over the first 10 days. At the end of the test, the laboratory measured a reduction of 12 % of the H_2 contained in the reactor, while the model predicts a reduction of 12.5 %.

As for the high pressure test, some CO_2 appears in the gas phase because of water outgassing in the reactor when put in contact with a 100 % H_2 atmosphere. This CO_2 is quickly transformed into CH_4 by bacterial methanogenesis reaction. However, methane generation in the simulations is low compared to the observed values in the laboratory: the formation of 0.85 mmol of CH_4 are predicted by the model, while the laboratory measured a maximal value of 2.7 mmol of CH_4, with an average value of 2.1 mmol.

Nevertheless, looking at the available data from the laboratory, the carbon balance does not seem completely equilibrated: too much methane seems to be generated (2.1 mmol in average) compared to the measured diminution of carbonates in water (1.5 mmol). A possible dissolution of calcite and dolomite could have provided additional carbonates for the methanogenesis reaction, but according to the model and the XRD analyses, in the short term only precipitation reactions would take place. Therefore, eventually there could be some uncertainty with the carbonates' measurement in water, which disequilibrates the balance, and prevents a more important methane generation in the model.

The model also predicts the formation of some H_2S, with a maximum value of 0.031 mmol, reached at day 9 (Figure 13). The H_2S decreases afterwards (6×10^{-4} mmol at the end of the tests). This H_2S decrease begins when most of sulphate reducing bacteria become inactive and stop SO_4 consumption, because of pH increase (Figure 15). This decrease in H_2S is likely related to a re-equilibration between the gas phase and the water phase, as the total pressure decreases.

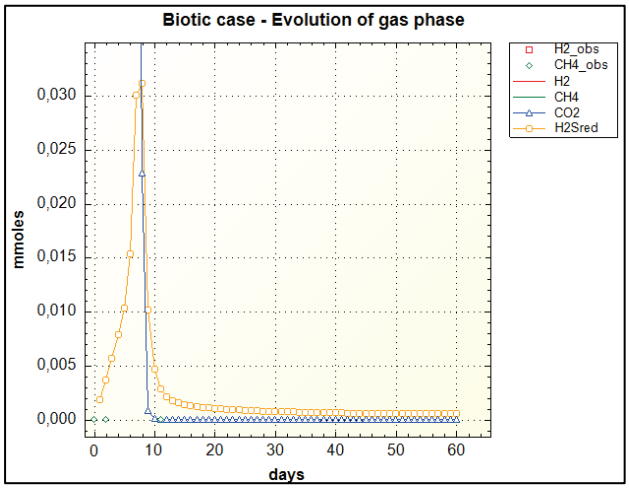


Figure 13: Biotic case at low pressure: H_2S in gas phase

Regarding the ions in water, a quick decrease of calcium, magnesium and carbonates is observed at the beginning of the test because of precipitation reactions and carbon outgassing as CO_2 (Figure 15). As it happens in the high-pressure test, the rate of ion depletion slows down afterwards but keeps going because of calcite and dolomite precipitation and because of bacterial methanogenesis. Once all the carbonates in water have been depleted, Ca^{2+} and Mg^{2+} precipitation stops as they cannot form calcite and dolomite anymore, and dissolution of the dolomite starts (Figure 14), increasing Ca^{2+} and Mg^{2+} contents in water. Dissolution of dolomite also provides carbonate to bacteria, so that the methanogenesis reaction can keep going to a certain extent, which explains the small but continuous decrease of H_2 in the gas phase.

SO_4 is not involved in precipitation reactions but it is reduced quickly by bacteria. However, as discussed in chapter 5.2.1, sulphate reduction is importantly slowed down when pH becomes higher than 8.7. This explains the inflection point in Figure 15 at day 9. After that, the sulphate consumption keeps going but at a much smaller rate.

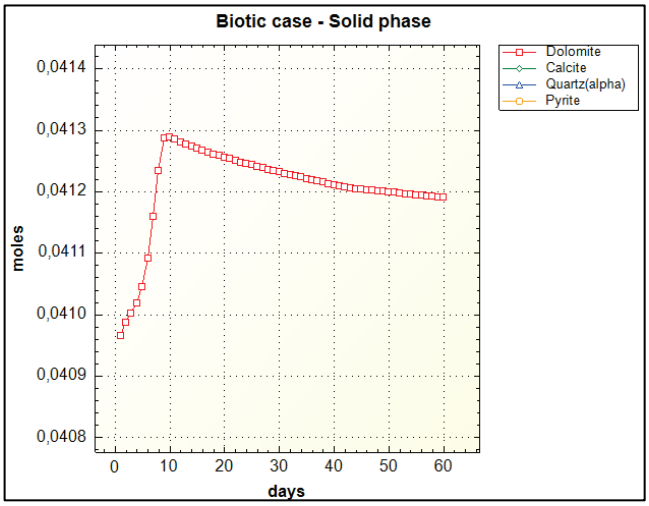
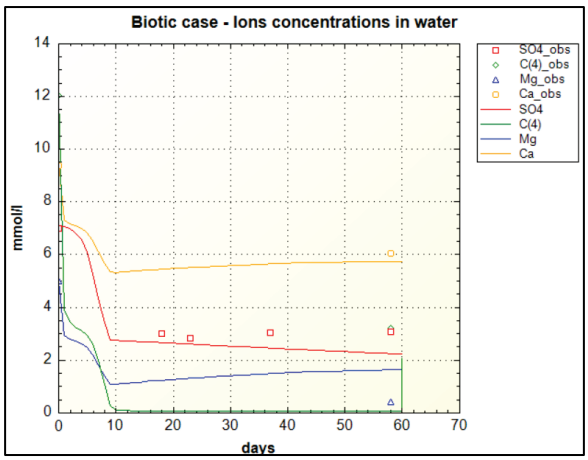


Figure 14: Biotic case at low pressure: evolution of dolomite



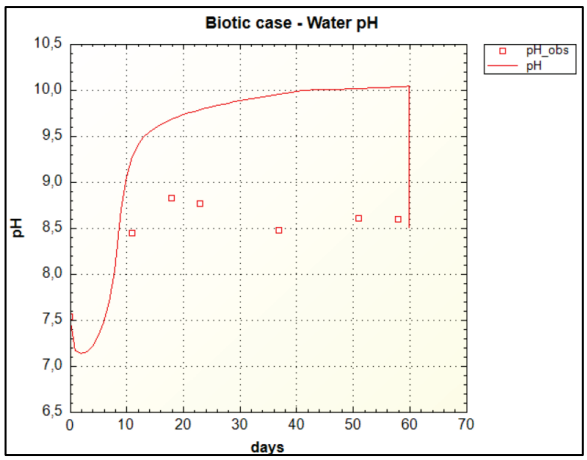


Figure 15: Biotic test at low pressure: evolution of the water phase

The predicted pH values by the model do not match accurately the measured values (Figure 15). The model predicts a pH increase up to 10.1 at the end of the test, while the value measured by the laboratory was 8.59. As in high pressure test, the hypothesis to explain this would be the re-equilibrium of CO_2 partial pressure of the water sample with atmospheric CO_2 during pH measurement. Since in low pressure test, the CO_2 partial pressure is very small (2.3×10^{-8} atm), dissolution of atmospheric CO_2 in water sample in expected, decreasing water pH. When this process is simulated with PHREEQC, the pH value decreases to 8.5, very close to the measured value. Likewise, the carbonate concentration in water increases from 0.046 mmol/l at the end of the tests to 2 mmol/l after the measurement (which is still a bit low compared to the measured value of 3.2 mmol/l, and once again, could be due to the inaccuracy of the carbon balance).

Finally, regarding bacteria, methanogenic bacteria grow quickly up to day 10 (Figure 16). Once the available carbonates in water have been consumed, bacteria growth is heavily slowed down, and can only be sustained by the slow dissolution of dolomite that provides a source of carbon. It needs to be pointed out that the model does not consider any bacteria mortality, and therefore their concentrations remain constant. Once the substrate has been mostly consumed, bacteria concentrations should decay.

In the same way, sulphate reducing bacteria grow quickly up to day 9. After that, pH becomes unfavourable, and the cells growth is slowed down importantly. As it happens with methanogenic bacteria, no bacteria mortality has been considered in their kinetics.

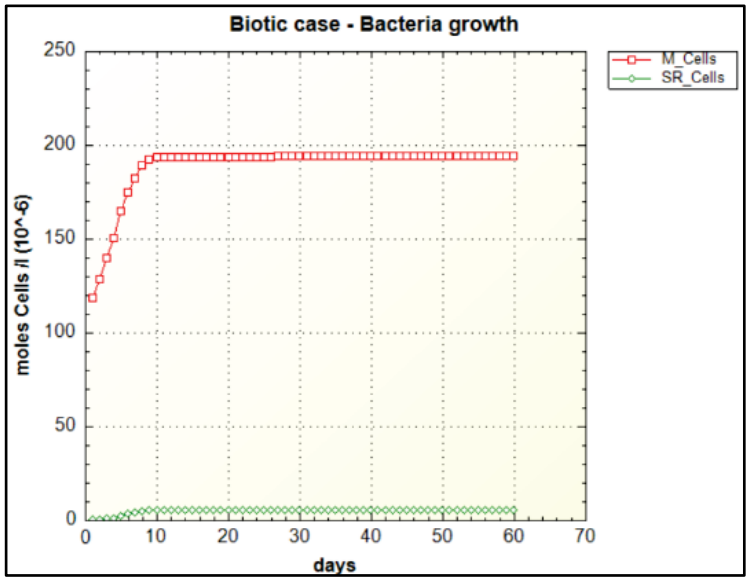


Figure 16: Biotic case at low pressure: active bacteria development

5.4. Intermediate conclusion on the modelling of laboratory test experiments

Laboratory tests of H_2 consumption in presence or in absence of bacteria were satisfactorily simulated. A biogeochemical model accounting for microbial kinetics on aqueous redox reactions induced by H_2 was established for this purpose. Model confirms that methanogenesis and sulphate-reduction reactions are responsible of the measured gas phase and solution composition evolution. Indeed, the decrease of H_2 and increase of CH_4 in the gas phase and the decrease of dissolved carbonates and sulphates can only be reproduced by simulating methanogenesis and sulphate-reduction reactions. The role of bacteria is crucial for the occurrence of these reactions and is proved by the fact that no H_2 is consumed in absence of methanogenic and sulphate-reducing bacteria. The model was also able to identify calcite and dolomite precipitation and an experimental artefact could be responsible of the evolution of some chemical parameters (pH and Ca, Mg and HCO_3^- concentrations).

The simulation of the laboratory tests allowed the determination of kinetic parameters to match the microbial catalysis of methanogenesis and sulphate-reduction reactions under H_2-rich conditions, at reactor scale. These kinetic parameters can now be used to estimate the microbial risk of H_2 consumption at reservoir scale.

It needs to be reminded that the kinetics measured in the laboratory represent the optimal conditions for bacteria growth and H_2 consumption, while at reservoir scale, the kinetics can be orders of magnitude lower because of the less favourable conditions and the multitude of bio-geo-chemical reactions that can take place. An approach for converting laboratory rates into expected reservoir rates is presented in next section.

6. 3-D Modelling

6.1. Methodology

STARS™ is a 3-D 3-phases compositional model design for the advanced modelling of recovery processes involving the injection of steam, solvents, air and chemicals. STARS™ was developed to model thermal processes (SAGD, expanding-solvent/hybrid SAGD, steam flooding, CSS, thermal VAPEX, air injection) and chemical EOR processes (emulsions, gels, foams, ASP, microbial EOR, VAPEX, low salinity waterflooding) for oil and gas. A key feature of STARS™ is the possibility to define reaction in any phase (gas, oleic, aqueous) between user defined components such as a reaction induced by bacterial activity. STARS™ has already been used to model sulphate-reduction microbial reaction [Coombe *et al.*, 2004]. In addition, recent developments include modelling the aqueous chemical equilibrium and heterogeneous kinetic reaction between minerals and aqueous ions. However, this is the first modelling attempt combining user-defined and geochemical reactions. As such, to extend this modelling approach to field cases, further validation would be required.

The modelling concept to bacterial reactivities assumes the reaction should occur at the interface between hydrogen and brine based upon qualitative laboratory experiences. Consequently, to enable localized reactions, bacteria concentration is defined spatially within the model. As detailed in the following sections, integrating the bacteria reactivity would then link the bacteria concentration to the amount of dissolved carbon (CO_2) and sulphate (SO_4) without interfering with other reactions.

6.1.1. Methanogenesis reaction

Due to STARS™ constraints which cannot directly handle Monod-type reactions, it is not possible to model the methanogenesis reaction as defined in PHREEQC (see section 5.1). Thus, the methanogenesis reaction is combined with the dissociation of CO_2 in the water phase:

$$\left.\begin{array}{c} 4H_2 + HCO_3^- + H^+ \xrightarrow{Mt\_bacteria} CH_4 + 3H_2O \\ CO_2 + H_2O \rightarrow HCO_3^- + H^+ \end{array}\right\} \Leftrightarrow 4H_2 + CO_2 \xrightarrow{Mt\_bacteria} CH_4 + 3H_2O$$

The reactant components are then CO_2, H_2 and the product components are CH_4 and H_2O.

The reaction rate is determined from the PHREEQC modelling. Gas water equilibriums of the components (CO_2, H_2, CH_4) are defined through equilibrium constant tables as a function of pressure and temperature.

