

PS H₂S Generation and Release in Salt Cavern Gas Storage*

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Abstract

Salt caverns are used for the underground gas storage to balance the fluctuations in the supply and demand of natural gas throughout the year. However, the storage of gas in the underground entails risks, e.g. the generation of hydrogen sulfide (H₂S_(g)) during methane storage in salt caverns. H₂S is toxic, leads to gas souring and corrosion of the storage facilities. Therefore, technical regulations determine that the H₂S_(g) concentration in stored gas is limited to 5 mg/m³.

The H₂S is generated by bacterial sulfate reduction (BSR) in the brine and the upper meters of the sump of a salt cavern. Generally, BSR occurs in aqueous anoxic environments. Sulfate-S is used by the bacteria as an electron acceptor to oxidize organic compounds and sulfide is generated. In salt caverns, the sulfate source is provided by anhydrite layers within the salt rock. The stored methane dissolves in the brine until saturation is established and serves continuously as reductant for BSR. Consumption of anhydrite and aqueous methane is accompanied by calcite formation. The H₂S_(g) generated in brine and sump contaminates the stored gas by outgassing. These processes are quantitatively retraced by a three dimensional hydrogeochemical mass-transport model based on chemical equilibrium thermodynamics using the software PHAST. Reaction kinetics of methane oxidation by sulfate are integrated into the model. The modeling approach simulates a semi-generic salt cavern with data from several caverns. Despite the semi-generic nature of the model, the modeling results give basic and quantitative insights into the mechanisms of H₂S_(g) generation in salt caverns induced by BSR.

By varying the input parameters, the factors controlling H₂S_(g) generation are identified and explain why H₂S_(g) is just generated in some salt caverns. An important factor is the availability of anhydrite as sulfate source. Whereas the occurrence of Fe-bearing minerals like goethite inhibit the release of BSR-generated H₂S into the stored gas. The sulfur (S-II/-I) reacts with Fe+II, and mackinawite (FeS) or pyrite (FeS₂) are formed. To identify early H₂S generation and protect the stored gas from souring, a monitoring system should be installed in the brine of the salt cavern. If the aqueous H₂S concentration increases, the addition of dissolved ferrous iron into the brine and the sump is a potential method to reduce H₂S release.

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1. Aim

- Quantitative description of the H₂S_(g) generation and release in salt caverns.
- Analyzing the restriction factors for the H₂S_(g) generation and release in salt caverns.
- Identifying technical approaches to decrease and inhibit the H₂S_(g) generation and release.

2. Introduction

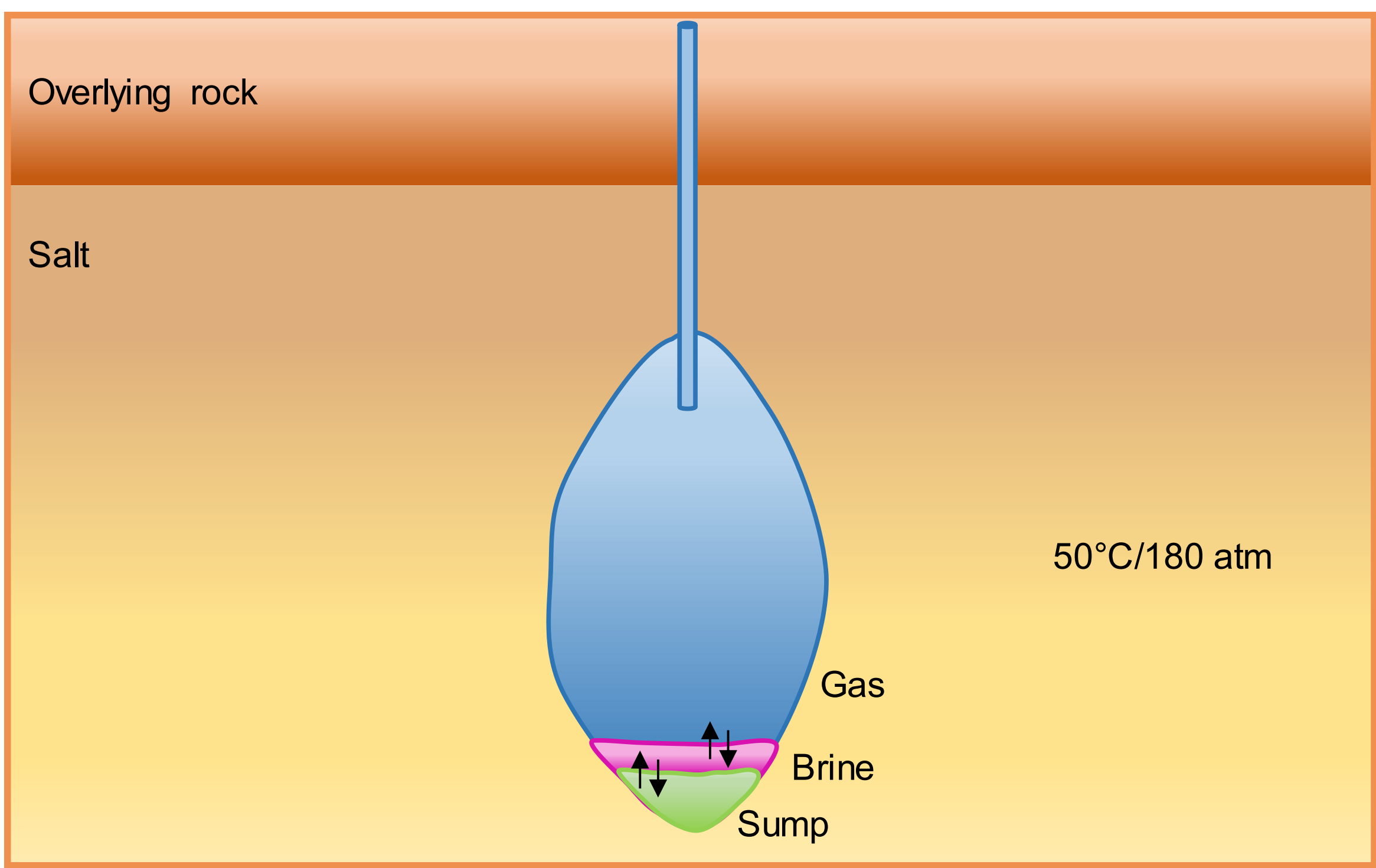


Figure 1. System sketch of the model. Arrows = time-dependent diffusive transport of aqueous components.