The reaction is approximated in STARS™ by a

$$K = K_{max} \frac{1}{(1+\alpha[H_2])^{\beta}} [Mt_{bacteria}][CO_2]$$

with α and β adjusted to match $\mu_{H_2} = \frac{[H_2]}{Ks_{H_2} + [H_2]}$ and $[Mt\_bacteria]$ being the concentration of methanogenesis bacteria.

The bacterial growth is obtained by integration of the bacteria reaction, i.e. the concentration of bacteria is assumed to be proportional to the amount of dissolved CO_2:

$$[Mt\_bacteria] = Y * [CO_2] * \frac{1}{(1 + \alpha[H_2])^{\beta}}$$

with α and β are ajusted to match $\mu_{HCO_3^-} = \frac{[HCO_3^-]}{Ks_{HCO_3^-} + [HCO_3^-]}$ and $[Mt\_bacteria]$ is the concentration of methanogenesis bacteria.

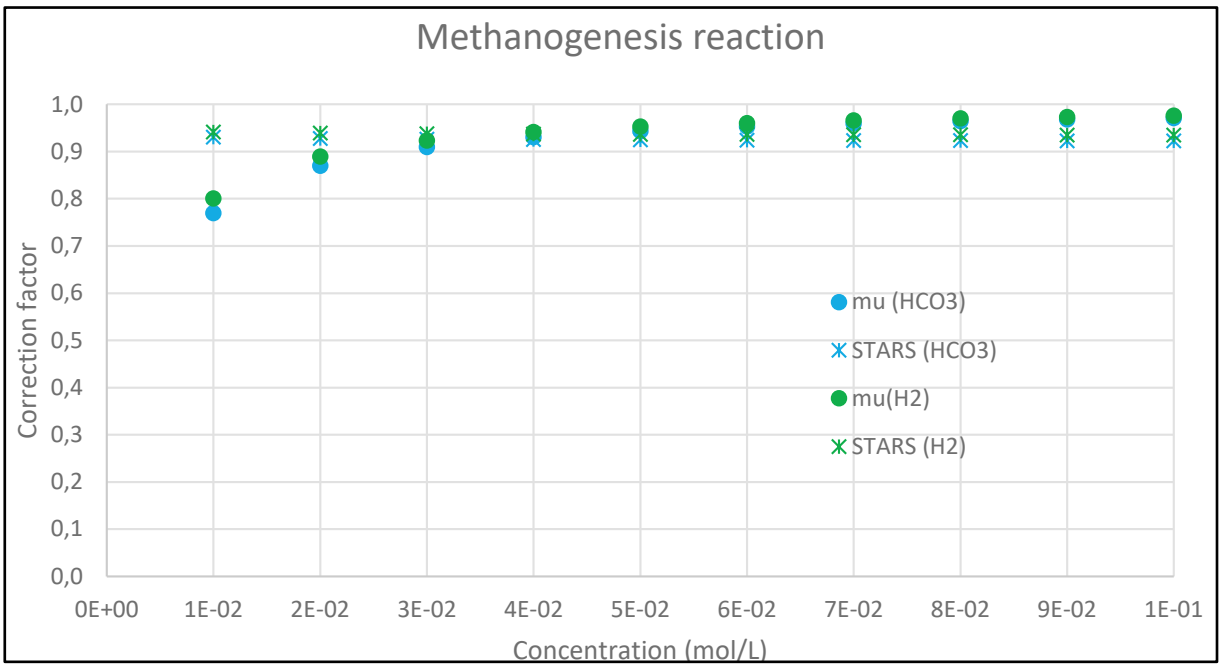


Figure 17: Comparison of STARS™ and Monod correction factors for the methanogenesis reaction

Given the different mathematical expressions, the agreement is diverging at low concentrations as shown in Figure 17.

6.1.2. Sulphate reduction reaction

Due to STARS™ constraints which cannot directly handle Monod-type reactions, it is not possible to model the sulphate reduction reaction as defined in PHREEQC (see section 5.1). Thus, the sulphate reduction reaction modelled in PHREEQC is combined with the hydrosulphide reaction as follows:

$$\left.\begin{array}{l} 4H_2 + SO_4^{--} + H^+ \xrightarrow{SR\_bacteria} HS^- + 4H_2O \\ HS^- + H^+ \rightarrow H_2S \end{array}\right\} \Leftrightarrow 4H_2 + SO_4^{--} + 2H^+ \xrightarrow{SR\_bacteria} H_2S + 4H_2O$$

The reactant components are then SO_4, H_2 and the product components are H_2S and H_2O.

The reaction rate is determined from the PHREEQC modelling. Gas water equilibriums of the components (H_2, H_2S) are defined through equilibrium constant tables as a function of pressure and temperature.

The reaction is approximated in STARS™ by:

$$\mathrm{K} = K_{max} \frac{1}{(1+\alpha[H_2])^{\beta}} [SR_{bacteria}][SO_4^{--}]$$

with α and β ajusted to match $\mu_{H_2} = \frac{[H_2]}{Ks_{H_2} + [H_2]}$ and $[SR\_bacteria]$ the concentration of sulphate-reducing bacteria.

The bacterial growth is obtained by integration of the bacteria reaction, i.e. the concentration of bacteria is assumed to be proportional to the amount of dissolved SO_4:

$$[SR\_bacteria] = Y * [SO_4^{--}] * \frac{1}{(1+\alpha[H_2])^{\beta}}$$

with α and β are adjusted to match$\mu_{SO_4^{--}} = \frac{[SO_4^{--}]}{Ks_{SO_4^{--}} + [SO_4^{--}]}$ and $[SR\_bacteria]$ is the concentration of sulphate-reducing bacteria.

Given the different mathematical expressions, the agreement is diverging at low concentrations as shown in Figure 18 and more than for methanogenesis reaction (Figure 17).

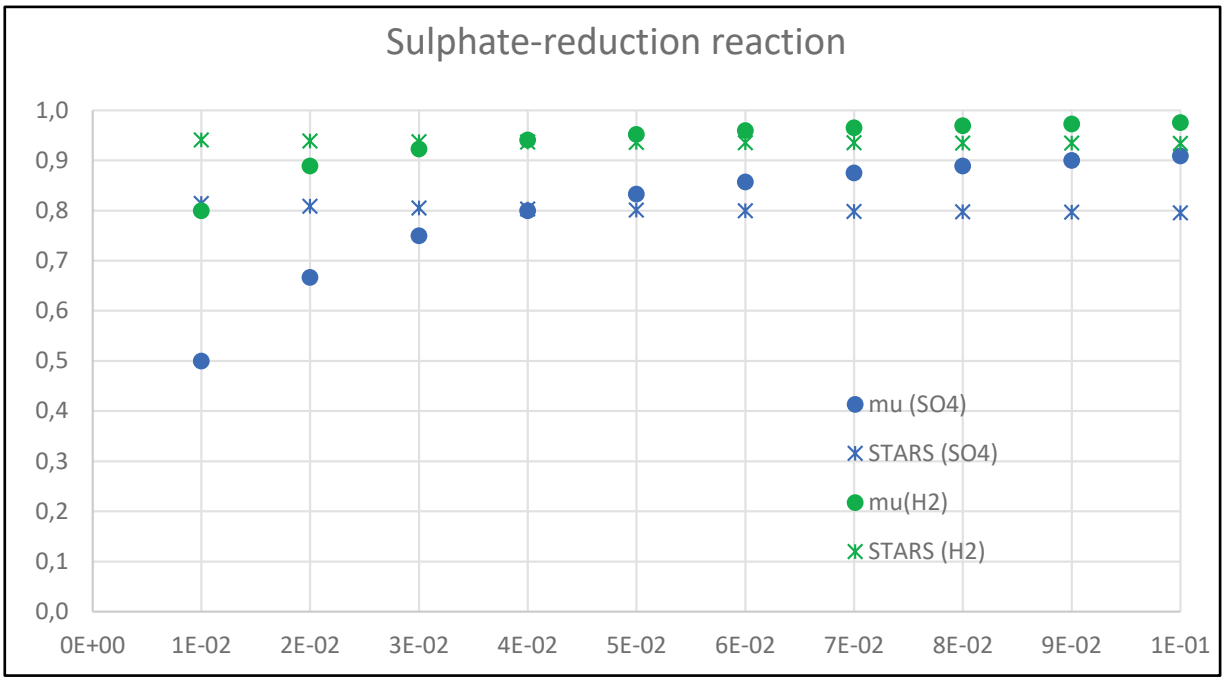


Figure 18: Comparison of STARS™ and Monod correction factors for the sulphate-reduction reaction

6.2. Simulation conditions

The synthetic geological model presented and used in D2.3 is taken as the application case. The model is assumed as a saline aquifer formation (initial gas saturation = 0 %). The model does not assume any brine recharge i.e. the model boundaries are closed: no brine influx from the surroundings.

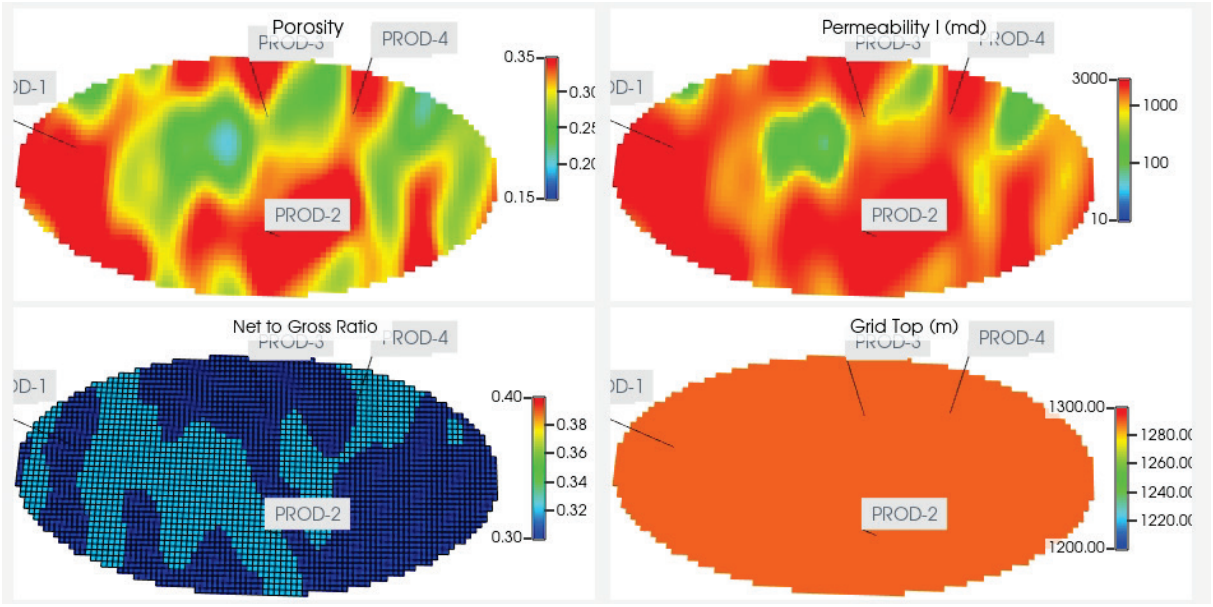


Figure 19: Distribution of the key petrophysical parameters of the storage and well locations

The initial pressure is assumed to be 130 bar, the temperature is constant at 50 °C and the water composition is given in Table 9. At this temperature conditions, the methanogenesis and sulphate reduction reactions are at their peak rate according to Thaysen *et al* (2021). This water composition is slightly modified compared to the one used in 0D Modelling, as the sulphate concentration was fixed close to zero (5 mg/l) to simplify the model. Sulphate reduction reactivity is thus underestimated on this first model and H_2S emission could be higher in real cases. The model aims to compute the evolution of the pressure and fluid composition within the storage assuming seasonal cycling (after 10 months of initial fill-up) and injection/withdrawal through 4 horizontal wells at a rate of 0.1 $MMSm^3/d$/well with a withdrawal rate equal to the injection rate as illustrated in Figure 20.

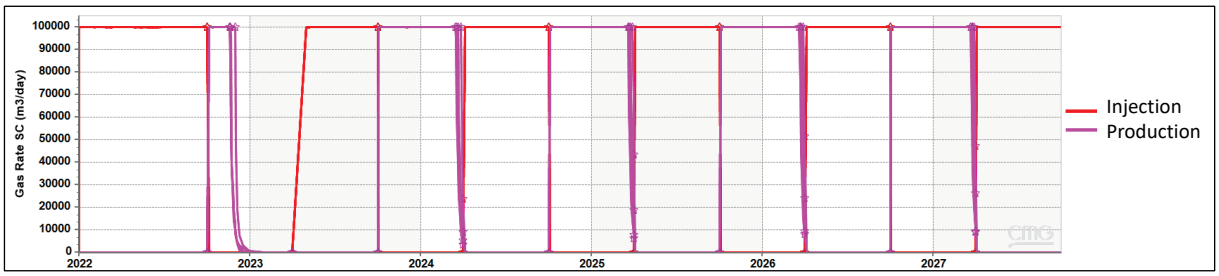


Figure 20: Well flowrates for the first five seasonal cycles

Table 9: Initial concentrations of aqueous components

ions	Initial concentration	units
HCO_3^-	720	mg/L
SO_4^{-2}	5	mg/L
Cl^-	4432	mg/L
Ca^{2+}	375	mg/L
Mg^{2+}	120	mg/L
Na^+	5 415	mg/L
K^+	140	mg/L
Salinity	15 104	mg/L

The model is set up with 4 gaseous components (CO_2, H_2, CH_4, H_2S) with equilibrium constants computed between 80 and 250 bar for the synthetic case. The model is set up for the carbonate case assuming 2 minerals, calcite and dolomite, in equal proportions.

The methanogenesis reaction is either as obtained from PHREEQC (see section 5.3) or upscaled due to volume difference between experiment and field scale as illustrated in Figure 21. The contact between fluids and minerals should induce a reduced level of reaction. Using a similar approach to the upscaling of chemical reactivity for water flooding upscaling (Islam and S. M. Ali., 1989&1990), a dumping factor of about 10^{-4} could be foreseen compared to laboratory conditions. Consequently, two simulation conditions will be investigated using the laboratory (matched by PHREEQC) or the upscaled reactivity and are summarized in Tables 10 and 11.

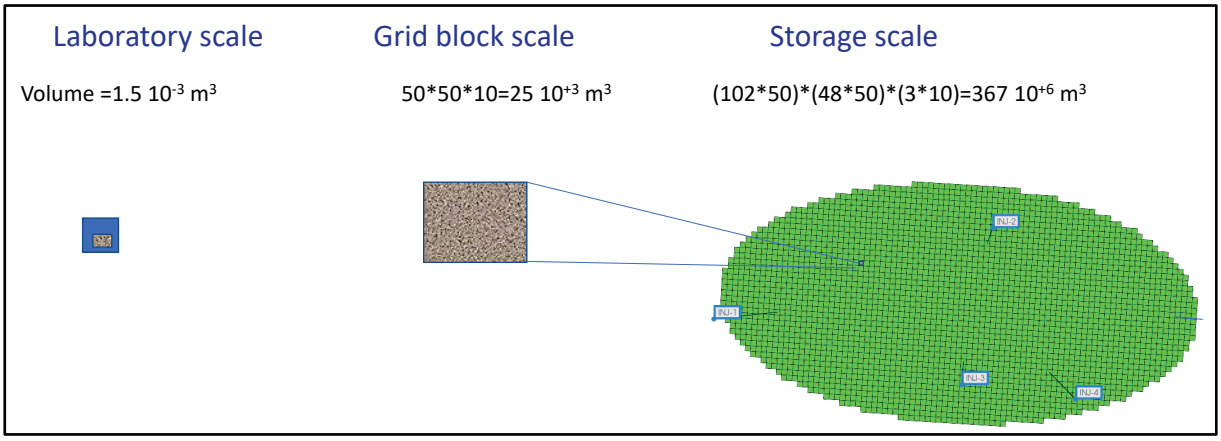


Figure 21: Upscaling models from Laboratory to storage scales

Table 10: Methanogenesis parameters used in the 3-D model

Parameter	laboratory scale	grid scale	units
[X] = concentration of methanogenic bacteria	$1.25\ 10^{-4}$	$1.25\ 10^{-4}$	$kg.mol/m^3$
Kmax = maximum substrate utilization rate (HCO_3)	$2.59\ 10^{-2}$	**$5.18\ 10^{-6}$**	$kg.mol/m^3/d$
Ks_{HCO3}= semi-saturation constant for HCO_3[5]	$3\ 10^{-3}$	$3\ 10^{-3}$	$kg.mol/m^3$
Ks_{H2} = semi-saturation constant for H_2	$2.5\ 10^{-3}$	$2.5\ 10^{-3}$	$kg.mol/m^3$
Y = yield factor methanogenic bacteria	$2\ 10^{-5}$	$2\ 10^{-5}$	$kg.mol/m^3$
D= decay/death-rate coefficient of bacteria	0	0	

Table 11: Sulphate-reduction parameters used in the 3-D model

Parameter	laboratory scale	grid scale	unit
[X] = concentration of sulphate reduction bacteria	$1.27\ 10^{-7}$	$1.27\ 10^{-7}$	$kg.mol/m^3$
Kmax = maximum substrate utilization rate (SO_4)	$6.9\ 10^{0}$	**$1.38\ 10^{-3}$**	$kg.mol/m^3/d$
Ks_{SO4}= semi-saturation constant for SO_4	10^{-2}	10^{-2}	$kg.mol/m^3$
Ks_{H2} = semi-saturation constant for H_2	$2.5\ 10^{-3}$	$2.5\ 10^{-3}$	$kg.mol/m^3$
Y = yield factor sulphate reduction bacteria	$4\ 10^{-7}$	$4\ 10^{-7}$	$kg.mol/m^3$
D= decay/death-rate coefficient of bacteria	0	0	

6.3. Simulation results

The simulations aim to model the impact of the methanogenesis reactions at the storage scale considering hydrogen injection in a saline formation. The amount of hydrogen injected is the same in both cases as shown in Figure 22.

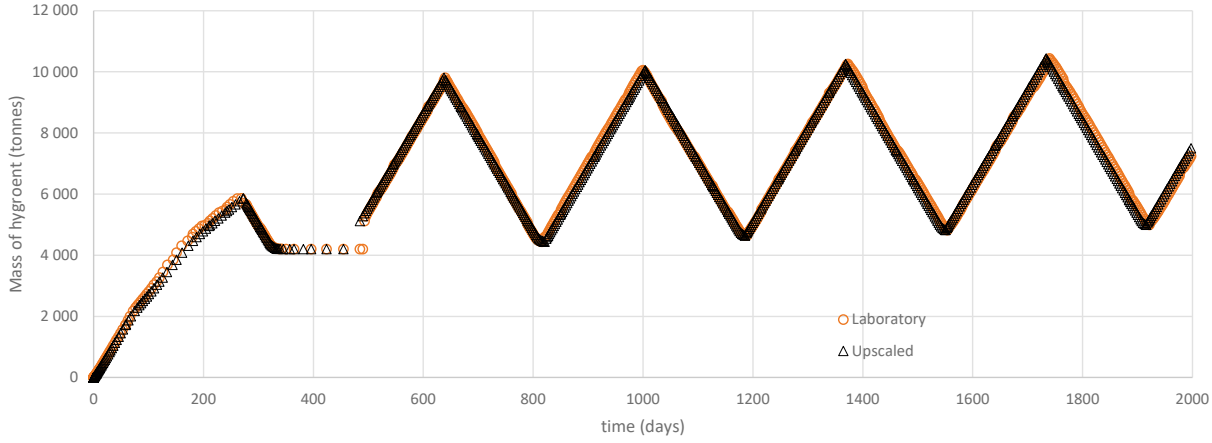


Figure 22: Comparison of the mass of hydrogen injected with laboratory and upscaled maximum substrate rate

[5] $KsHCO_3$ was modified for PHREEQC last simulations after 3D modelling simulations. Therefore, this value is different between 0D Modelling and 3D Modelling.

Limited reactivity of the minerals is expected from hydrogen as shown in Figure 23 and Figure 24. The computed changes in calcite are not correlated with hydrogen either dissolved or gaseous and reflects adjustment of minerals (dissolution of calcite) to the brine composition as the same behaviour is obtained irrespective of the reaction parameters. The coupling between component reactions such as methanogenesis or sulphate reduction reactions as defined and the geochemical reactions within the brine or with the minerals does not seem to be fully adequate in the current version (2022.10) of STARS™ and is currently under review by the software development team as this is the first test carried out with such a modelling approach.

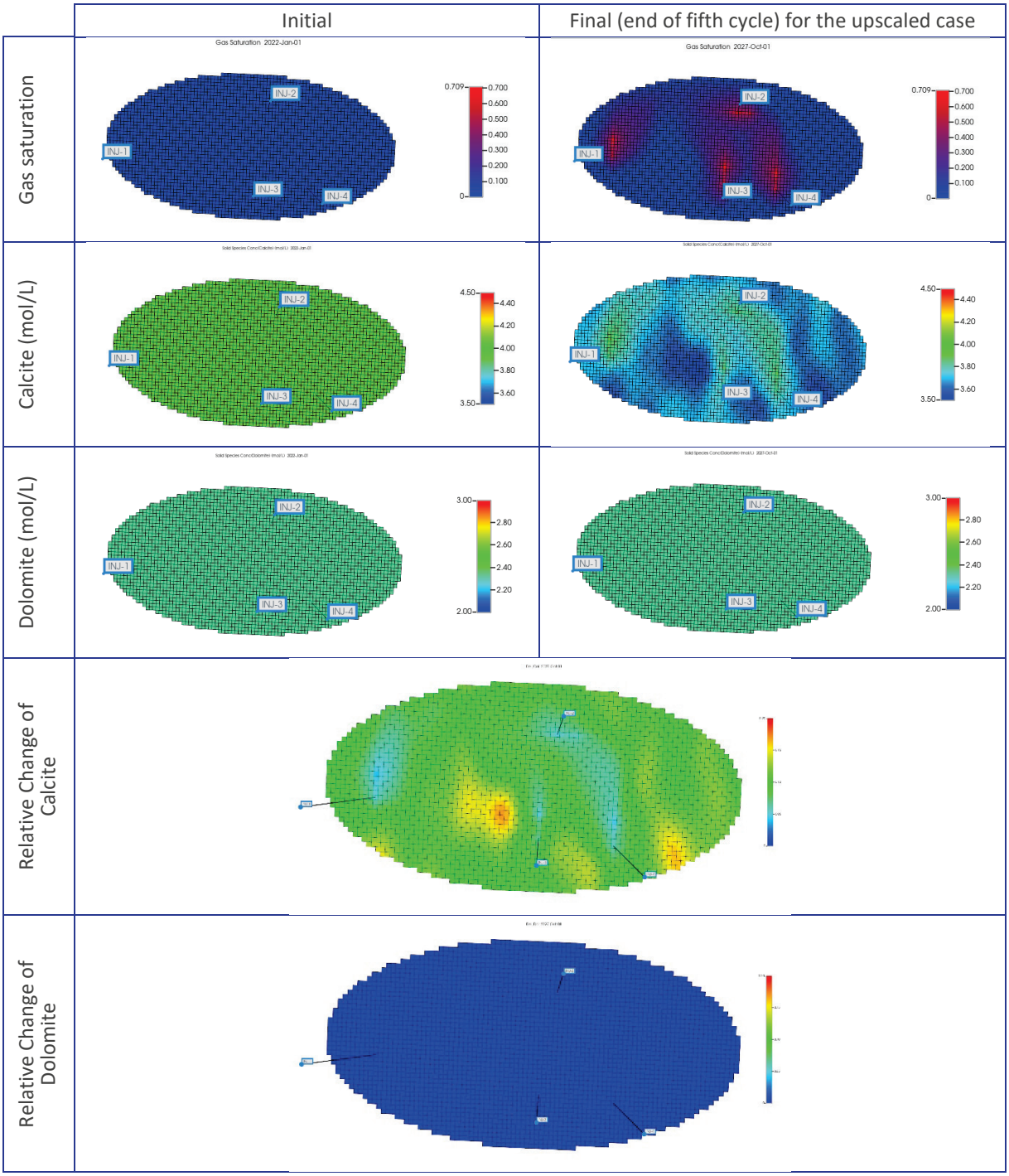


Figure 23: Changes in gas saturation, and solid concentrations for upscaled reaction parameters

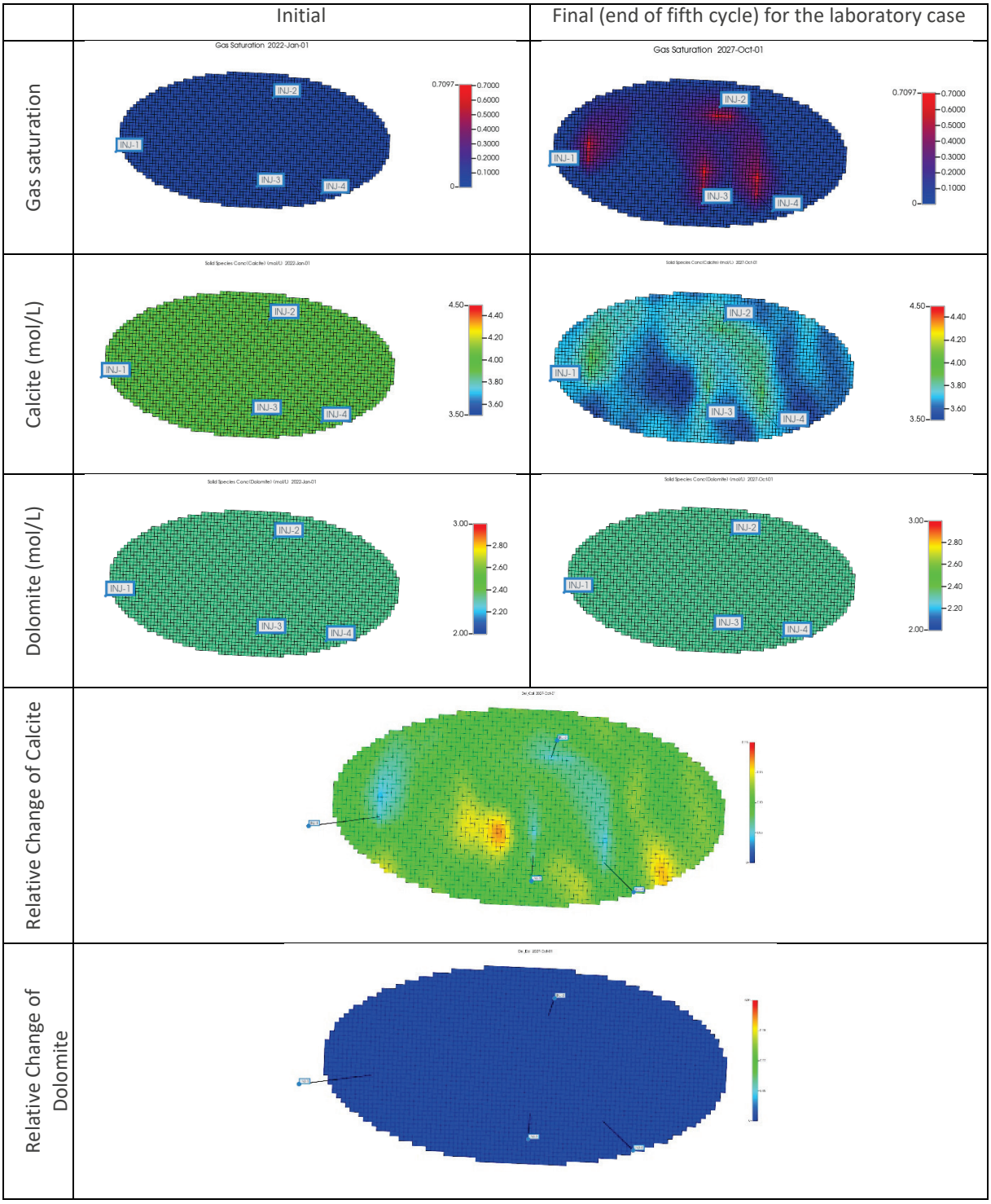


Figure 24: Changes in gas saturation, and solid concentrations for laboratory-scale reaction parameters