- Salt caverns are used for the underground gas storage to balance the fluctuations in the supply and demand of natural gas throughout the year.
- A risk in salt cavern gas storages is the potential generation and release of hydrogen sulfide (H₂S).
- H₂S is toxic if inhaled, aggressive towards the storage facilities, and can pose a risk for the environment.
- H₂S contaminates the stored gas and can affect the gas quality.
- The maximum of 5 mg/m³ H₂S_(g) in the stored gas must not be exceeded (DVGW, 2013).

3. Indications for the potential risk of H₂S generation in salt caverns

- H₂S is observed in hydrocarbon reservoirs where it originates from sulfate reduction (Machel, 2001).
- Anaerobic oxidation of methane (AOM) is possible. This is also observed in non-marine environments (Meulepas et al., 2010).
- Bacterial sulfate reduction (BSR) is observed in saline environments where high rates of sulfate reductions are measured (Kielsen et al., 2007).
- H₂S is detected in the underground storage of town gas (Crotogino, 2016).
- H₂S is noticed in the underground gas storage in porous media (Kleinitz and Böhling, 2005).
- The activity of sulfate reducing bacteria is observed in salt caverns examined for hydrogen storage where they live in the sump and in the brine, generating biofilms at the cavern walls (Panilov, 2016).

4. Conceptual model

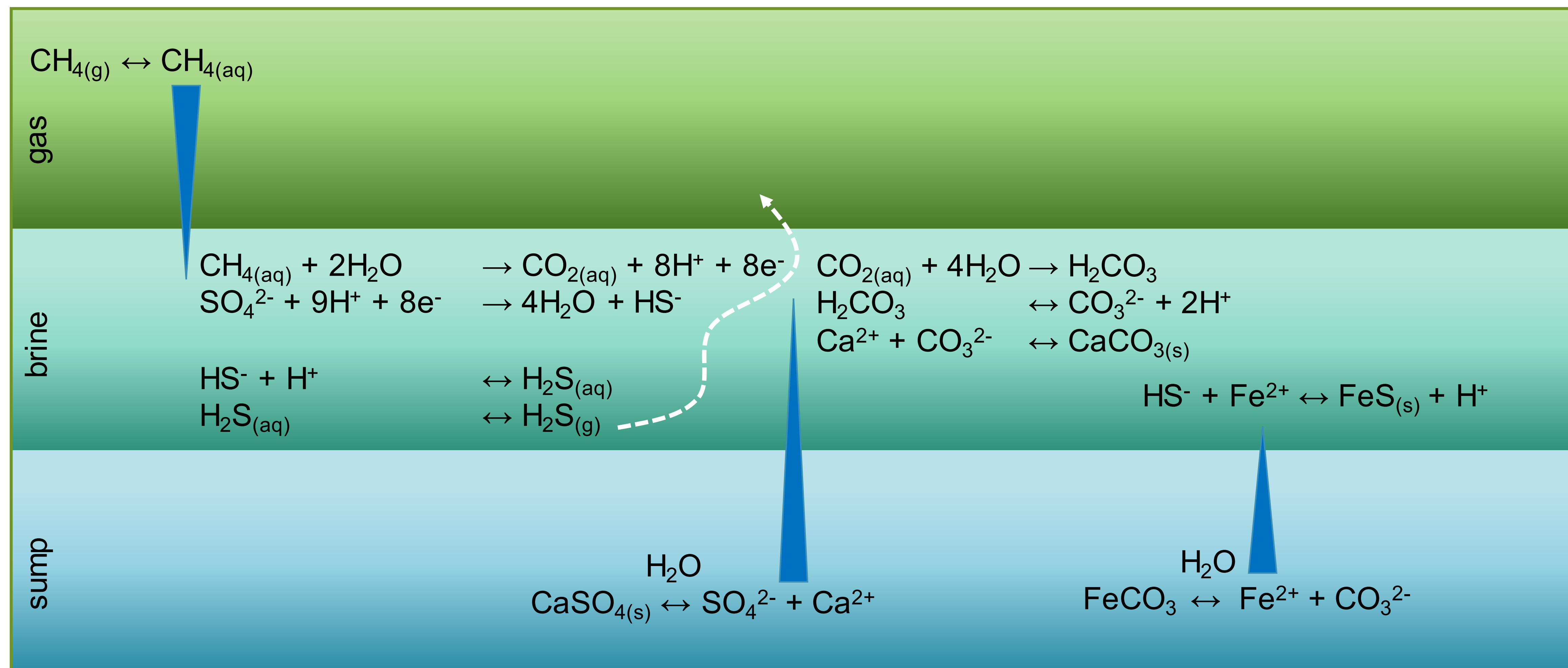
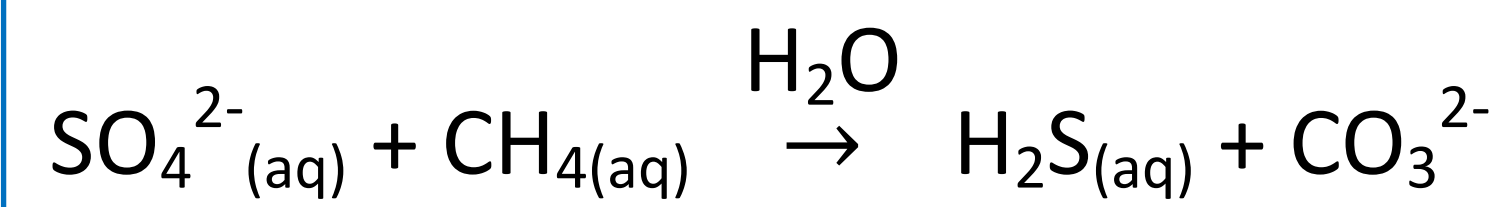


Figure 2. Selected reactions and processes coupled to bacterial sulfate reduction. Single arrow (→) = kinetic-controlled reactions; double arrow (↔) = equilibrium reactions; blue triangles = time-dependent diffusive transport of aqueous components; white dashed arrow = release of generated H₂S_(g) into the stored gas.