6.3.1. Deep saline formation using laboratory-scale reactivity

Using the laboratory-scale reaction parameters (Tables 10 and 11), a strong reaction occurs due to the methanogenesis reaction which create a large number of moles of methane and significant amount of hydrogen sulphide as shown in Figure 25 and correlated with the hydrogen in the structure (Figure 26).

Within the storage, the amount of hydrogen involved in bacterial reactions decreases quickly during the first hydrogen injection and stabilize to about 5.6 % towards the end of the initial fill-up (Figure 26). This reactivity of significantly larger than what is observed on existing analogue cases. Thaysen *et al* (2021) estimated the hydrogen loss in depleted oil and gas fields to be negligible to small (<0.01–3.2 % of the stored hydrogen). They also acknowledged that laboratory derived rates overpredict the conditions within real aquifers for 1 to five order of magnitude based upon the analogy of sulphate-reduction and methanogenesis in oil and natural gas reservoirs. Our modelling results leads to higher estimate of hydrogen reactivity but much less than in town gas analogues as reported in Hystories D7.2. Such comparison is even more difficult as different town-gas storage exhibit drastically different behaviour as indicated in Hystories D7.2.

The mass of hydrogen which reacts is about 360 tonnes out of 6450 tonnes injected over the period. The sulphate reduction reaction produces about 80 tonnes of H_2S mainly over the period as shown in Figure 26.

Figure 27 shows the production of hydrogen, methane and hydrogen sulphide for the storage after the five seasonal cycles which were modelled. The H_2S production through the wells is significative when using the laboratory reaction rate at about $1/10^{th}$ of the CH_4 production during all the cycles. The gaseous H_2S is about 10 times less mobile than methane due to its viscosity. The maximum production of H_2S and CH_4 (Table 12) generally occur in the second half of each cycle (Figure 27) when long enough contact between hydrogen and fresh water takes place. Both maximum production of H_2S and CH_4 decrease with the number of cycles (Table 12).

As assumed in the modelling concept, the bacterial reactions, methanogenesis and sulphate reduction, develop further and further away from the injection well with the number of cycles (Figure 28). H_2S and CH_4 are produced at the interface between hydrogen and fresh brine as the model does not assume any brine recharge.

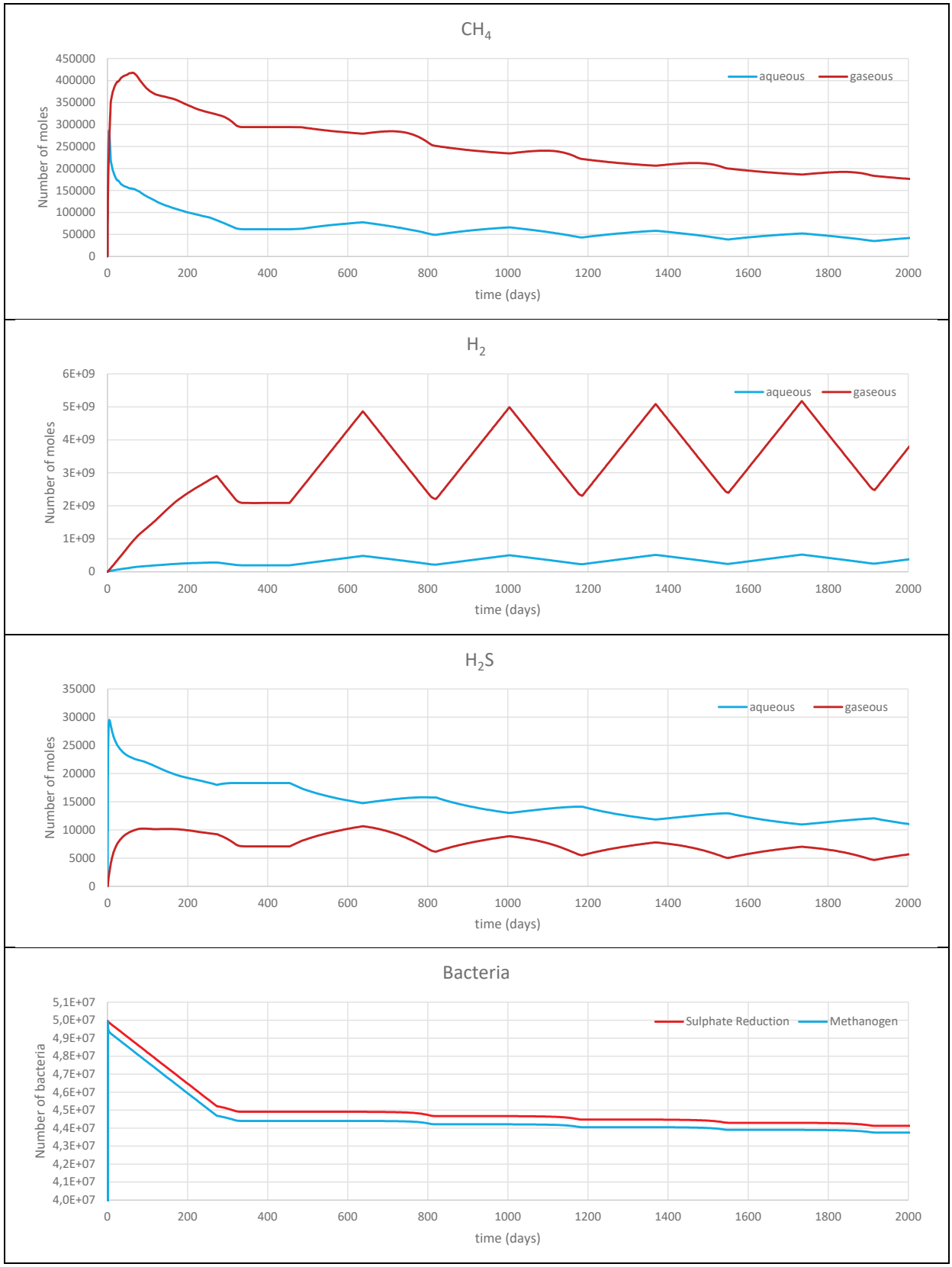


Figure 25: Evolution of the number of moles for methane, hydrogen and hydrogen sulphide for laboratory-scale reaction parameters

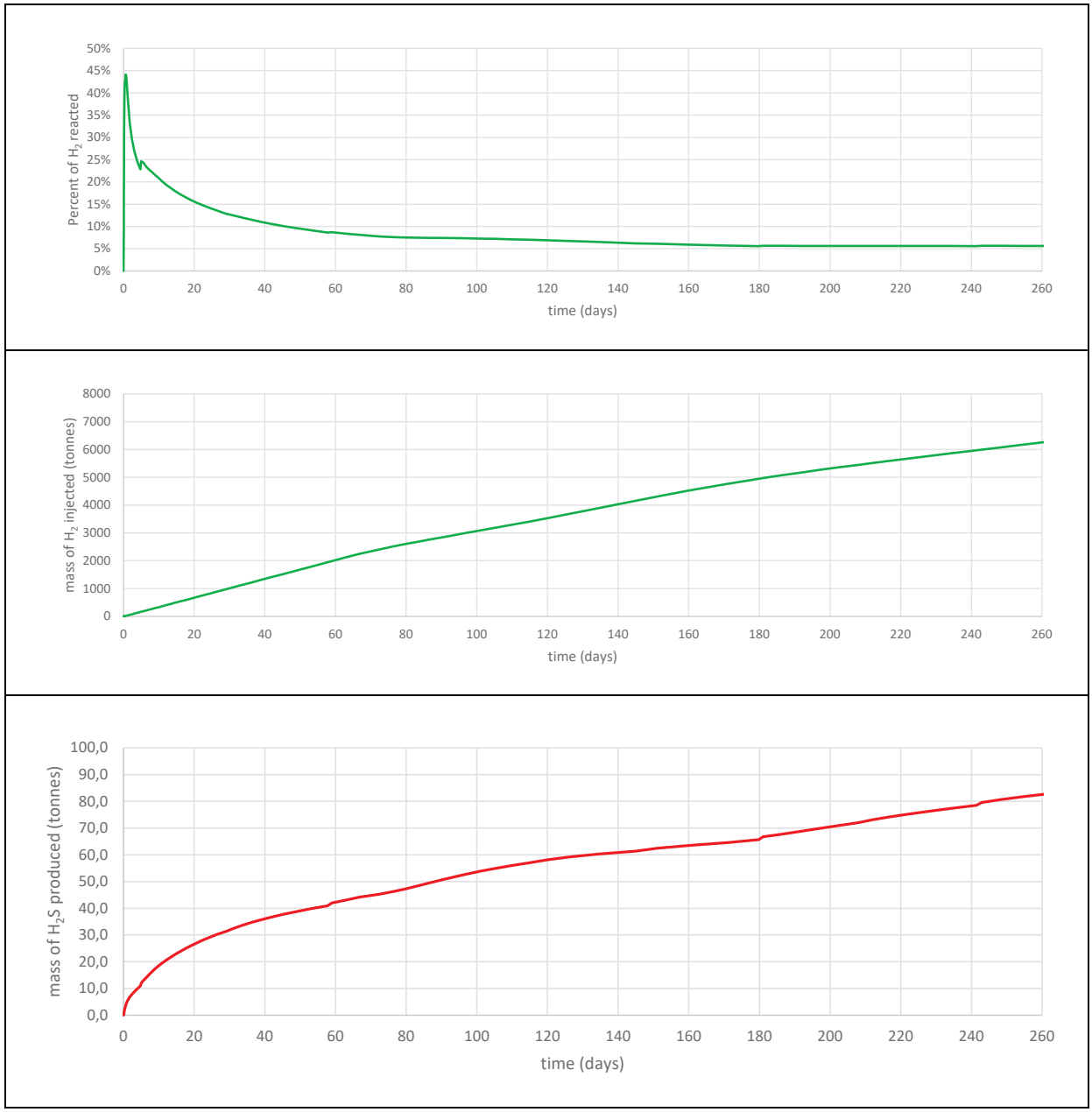


Figure 26: Evolution of the hydrogen reacting and hydrogen sulphide generated through methanogenesis and sulphate for laboratory-scale reaction parameters during the initial fill-up.

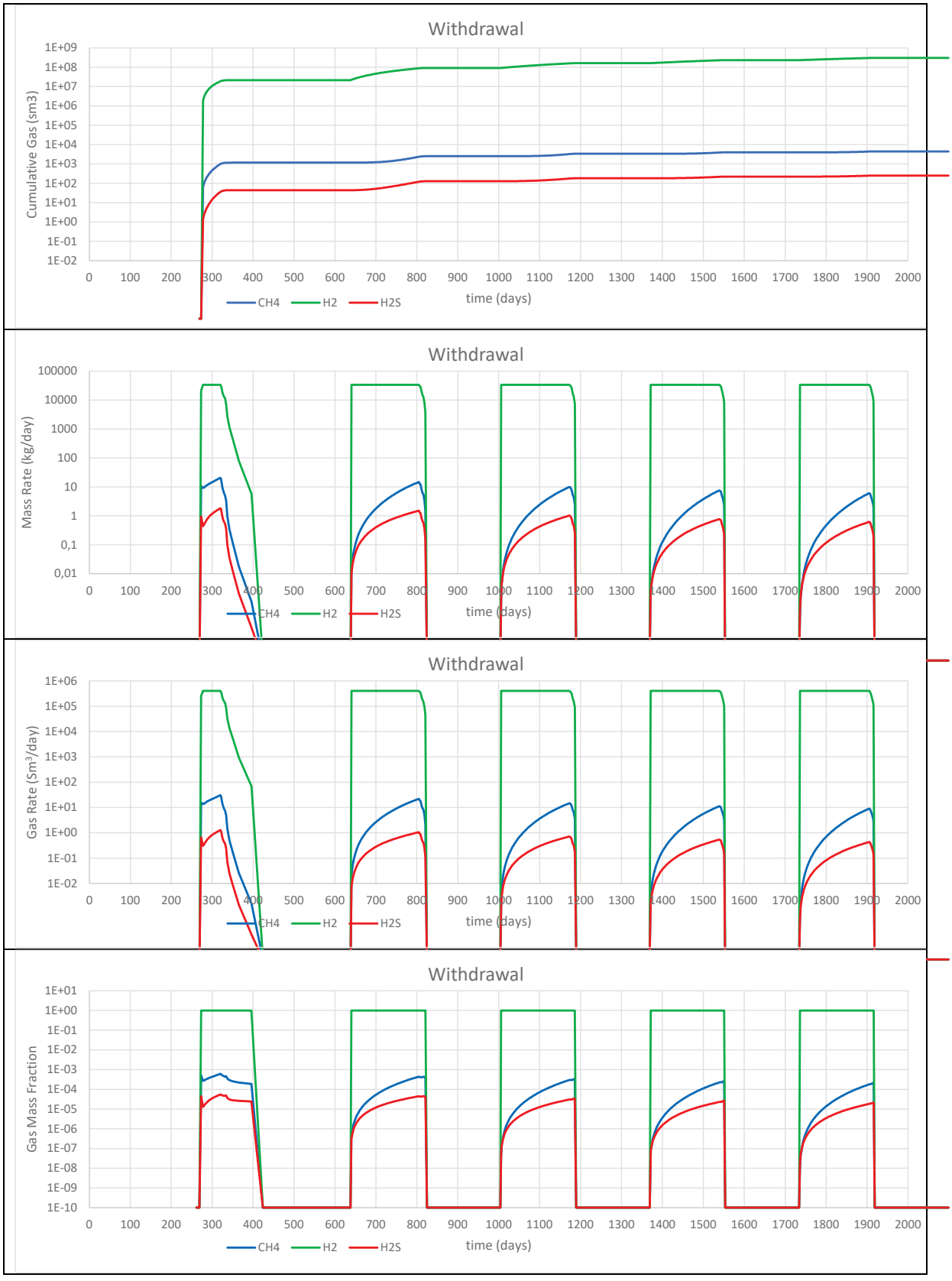
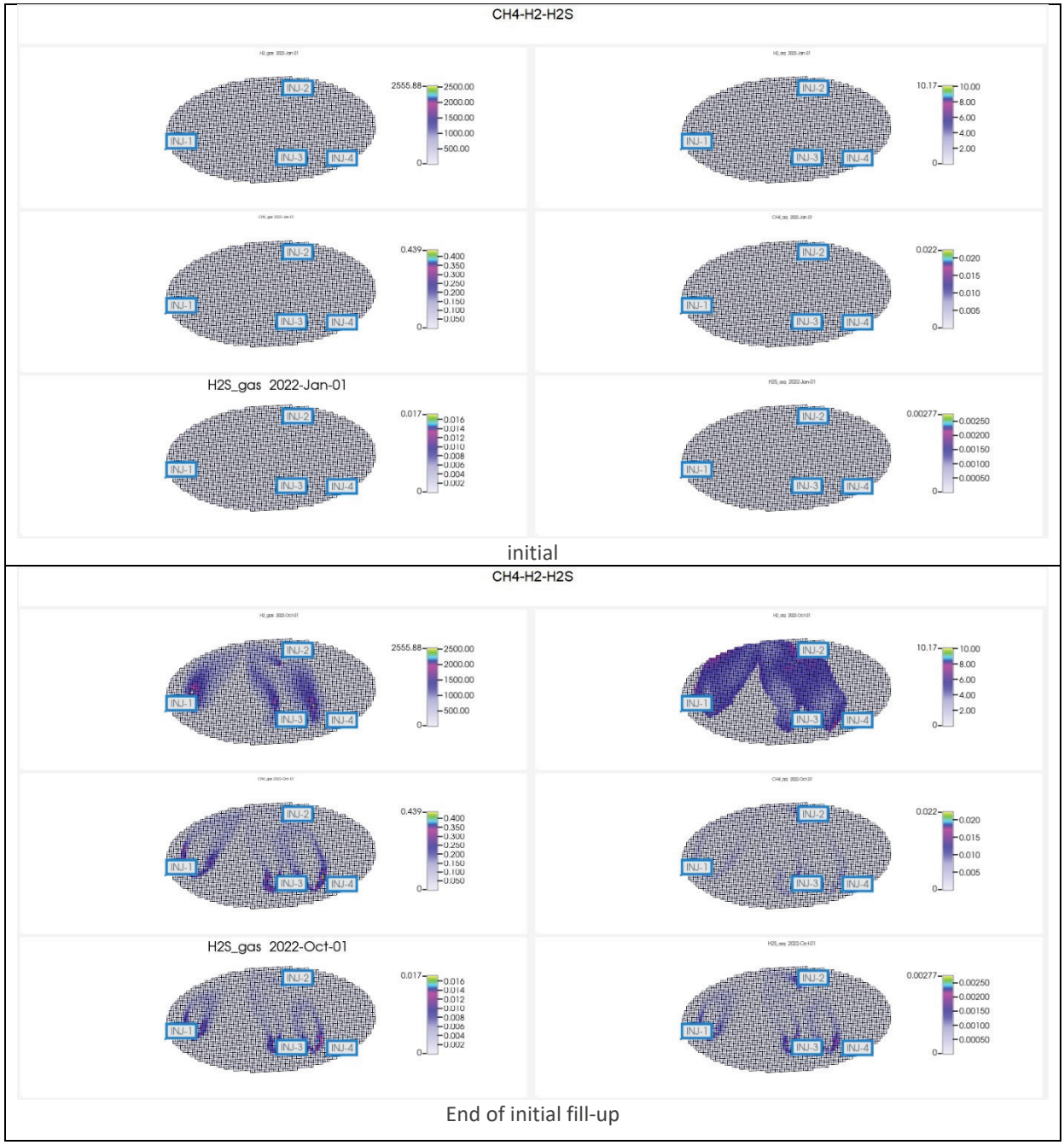
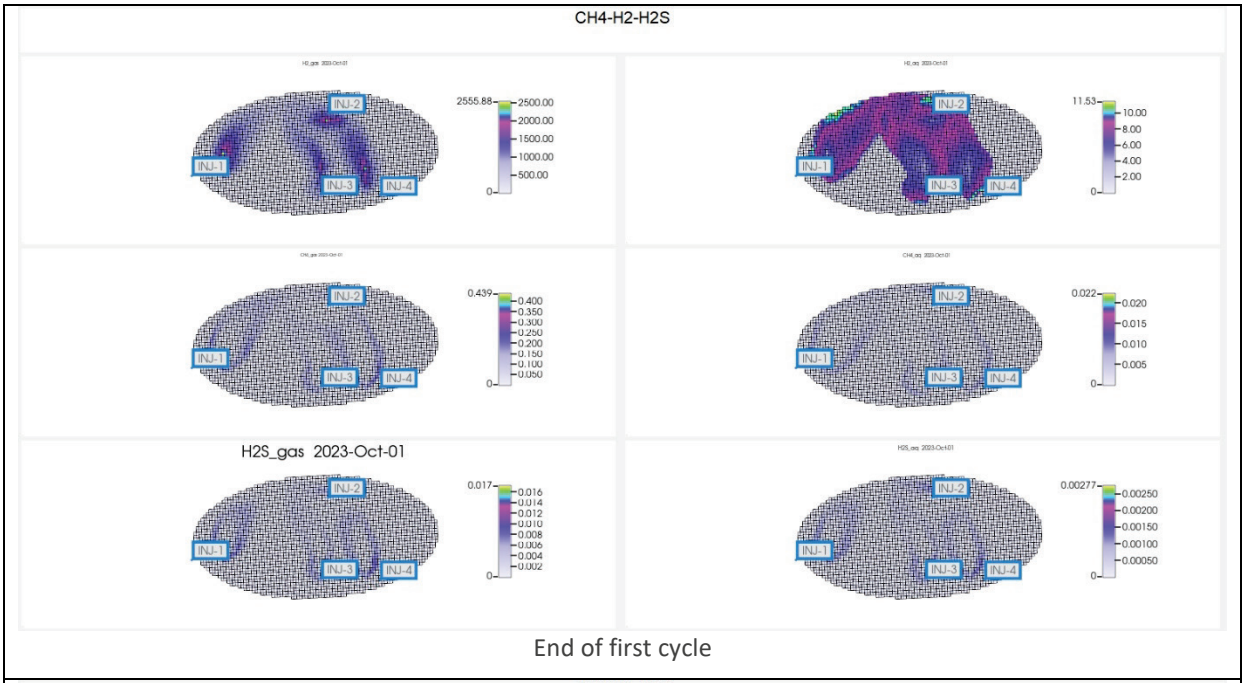


Figure 27: Evolution of withdrawal mass and volume for the synthetic storage for laboratory-scale reaction parameters

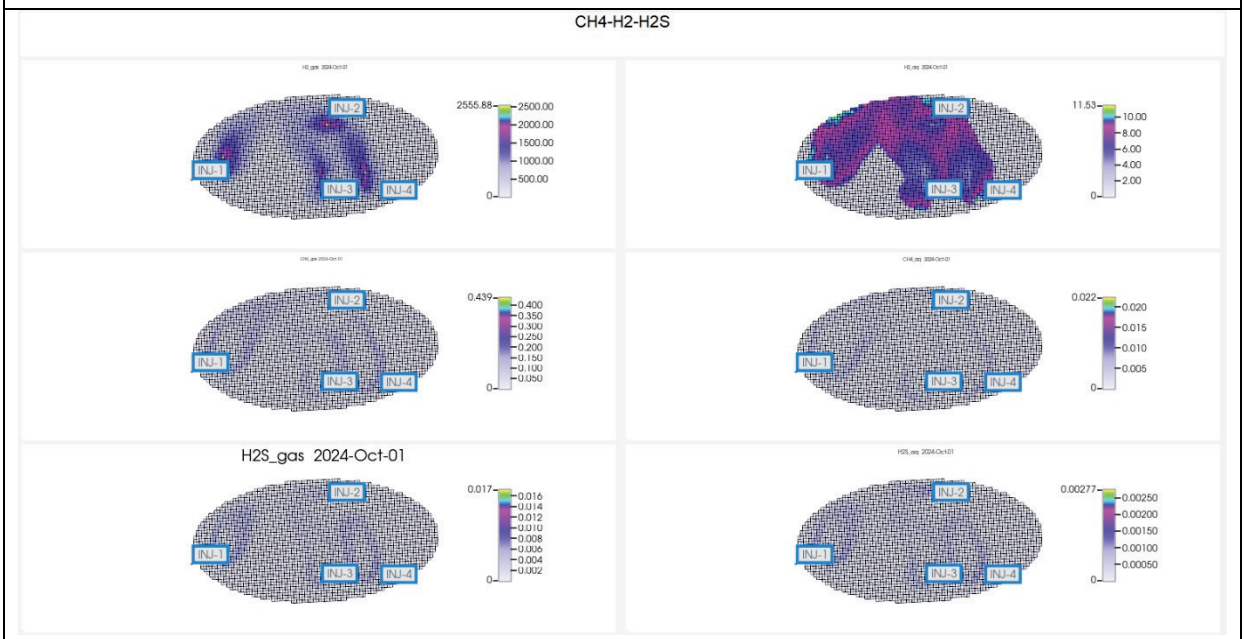
Table: 12 Evolution of the maximum mass concentration during the cycles for the synthetic storage for laboratory-scale reaction parameters

Cycle	CH_4 maximum (%)	H_2S maximum (ppm)
1	0.06	54
2	0.04	46
3	0.03	34
4	0.03	27
5	0.02	21