Bacterial Sulfate Reduction



4.1. Modeling approach and tools

- The processes are identified and quantified by 1-D and 3-D reactive mass transport models and are described by their spatial and temporal development, based on
 - chemical and thermodynamic principles,
 - the reaction kinetics of bacterial sulfate reduction,
 - the principles of diffusive mass transport.
- The tool for the one-dimensional (1-D) modeling: PHREEQC (Parkhurst and Appelo, 2013; provided by the U.S. Geological Survey). The calculations are based on mass action laws including all species and their corresponding equilibrium constants.
- The tool for the three-dimensional (3-D) modeling: PHAST (provided by the U.S. Geological Survey). The geochemical reactions in PHAST are simulated with PHREEQC. The mass transport calculations are based on HST3D, both are embedded in PHAST (Parkhurst and Charlton, 2010). The results are visualized using the software Model Viewer (Hsieh and Winston, 2002).

- Database: phreeqc.dat (provided by the U.S. Geological Survey)

4.2. Model setup

- The model reproduces a column of 8 cells with a cell length of 1.0 m each.
- Cell 1 delivers CH₄ (C(-4)) continuously by diffusion. Cell 2 is located at the brine-gas interface, cell 3 is placed in the brine, and cells 4-8 in the sump.
- Each cell is defined by specific mineralogical and hydrochemical properties.

PARAMETERS FOR 1-D AND/OR 3-D MODEL

- Cavern height: 350.0 m (300.0 m gas, 2.0 m brine, 48.0 m sump)
- Temperature: 50.0 °C
- Pressure 180.0 atm
- Porosity in the sump: 20 %
- Mass transport: molecular diffusion
- Diffusion coefficient: 5.0 x 10⁻⁹ m²/s (for all aqueous species)
- Dispersivity: 0.05 m
- Tortuosity: 0.1 [-]

Table 1. Initial mineralogical composition of the sump (20 % porosity). The data are modified after Kyle and Posey (1991). Mackinawite, sulfur and calcite are potential secondary phases which may form at saturation.

Primary mineral phases	Weight percent [wt%]	Amount [mol/kgw]
Halite	97.0	144.62
Anhydrite	2.75	1.76
Siderite	0.05	0.04
Quartz	0.05	0.07
Barite	0.05	0.02
Pyrite	0.05	0.04
Dolomite	0.05	0.02

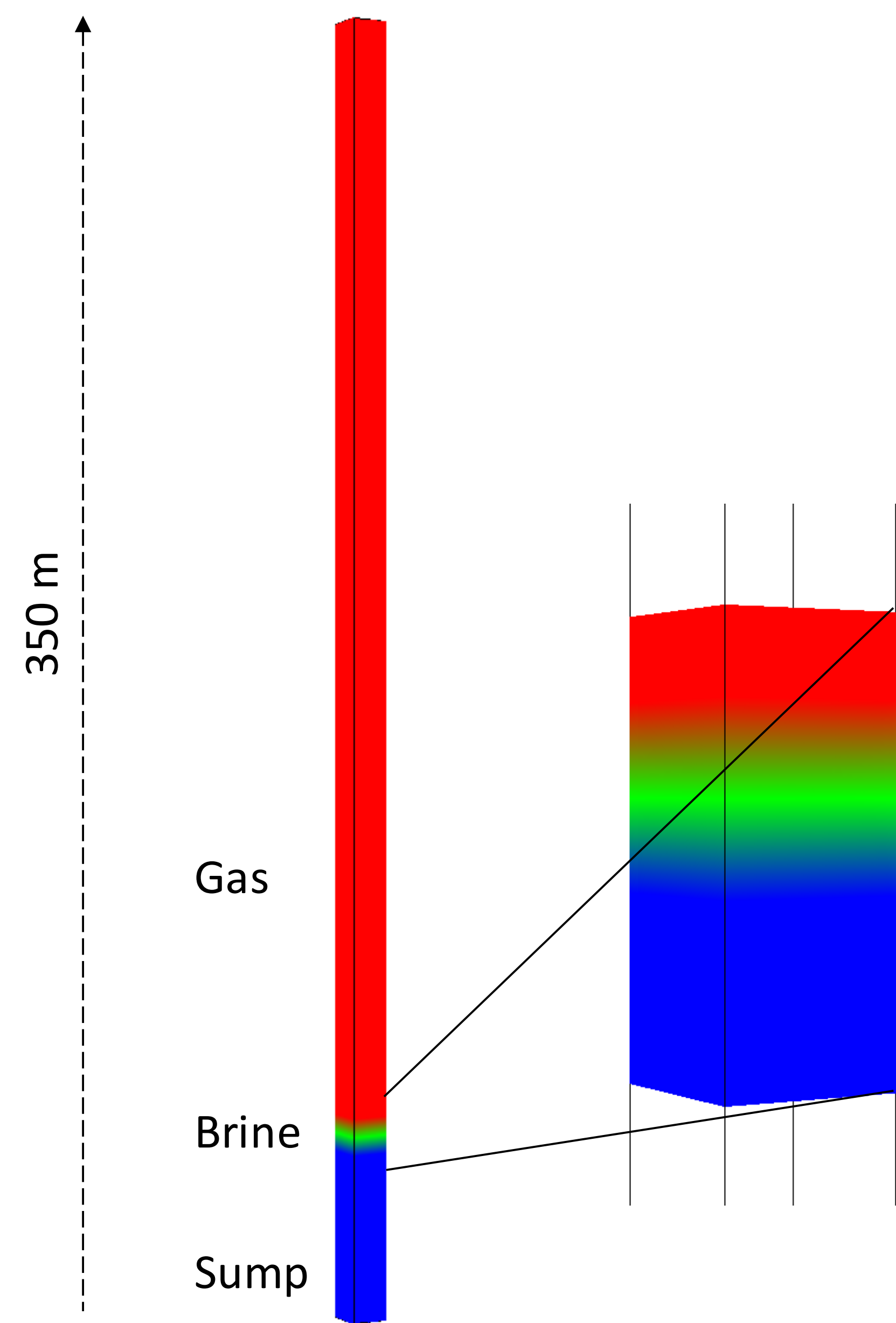


Figure 3. Model setup in PHAST (USGS).

Table 2. Groundwater composition used for leaching (NLWKN 2015), initial composition of the brine and the pore water in the sump.