End of first cycle



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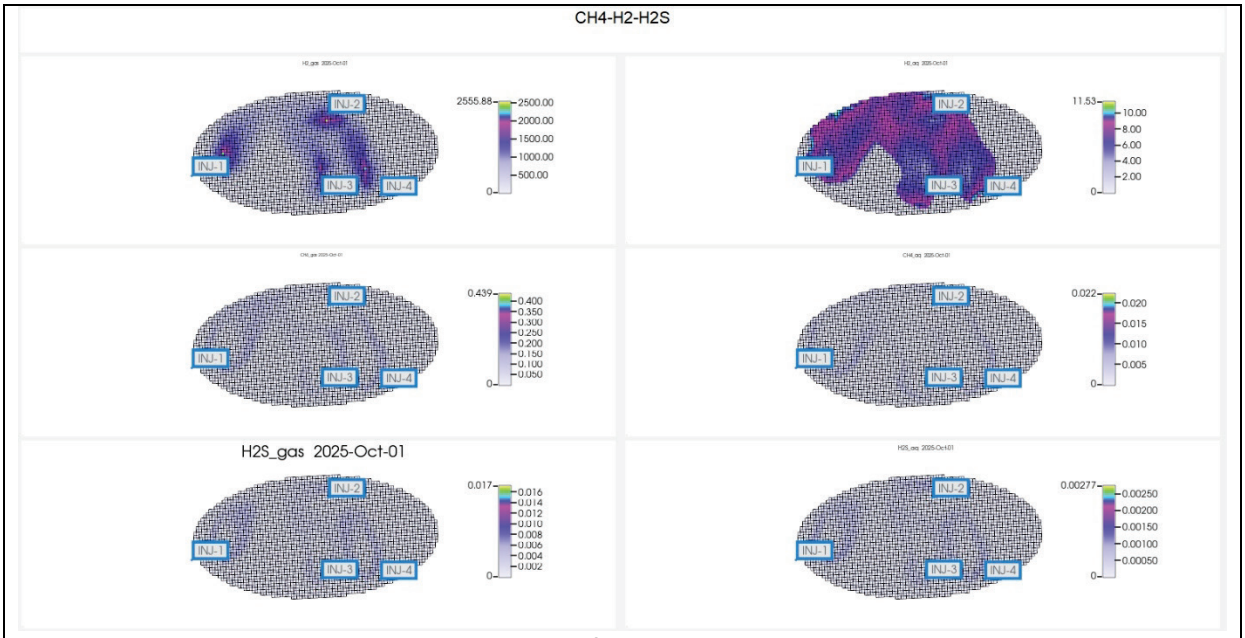
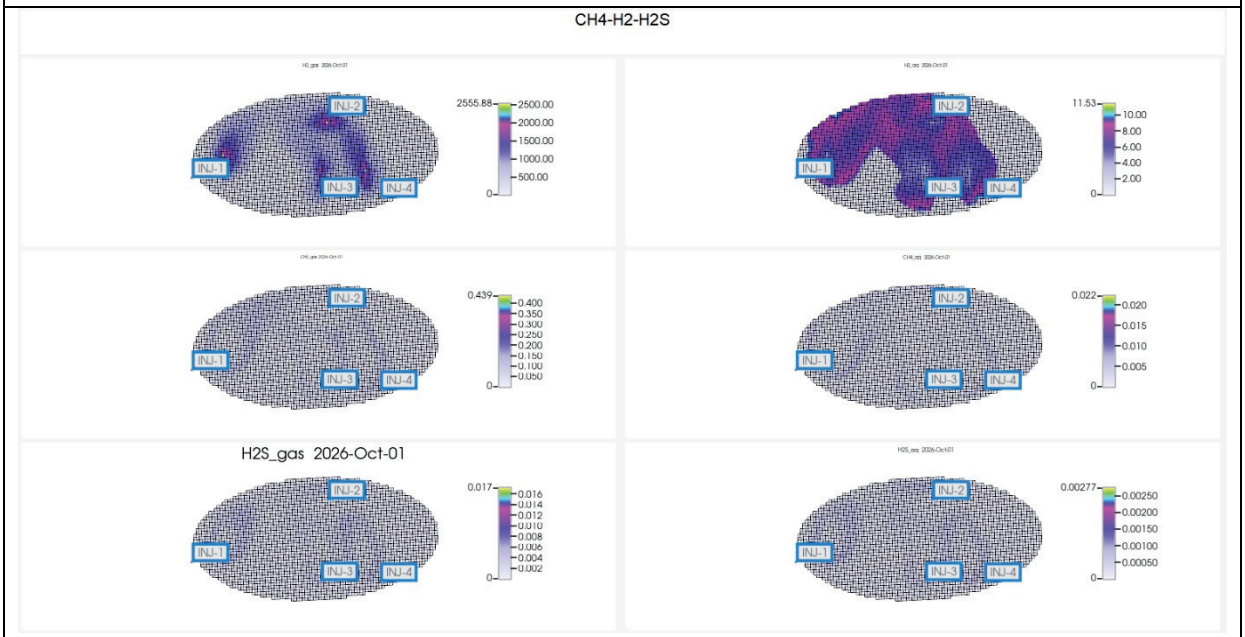


End of third cycle



End of fourth cycle

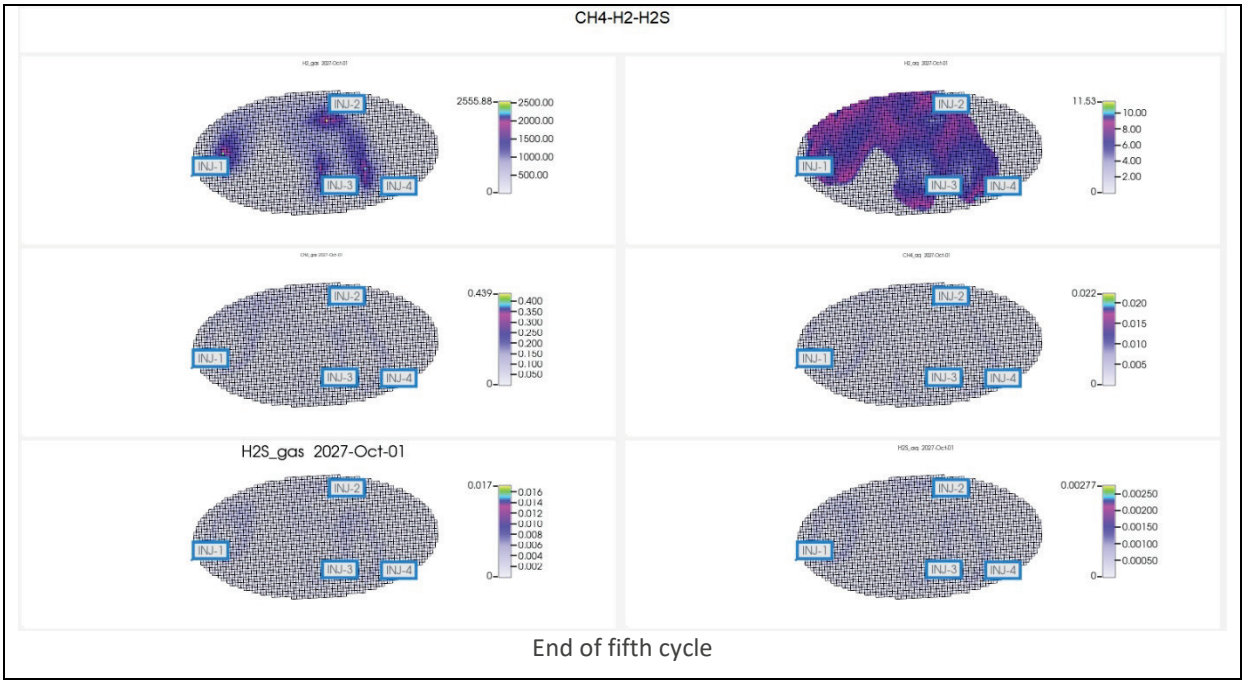


Figure 28: Evolution of the hydrogen, methane and hydrogen sulphide volume in gaseous and aqueous phases for laboratory-scale reaction parameters

6.3.2. Deep saline aquifer formation using upscaled reactivity

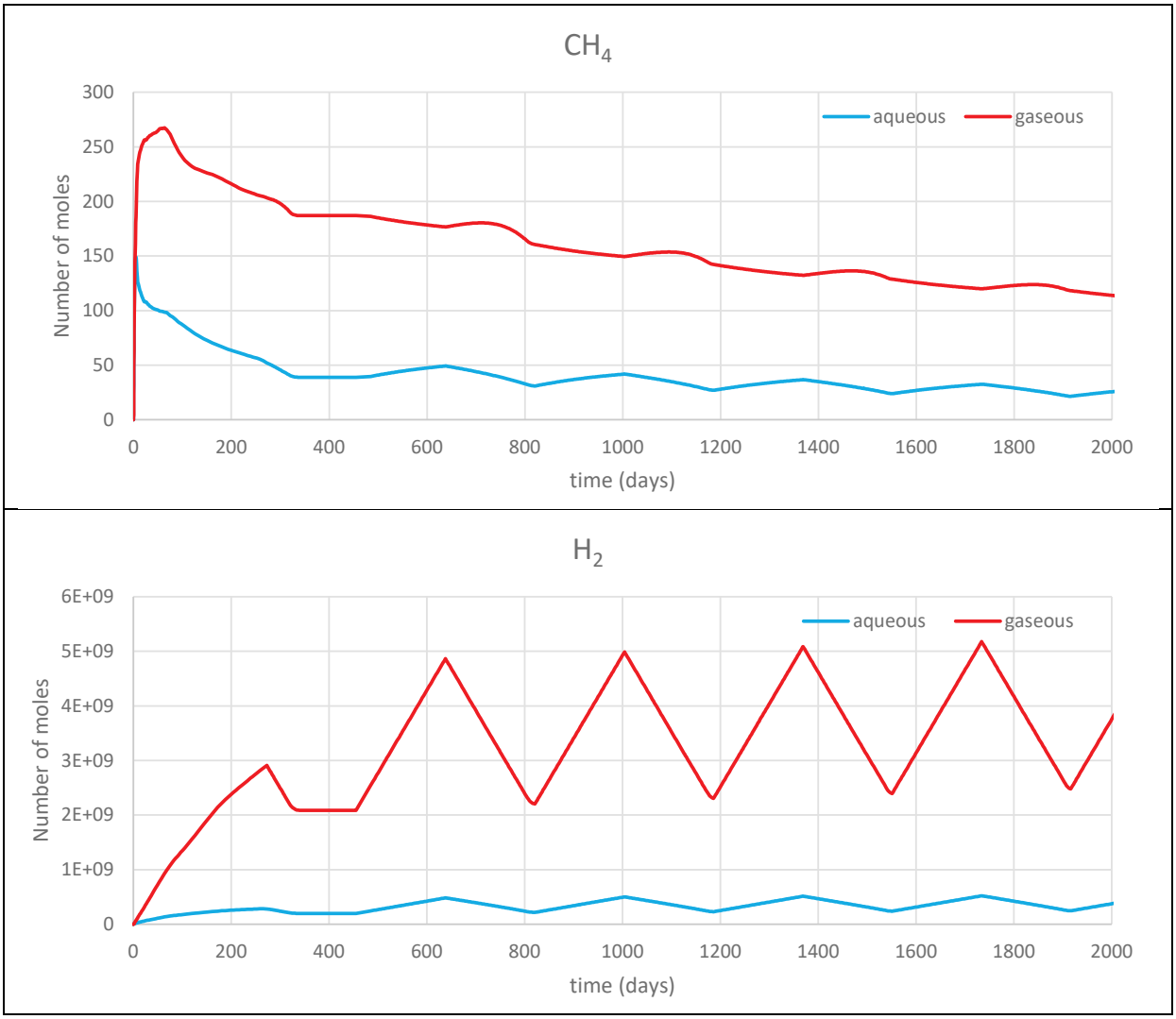
Using the upscaled reaction parameters (Tables 10 and 11), a weak reaction occurs due to the methanogenesis reaction which creates a small number of moles of methane and no hydrogen sulphide as shown in Figure 29. As expected, the methane generation occur at the edge of the hydrogen front where hydrogen meet fresh brine with dissolved CO_2. Within the hydrogen rich zone, all the bacteria consume the dissolved CO_2 which is the limiting reactant as shown in Figure 32.

Within the storage, the amount of hydrogen involved in bacterial reactions decreases quickly during the first hydrogen injection and stabilize to about 0.003 % towards the end of the initial fill-up (Figure 30). This reactivity of significantly smaller than what is observed on existing analogue cases and consistent with the conclusion from Thaysen *et al* (2021) who estimated the hydrogen loss in depleted oil and gas fields to be negligible to small (<0.01–3.2 % of the stored hydrogen). They also acknowledged that laboratory derived rates overpredict the conditions within real aquifers for 1 to five orders of magnitude based upon the analogy of sulphate-reduction and methanogenesis in oil and natural gas reservoirs. This estimates of the reduced reactivity at the field scale is consistent with our upscaling approach but lead to much smaller estimate of hydrogen reactivity than expected in town gas analogues as reported in Hystories D7.2. Our modelling was not representative of the conditions of the town gas analogues which should require site specific models. This is even more difficult as different town-gas storage exhibit drastically different behaviour as indicated in Hystories D7.2.

The mass of hydrogen which reacts is about 0.214 tonnes out of 6450 tonnes injected over the period. The sulphate reduction reaction does not significantly produce any H_2S over the simulated period. The maximum production of CH_4 (Table 13Table *13*) generally occur in the second half of each cycle (Figure 31) when long enough contact between hydrogen and fresh water takes place. This maximum production decreases with the number of cycles (Table 13).

Figure 31 shows the production of hydrogen and methane for the storage after the five seasonal cycles which were modelled.

As assumed in the modelling concept, the bacterial reactions, methanogenesis and sulphate reduction, develop further and further away from the injection well with the number of cycles (Figure 32). CH_4 is produced at the interface between hydrogen and fresh brine as the model does not assume any brine recharge.