	Groundwater	Sump	Brine
pH	6.4	8.2	5.7
Temperature [°C]	10.1	50.0	50.0
Elements	Concentration [mol/kgw]	Concentration [mol/kgw]	Concentration [mol/kgw]
Ba	- ^a	8.136e-07	9.097e-07
C	- ^a	2.901e-05	7.077e-03
Ca	1.622e-03	5.488e-02	6.333e-02
Cl	8.380e-04	6.306e+00	6.310e+00
Fe	1.522e-06	2.257e-03	1.415e-03
K	1.010e-04	1.010e-04	1.010e-04
Mg	3.150e-04	1.464e-02	1.315e-03
Mn	9.100e-07	9.100e-07	9.100e-07
N _{tot} ^b	1.150e-03	1.152e-03	3.008e-04
Na	7.050e-04	6.306e+00	6.310e+00
O(0)	6.600e-05	- ^a	- ^a
P	4.840e-07	4.840e-07	4.840e-07
S _{tot} ^c	8.540e-04	7.108e-02	6.262e-02
Si	2.560e-04	5.242e-05	3.368e-02

^a: Not present.

^b: N_{tot}: summed concentration of aqueous N(-III), N(+III), N(+V) species.

^c: S_{tot}: summed concentration of aqueous S(+VI) and S(-II) species.

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5. H₂S generation in salt caverns – results

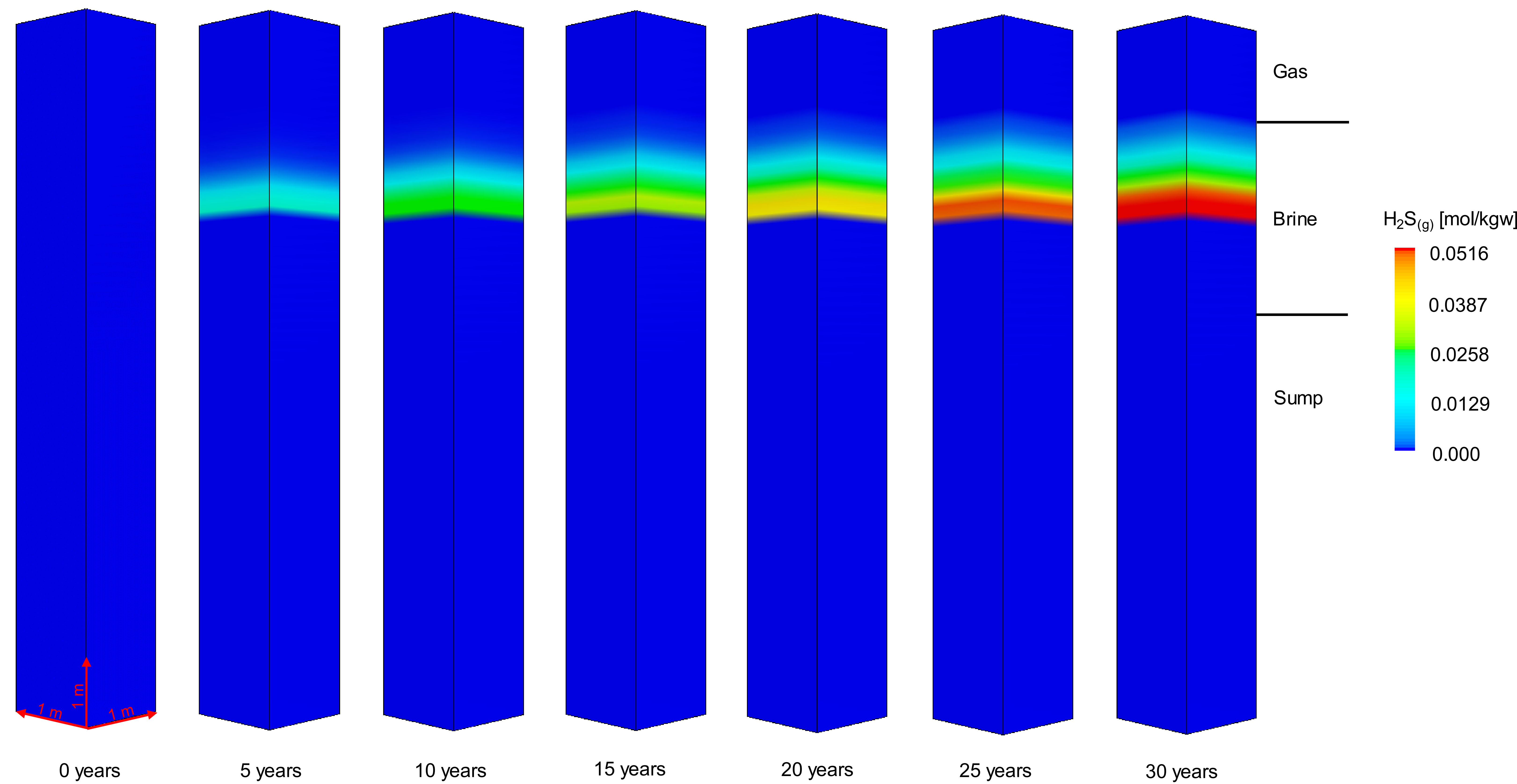


Figure 4. H₂S_(g) generation and the increasing H₂S_(g) amounts with ongoing time and bacterial sulfate reduction.

3-D MODELING RESULTS

H₂S_(g) generation in salt caverns by bacterial sulfate reduction mainly occurs along the diffusive path where methane and sulfate meet and react with each other. At this meeting point, the highest total H₂S_(g) concentrations are identified.

⇒ Diffusion and reaction kinetics of bacterial sulfate reduction mainly control the amount of generated H₂S_(g).

1-D MODELING RESULTS

H₂S is formed as a gas bubble in the brine and is released into the stored gas above if the sum of the partial pressures of all dissolved gases_(aq) is greater or equal to the total gas pressure in the stored gas.

At 50.0 °C and 180.0 atm a total of 7.2 mg/m³ H₂S_(g) is released into the stored gas after 30 years (under given conditions). This value lies above the allowed limit of 5 mg/m³.