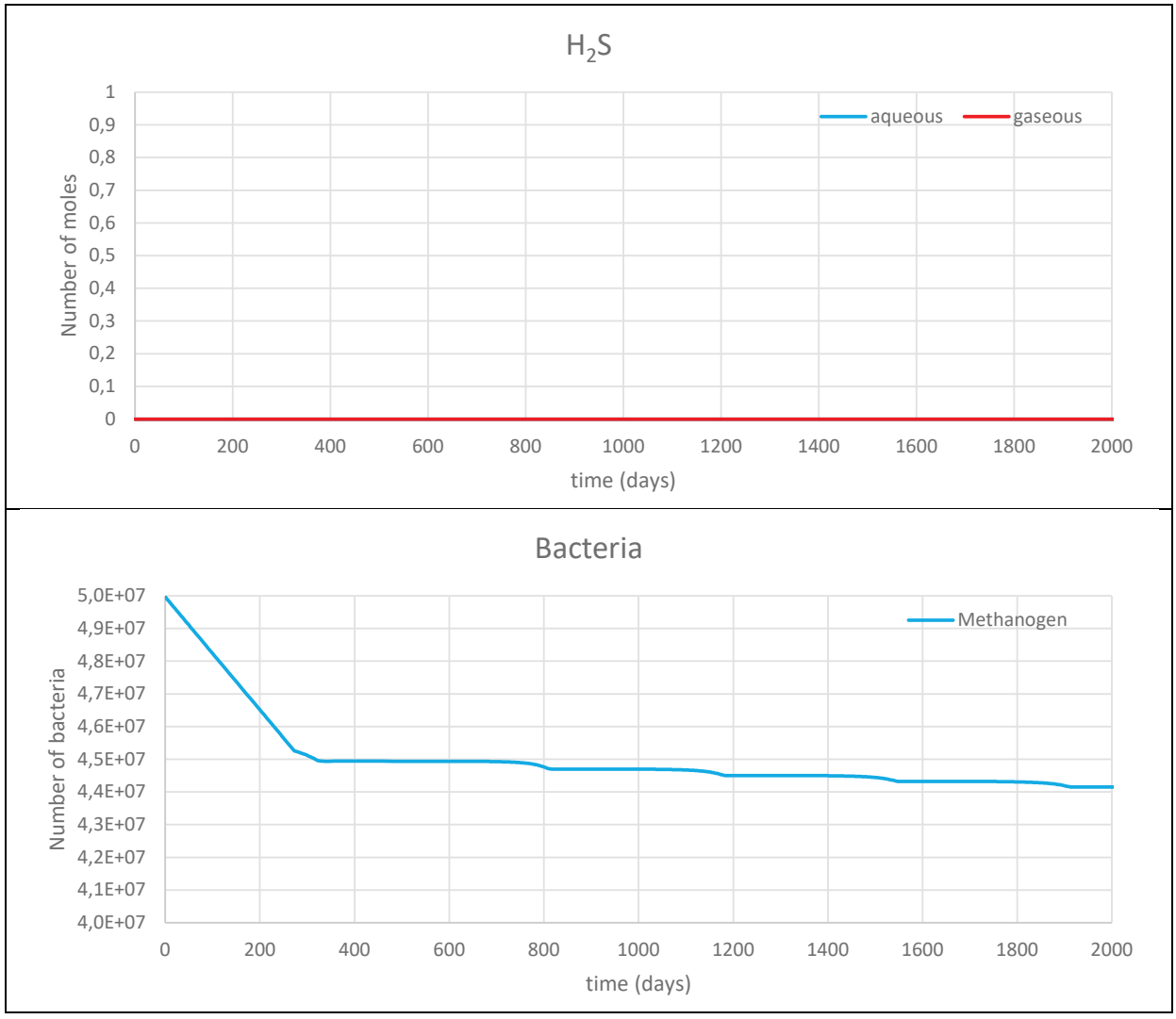


Figure 29: Evolution of the number of moles for methane, hydrogen and hydrogen sulphide for upscaled reaction parameters

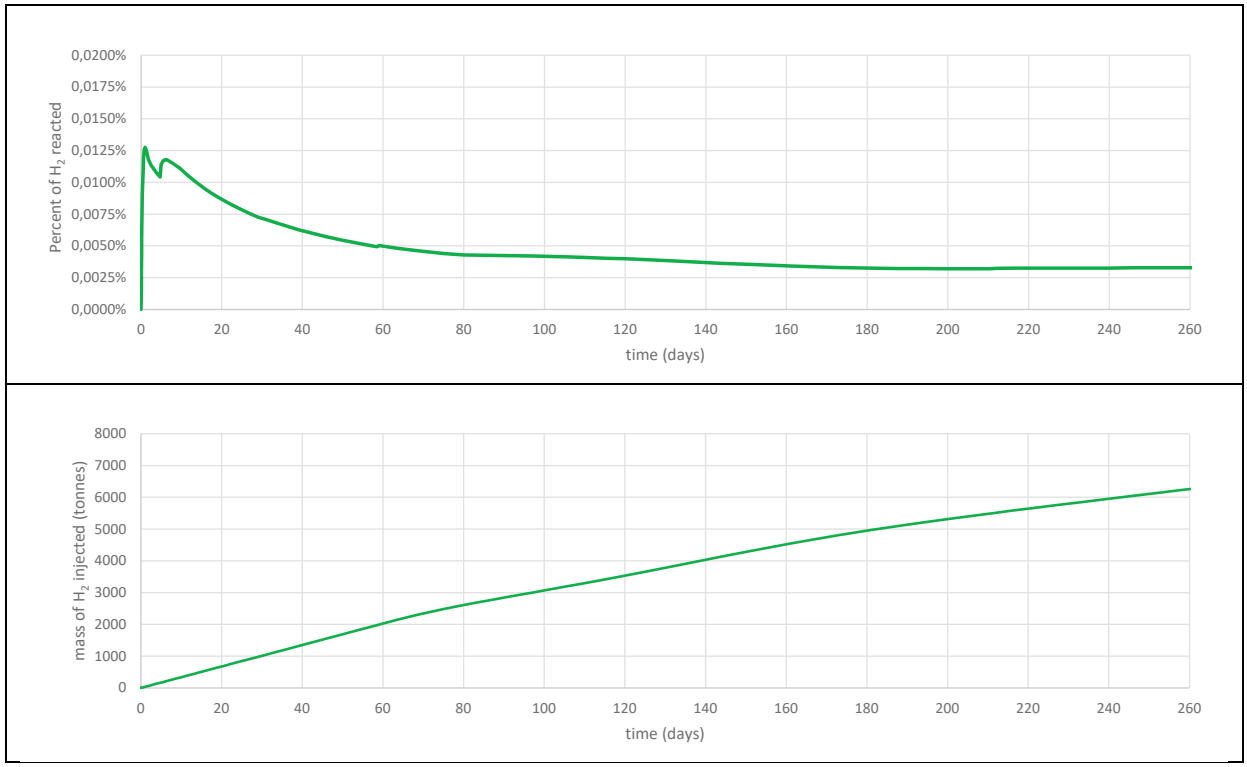


Figure 30: Evolution of the hydrogen reacting through methanogenesis and sulphate for upscaled reaction parameters during the initial fill-up

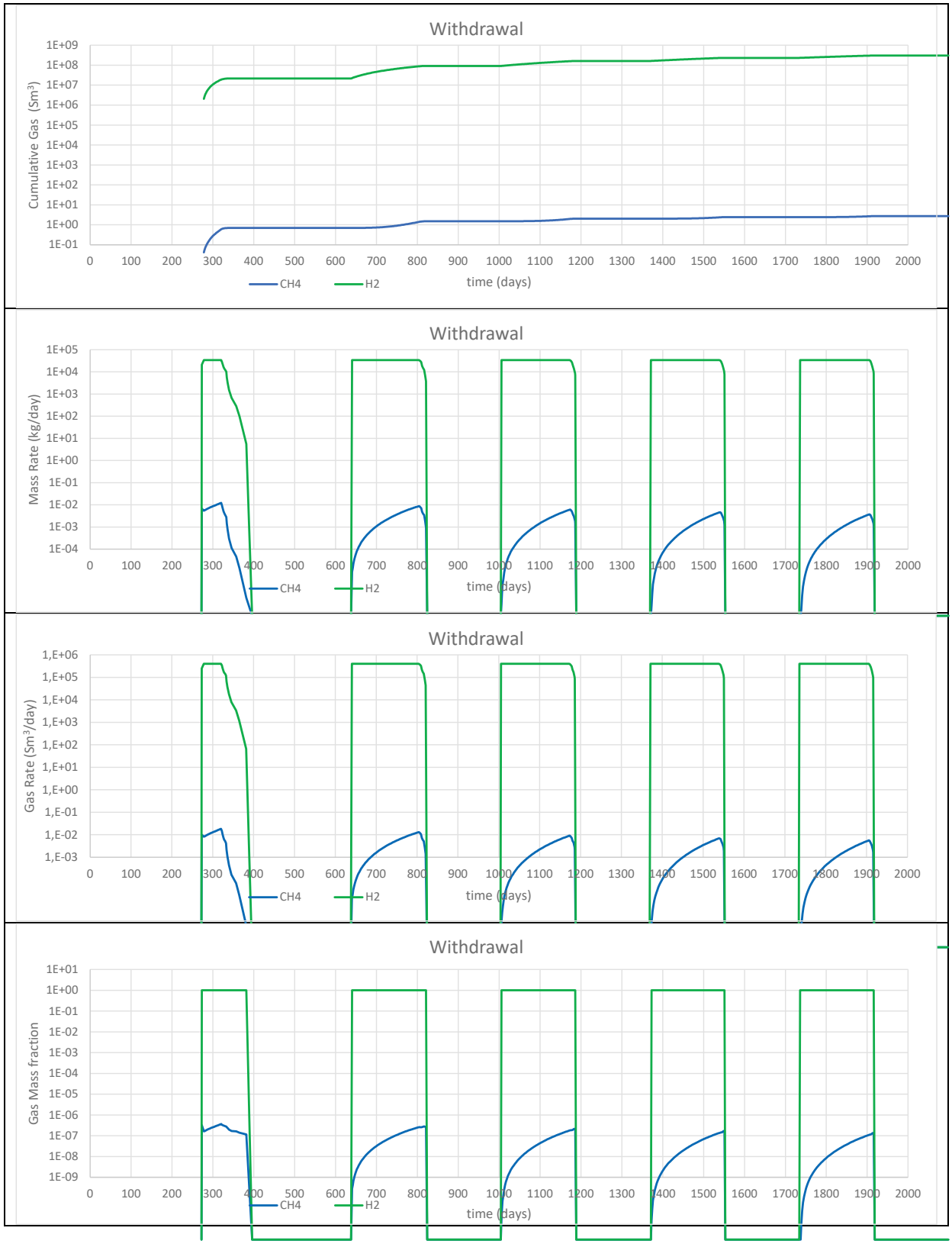
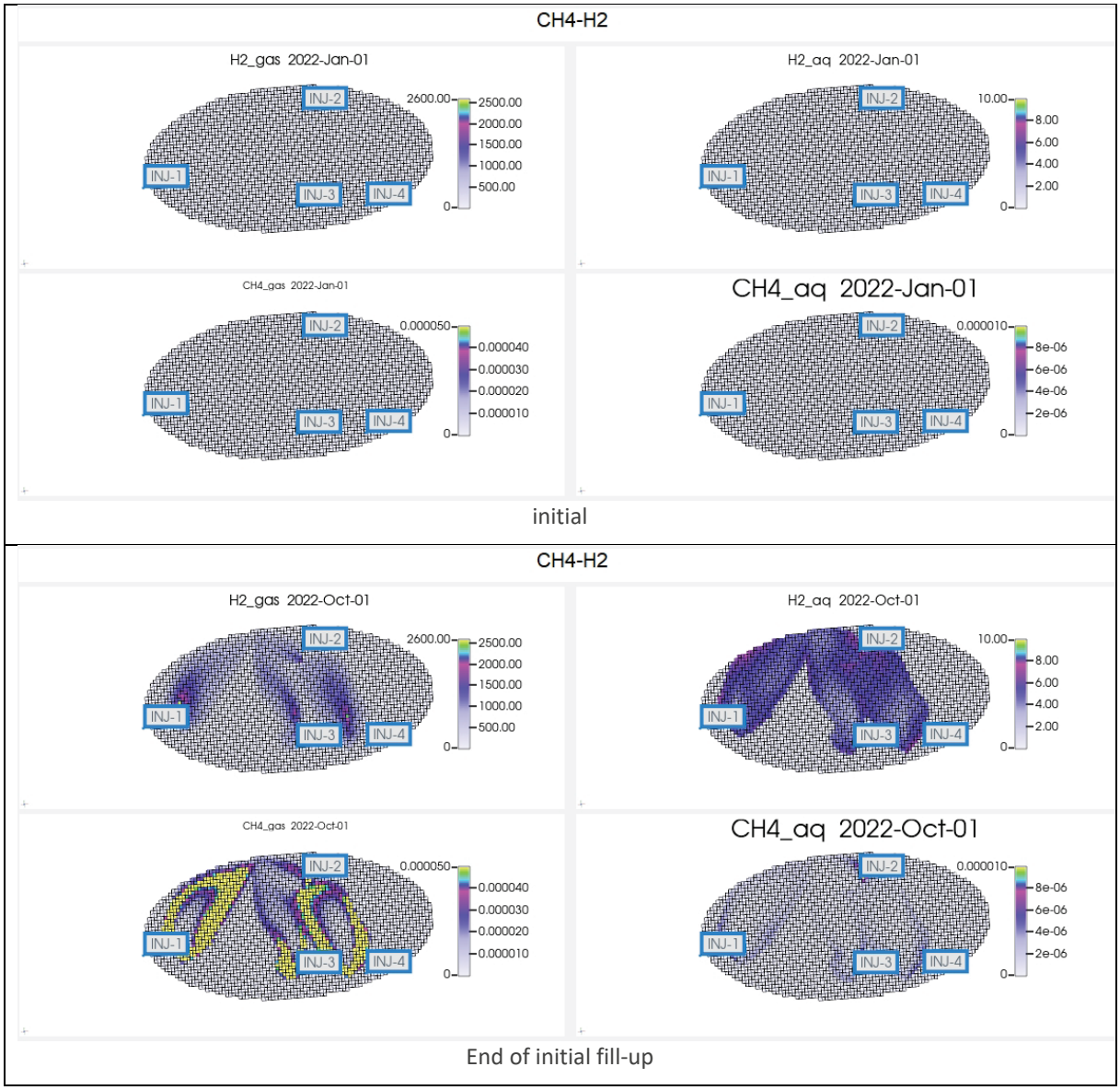
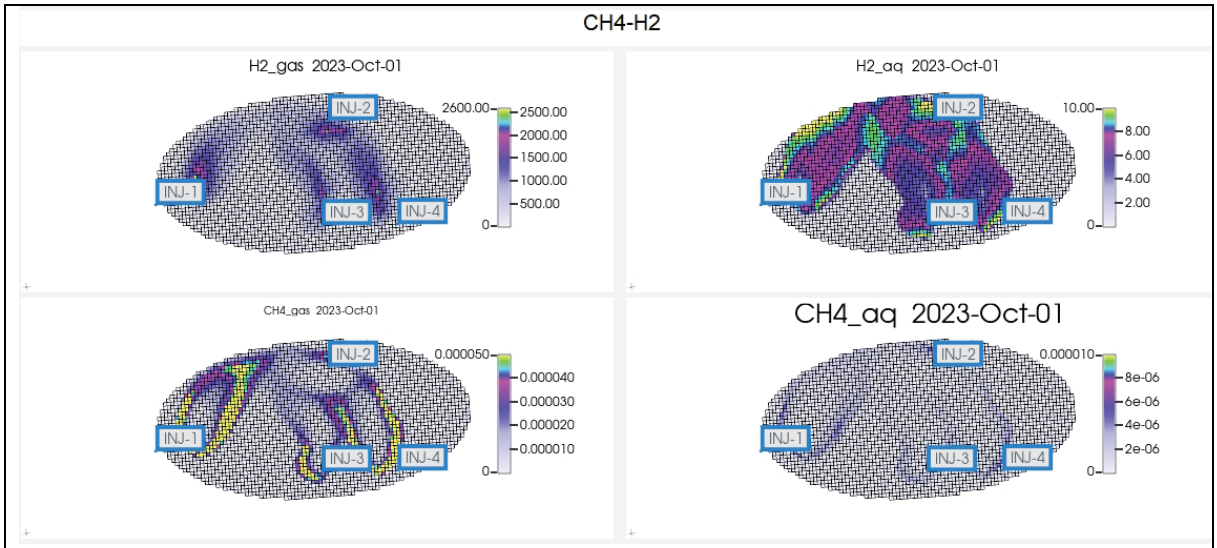