6. Calcium and calcite – results

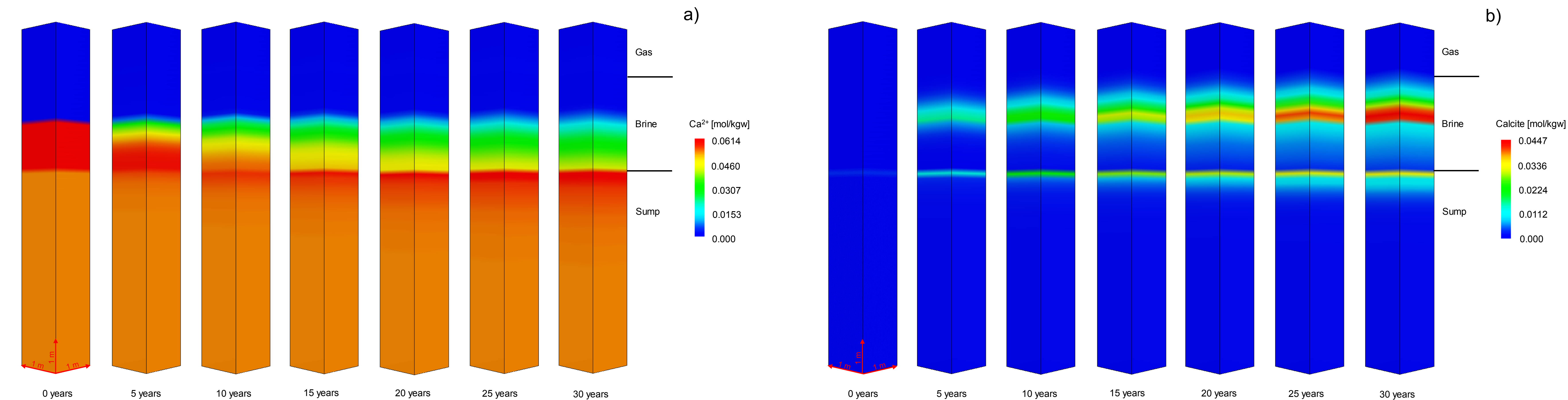
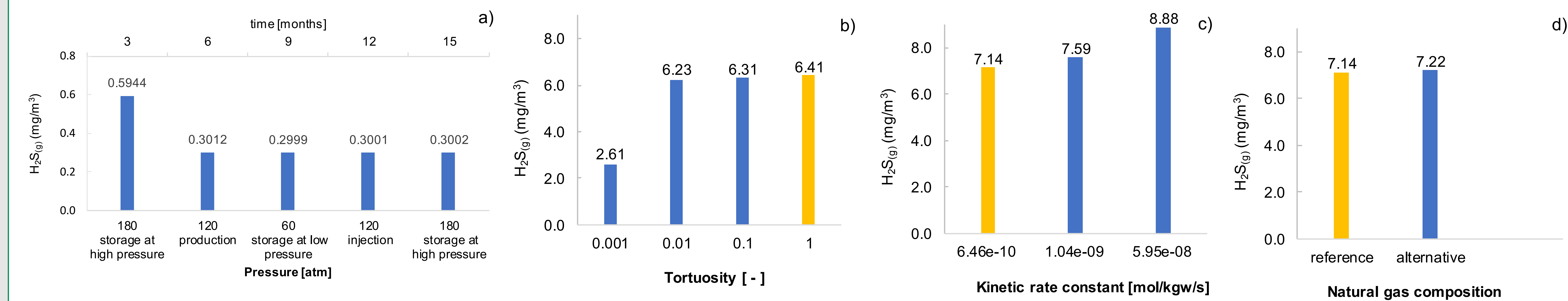


Figure 5. a) Concentrations of aqueous calcium; b) amount of precipitated calcite with ongoing time and bacterial sulfate reduction.

The dissolution of anhydrite contributes Ca²⁺ into the brine and calcite precipitates. Carbonate carbon is provided by methane oxidation. In 30 years: 0.0447 mol/kgw calcite precipitates in the brine.

7. Influencing factors – results

H₂S_(g) GENERATION INFLUENCED BY:



a) The change in pressure conditions has a minor influence on H₂S_(g) generation and release. When the amount of sulfate in the brine is consumed, the sulfate is delivered only by diffusion.
⇒ Diffusion of dissolved methane and dissolved sulfate through the brine is the limiting factor.

b) With increasing tortuosity, the maximum amount of generated H₂S_(g) increases.
⇒ Diffusion of dissolved methane and dissolved sulfate through the brine is the limiting factor.

c) With increasing BSR rate constant, the H₂S_(g) generation increases.
⇒ It is important to get knowledge about the kinetic rate constants at elevated levels of temperature and pressure of (site-specific) cavern conditions as exactly as possible.

d) The chemical composition of the gas used for storage can influence the final H₂S_(g) generation. In this case the effect is small.
⇒ However, knowledge of the exact natural gas composition used for storage is important.

Figure 6. H₂S_(g) generation influenced by a) pressure changes (after 3 months) b) tortuosity (after 30 years) c) kinetic rate constant (after 30 years) d) stored gas composition (reference = typical compositions of natural gas from Russia: 178.128 atm CH_{4(g)}, 1.548 atm N_{2(g)}, 0.324 atm CO_{2(g)}, 0.00018 atm H₂S_(g) and alternative = typical composition of natural gas from the North Sea: 175.032 atm CH₄, 1.476 atm N₂, 3.492 atm CO₂, 0.000288 atm H₂S; data from DVGW 2013; after 30 years) . H₂S_(g) in mg/m³ in the stored gas. Yellow = reference scenario, blue = modified parameters. a), c) and d) are modelled 1-D in PHREEQC and b) is modelled 3-D in PHAST.

H₂S Generation and Release in Salt Cavern Gas Storage

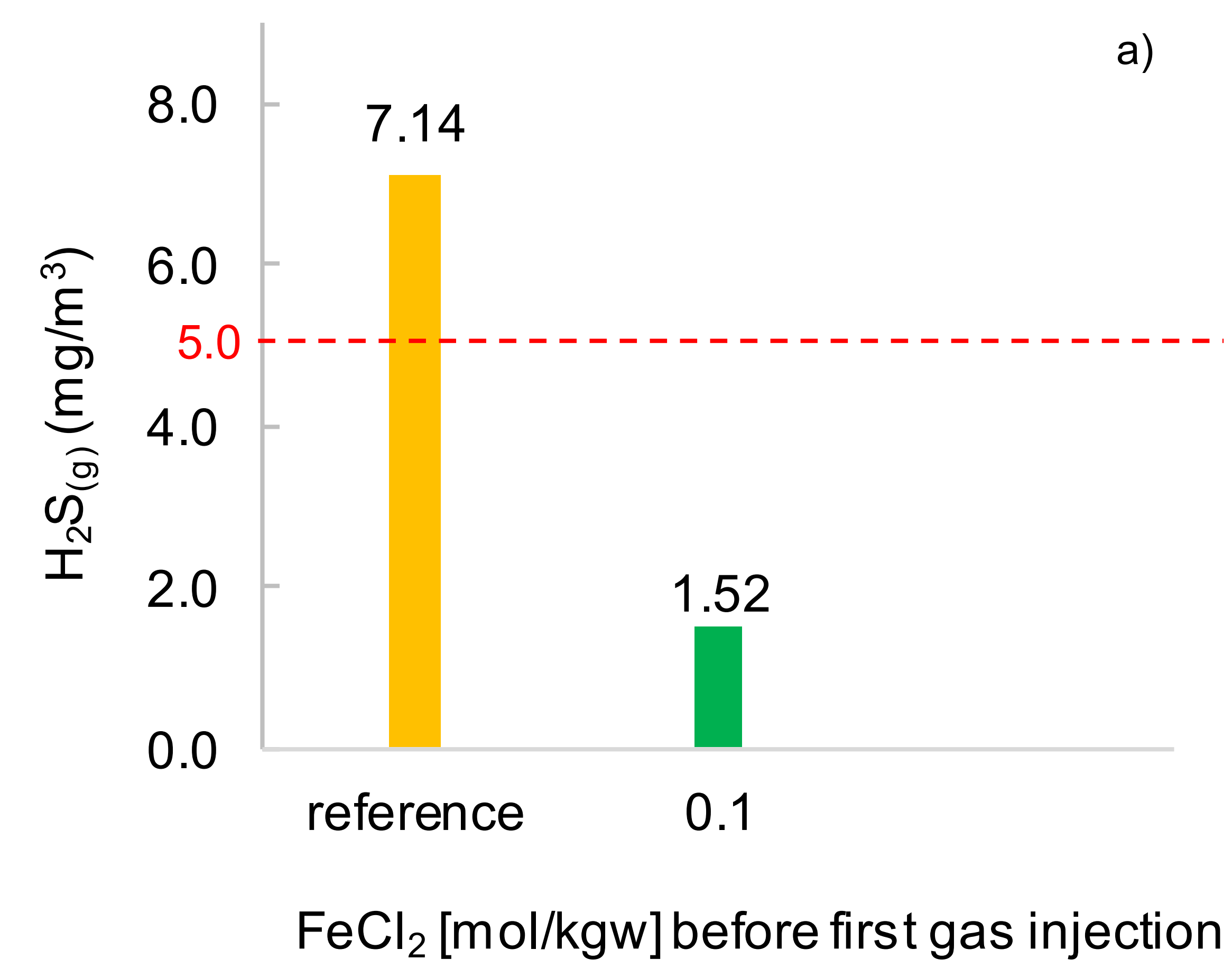


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8. Technical approaches to inhibit H₂S generation and release

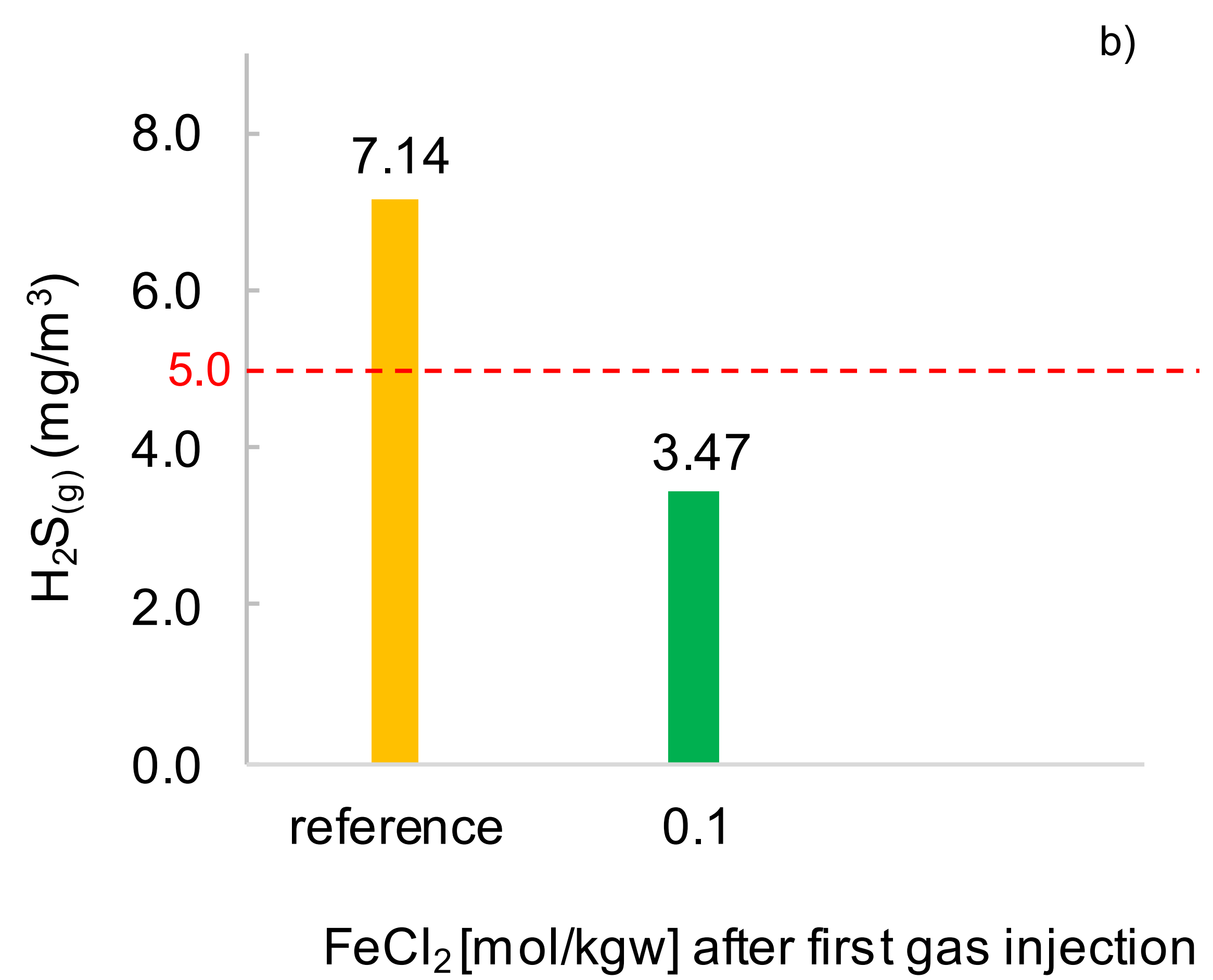


If the H₂S_(g) concentration in the stored gas exceeds the limit of 5 mg/m³ (DVGW, 2013), the stored gas is polluted. Therefore, three possible approaches could be applied to inhibit H₂S_(g) generation and release.

a) Addition of FeCl₂ to the brine directly after leaching (before the first gas injection), inhibits the H₂S_(g) generation (the amount of H₂S_(g) decreases from 7.14 mg/m³ in the reference scenario to 1.52 mg/m³).