Figure 31: Evolution of withdrawal mass and volume for the synthetic storage for upscaled reaction parameters

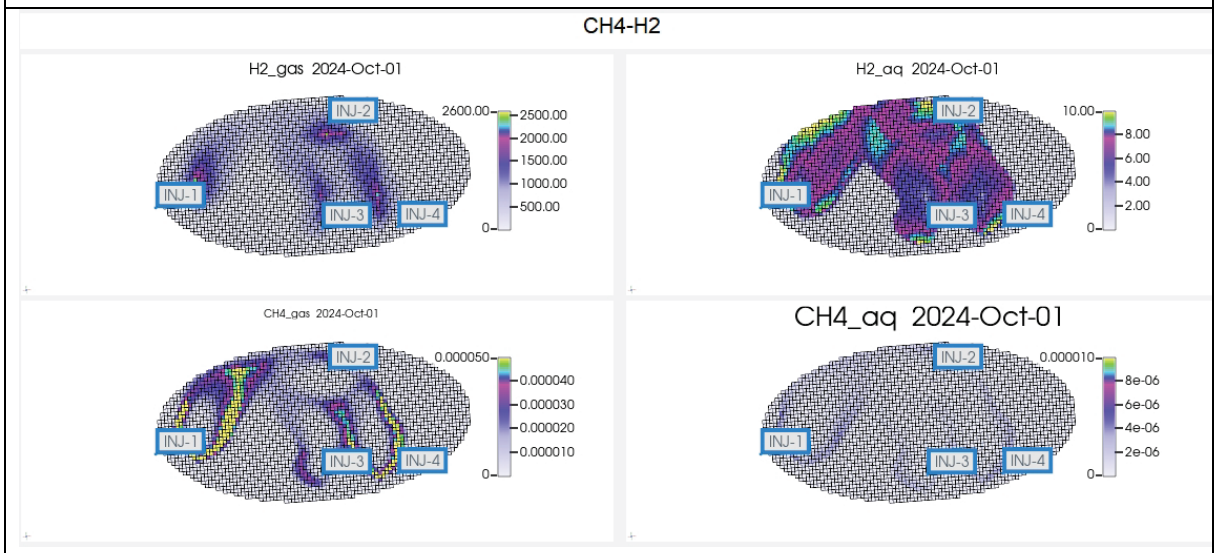
Table 13: Evolution of the maximum mass concentration during the cycles for the synthetic storage for upscaled reaction parameters

Cycle	CH_4 maximum (ppm)	H_2S maximum (ppm)
1	0.4	0
2	0.3	0
3	0.2	0
4	0.2	0
5	0.1	0

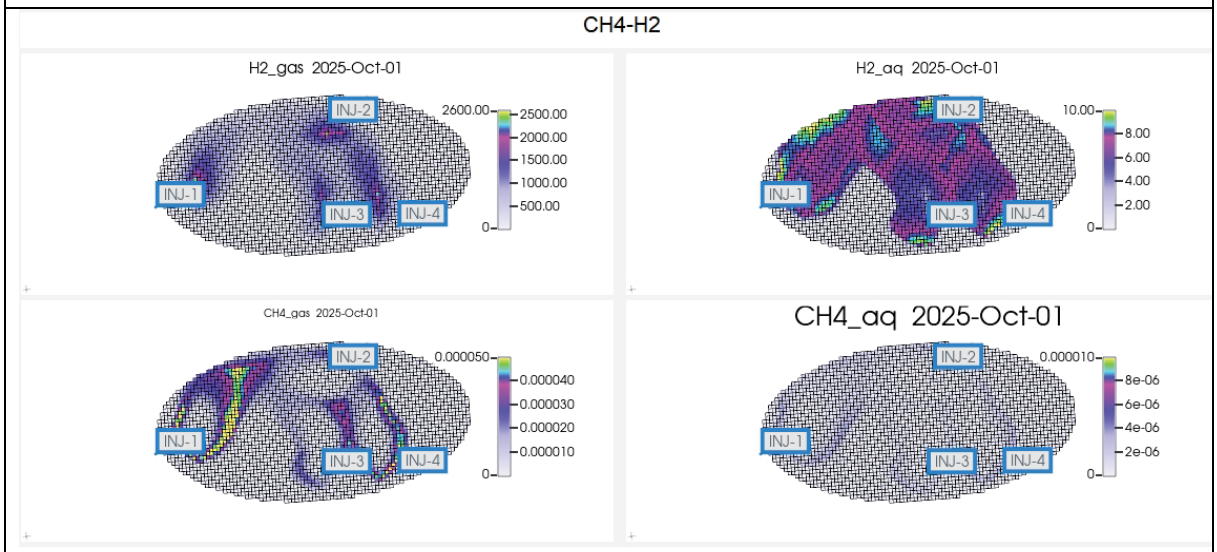




End of first cycle



End of second cycle



End of third cycle

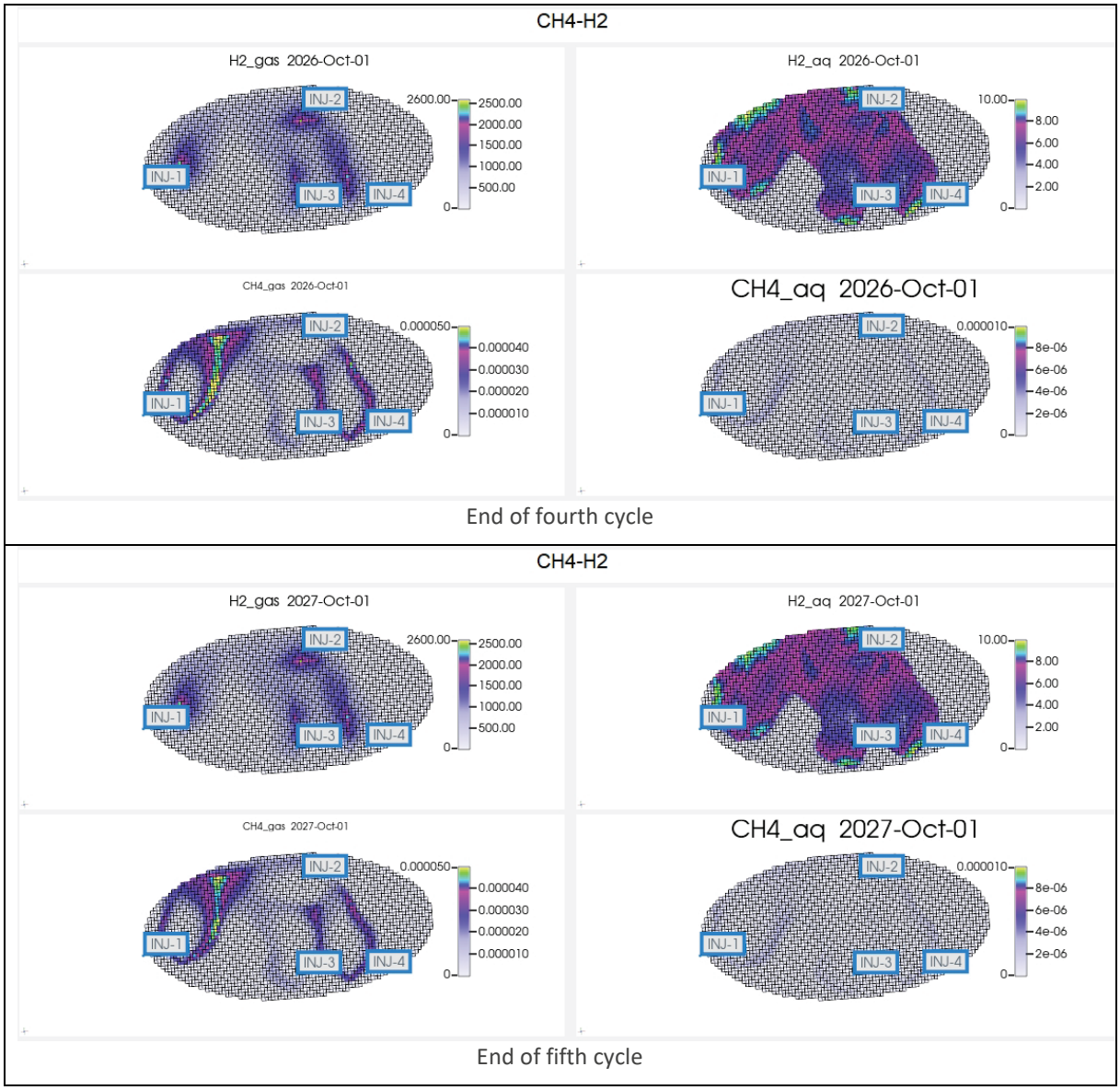


Figure 32: Evolution of the hydrogen and methane volume in gaseous and aqueous phases for upscaled reaction parameters

7. Conclusion

A microbial reactivity model was established using PHREEQC to simulate the methanogenesis and sulphate-reduction reactions observed in the laboratory tests made in Hystories WP3 by MicroPro GmbH. It is underlined that these laboratory tests and modelling were carried out at a specific salinity: 16 300 mg/l. Bacteria development and reactivity are highly dependent on salinity. Therefore, the model and kinetics presented below are valid only for this range of salinity.

Laboratory trend over 70 days at high pressure were well reproduced by the 0D model. Especially, at laboratory scale, the model predicts a consumption of 5 % of hydrogen at the end of the experiment. A production of methane and H_2S (up to 5300 ppm) in the gas phase was also modelled. This concentration is overestimated.

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.

The methanogenesis and sulphate reduction reactions are 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. An approach is proposed based upon water flooding experiences in oil and gas production. As expected, reaction parameters with or without upscaling strongly influence the hydrogen consumption and production of methane and/or hydrogen sulphide in the storage.

According to the model, most of the reactivity occurs at the start of hydrogen injection as in the current approach the bacteria activity, either methanogen or sulphate reduction, are correlated to the aqueous concentration of CO_2 and SO_4 respectively. As implied by the model concept, most of the reactions take place at the interface between hydrogen-rich and hydrogen- poor zones. In the zone swept by hydrogen, the reactivity decreases due to reactant impoverishments. Depending on the selected scale (laboratory scale or upscaled reactivity), the 3D model indicates a maximum amount of impurities between 4.10^{-5} and 0.06 % for methane and 0 and 54 ppm for H_2S. 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.

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APPENDIX 1

PROPOSED PROTOCOL FOR BACTERIA MODELLING REV. C FINAL

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The Project is co-founded by European Union

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