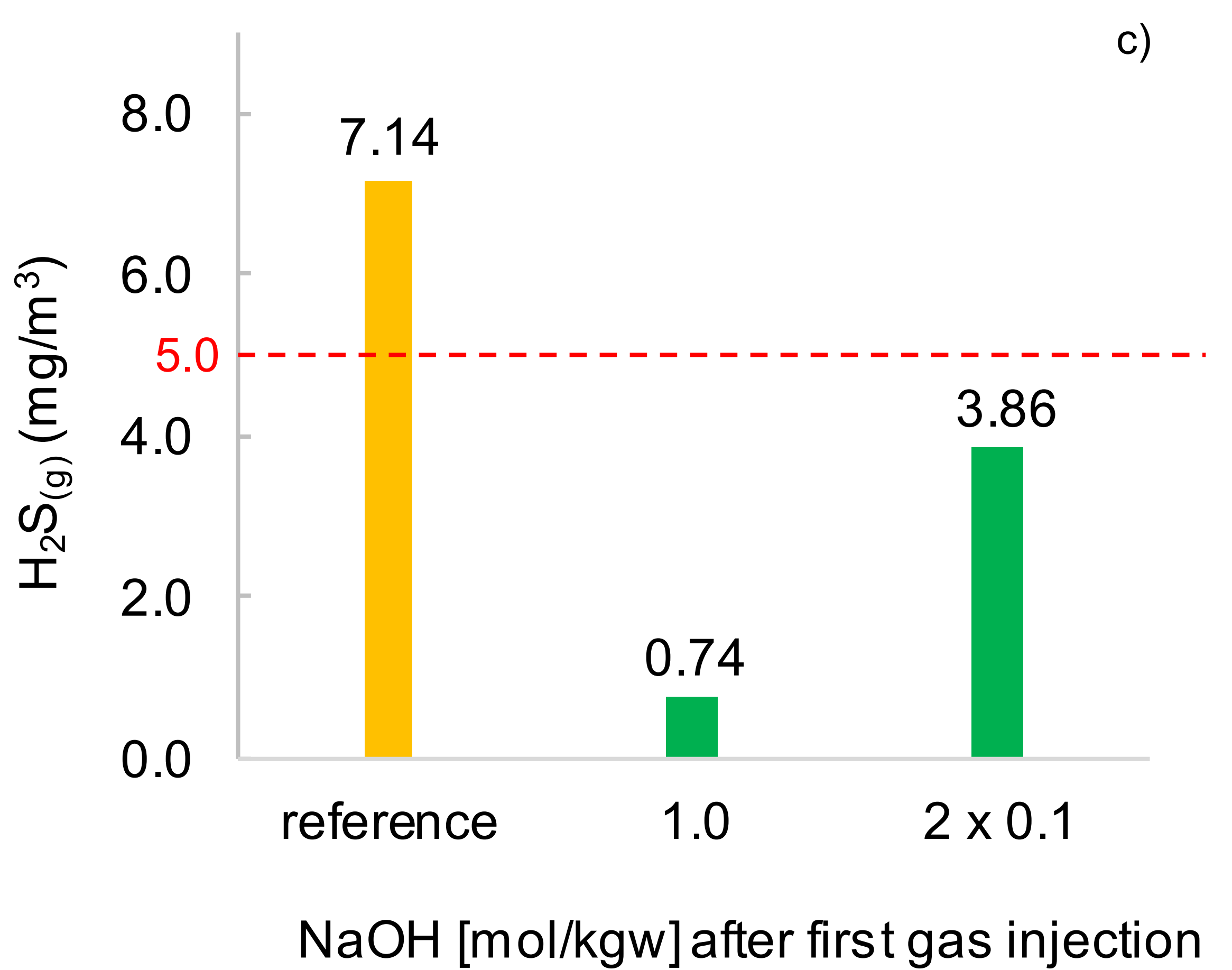
The available Fe²⁺ reacts with aqueous sulfide to form mackinawite (FeS_(s)), so that the aqueous sulfide is no longer available for H₂S_(g) generation. The amount of precipitated mackinawite increases from 0.003 mol/kgw (in the reference scenario) to 0.08 mol/kgw.

Two other approaches could be used when an increase in H₂S_(g) is measured in the stored gas.



b) Addition of FeCl₂ to the brine after gas injection. The available aqueous sulfide reacts with the aqueous ferrous iron and mackinawite precipitates. The aqueous sulfide is no longer available for H₂S_(g) release.

When adding 0.1 mol FeCl₂ after 5 years of storage, a total of only 3.47 mg/m³ H₂S_(g) are generated and released after 30 years. The pH decreases from 6.3 to 5.7, less calcite precipitates (from 0.03 to 0.005 mol/kgw) and mackinawite precipitation increases strongly from 0.004 to 0.05 mol/kgw.



c) Addition of NaOH to the brine increases the pH and inhibits H₂S_(g) generation. The pH shifts the type of sulfide-S from H₂S_(g) to S²⁻_(aq).

When adding 1.0 mol NaOH after 5 years of storage, the total amount of generated and released H₂S_(g) after 30 years is decreased to 0.74 mg/m³. The pH increases from 6.3 (in the reference scenario) to 11.8.

Calcite precipitation decreases from 0.03 to 0.02 mol/kgw and less mackinawite precipitates (from 0.004 to 0.001 mol/kgw).

Another possibility is the addition of 0.1 mol NaOH after 5 years of storage and repetition of the same input after 10 years of storage. The total amount of generated H₂S_(g) decreases to 3.9 mg/m³ after 30 years.

NaOH is available as a waste product from the industry.

Figure 7. H₂S_(g) in mg/m³ in the stored gas after 30 years. Inhibition of H₂S_(g) generation and release by addition of a) FeCl₂ before gas injection, b) FeCl₂ after gas injection c) 1.0 mol/kgw NaOH after 5 years of storage, and 0.1 mol/kgw NaOH after 5 years and after 10 years of storage to the brine. Reference is without any approaches. Yellow = reference scenario, green = inhibition factors. Red line = max. allowed H₂S_(g) concentration in stored gas.

9. Decision flow chart: identifying risks and technical approaches

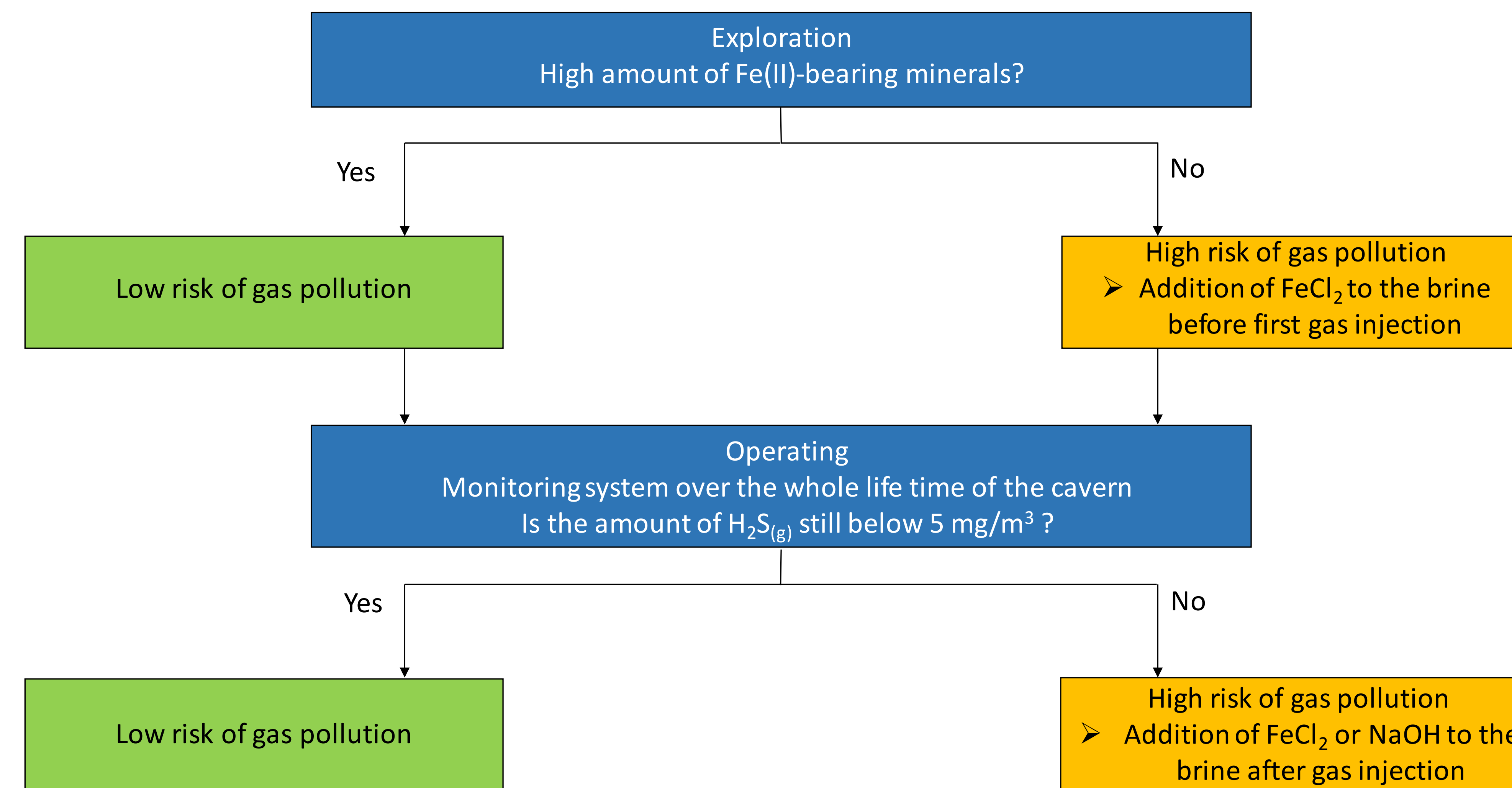


Figure 8. Decision flow chart for the possible approaches to inhibit H₂S_(g) generation and release in salt caverns.

Generally, salt caverns should be constructed in rock salt formations with low amounts of anhydrite and other sulfate sources. However, this is not always possible. In case, the geogenic conditions favor the H₂S_(g) generation, prevention measures should be applied.

We focus on **hydrogeochemical approaches to decrease** the generation and release of **H₂S_(g) into the stored gas**.

⇒ H₂S_(aq/g) measurements and monitoring in the brine and gas could be used as an early warning system.

To inhibit H₂S_(g) generation and release, three possible approaches could be applied:

1. Addition of FeCl₂ to the brine after leaching, before gas injection.
2. Addition of FeCl₂ to the brine after gas injection.
3. Addition of NaOH to the brine after gas injection.

10. Conclusions

- H₂S_(g) generation and related pollution of the stored gas is a possible risk in salt caverns.
- The amount of generated H₂S_(g) mainly depends on the diffusive mass transport, the kinetic rate constant for bacterial sulfate reduction and the amount of available sulfate in the rock salt formation.
- The change in pressure conditions has minor influence on generated H₂S_(g).
- The composition of the stored natural gas has a minor influence on the H₂S_(g) generation.
- There are technical approaches to inhibit the generation and release of H₂S_(g): a) addition of FeCl₂ to the brine directly after leaching, b) addition of FeCl₂ after gas injection and c) addition of NaOH to the brine after gas injection.

Take Home Message

1. Risk of H₂S_(g) pollution in salt caverns exists.
2. H₂S_(g) is generated by bacterial sulfate reduction.
$$\text{SO}_4^{2-}(\text{aq}) + \text{CH}_4(\text{aq}) \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{S}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}$$
3. H₂S_(g) generation can be inhibited by addition of FeCl₂ or NaOH to the brine.

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