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Potential risk of H_2S generation and release in salt cavern gas storage

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ABSTRACT

The storage of natural gas in salt caverns can entail the risk of H_2S generation, which in turn leads to gas pollution. H_2S is generated by bacterial sulfate reduction. The bacteria use aqueous sulfate$_{(aq)}$ as an electron acceptor to oxidize the dissolved hydrocarbons and generate sulfide. Anhydrite is available in the rock salt surrounding the cavern and acts as a sulfate$_{(aq)}$ source. The stored natural gas, with its main component, methane, is in solubility equilibrium with the brine and is additionally delivered by diffusion into the brine. The generated H_2S reaches the stored gas by outgassing from the brine. In this study, these processes are simulated by one- and three-dimensional hydrogeochemical diffusive mass transport models, which are based on equilibrium reactions for gas-water-rock interactions and kinetic reactions for sulfate reduction. Modelling results show that the greatest amount of H_2S is generated in the brine. The amount of generated $H_2S_{(g)}$ is mainly controlled by the amount of available sulfate$_{(aq)}$ as well as the rate of diffusion, which is coupled with the maximum operating live time of salt caverns. Additionally, the amount of generated and released $H_2S_{(g)}$ is sensitive to the chosen kinetic rate constant.

To ensure constant gas quality over time, the gas and the brine must be analyzed continuously and technical methods must be applied when the $H_2S_{(g)}$ concentration increases. According to the modelling results, $H_2S_{(g)}$ generation is inhibited by addition of dissolved ferrous iron to the brine. Dissolved ferrous iron reacts with sulfide-sulfur to form mackinawite ($FeS_{(s)}$) so that aqueous sulfide is no longer available for $H_2S_{(g)}$ generation. Another method is the addition of NaOH to increase the pH of the brine. Then, higher fractions of generated sulfide-sulfur are transformed to free $S^{2-}{}_{(aq)}$ instead of $H_2S_{(g)}$ and $H_2S_{(aq)}$.

1. Introduction

Natural gas is stored in salt caverns to balance the supply and demand of natural gas throughout the year. Salt caverns are highly qualified for hydrocarbon storage because of numerous physical properties and mechanical behaviors of the rock salt halite, like its self-healing forces and its impermeability below 300 m (Evans, 2008; Yang et al., 2013). However, Evans (2008) has stated that “there is a need to assess the safety record of previous and existing underground fuel storage facilities.” One risk is the potential generation and release of gaseous hydrogen sulfide ($H_2S_{(g)}$) in natural gas storage systems. H_2S is toxic if inhaled, is aggressive towards storage facilities (Cord-Ruwisch et al., 1987; Kleinitz and Böhling, 2005), and can pose a threat to the environment (Reitenbach et al., 2015). The presence of H_2S can lead to corrosion of metallic iron under anaerobic conditions and to the precipitation of amorphous ferrous sulfide, which in turn may cause plugging (Cord-Ruwisch et al., 1987). Even more importantly, H_2S contaminates the stored gas and can affect the gas quality (Cord-Ruwisch et al., 1987). Therefore, in Germany, technical regulations determine that the concentration of 5 mg/m^3 $H_2S_{(g)}$ in stored gas must not be exceeded (DVGW, 2013).

There are considerable indications that $H_2S_{(g)}$ generation could be a potential risk in salt caverns used for gas storage. First, H_2S is observed in hydrocarbon reservoirs where it originates from sulfate reduction (Machel, 2001), either via abiotic reactions or via reactions catalyzed by bacteria. The abiotic reaction, so-called thermochemical sulfate reduction (TSR), is common in geological settings with temperatures ranging from 100 to 180 °C, while the bacterial sulfate reduction (BSR), occurs in low-temperature geological settings ranging from 0 °C to 60–80 °C (Ehrlich, 1990; Machel, 2001; Postgate, 1984). In some cases, BSR has been

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observed above 80 °C. Hyperthermophilic sulfate-reducing bacteria may live at temperatures up to 110 °C (Jorgensen et al., 1992). However, BSR does not necessarily occur in all hydrocarbon-bearing geosystems with temperatures below 80 or 110 °C. Otherwise, all hydrocarbon reservoirs below this temperature would be sour, meaning H_2S-bearing (Machel, 2001), and would display higher total sulfide concentrations in the aqueous and the gas phase. Therefore, in this study, we focus on salt caverns filled by natural gas and exposed to temperatures ranging from 50 to 80 °C. Our focal point is the formation of sulfide-sulfur (S(-II)) from sulfate-sulfur (S(+VI)) via BSR and the subsequent release of formed sulfide-sulfur (S(-II)) as $H_2S_{(g)}$ into the stored natural gas.

An additional indication of H_2S generation by BSR in salt caverns is the possible anaerobic oxidation of methane (AOM), which is observed in marine as well as in non-marine environments (Meulepas et al., 2010). In aqueous anoxic environments, sulfate-reducing bacteria (SRB) use sulfate as an electron acceptor to oxidize organic compounds and generate sulfide (Eq. (1)). This generated sulfide-S could be available as aqueous H_2S, $HS^-{}_{(aq)}$, and $S^{2-}{}_{(aq)}$ and gaseous H_2S. SRB use the produced energy from sulfate reduction to sulfide for cell growth (Cord-Ruwisch et al., 1987). The sulfate for BSR could be derived from the aqueous dissolution of calcium sulfide-sulfur mineral phases like gypsum $(CaSO_4[2H_2O])_{(s)}$ and anhydrite $(CaSO_4)_{(s)}$.

$$SO^{2-}_{4(aq)} + CH_{4(aq)} \xrightarrow{H_2O} H_2S_{(aq)} + CO^{2-}_{3(aq)} + H_2O \tag{1}$$

The increasing demand for storage capacity in salt caverns requires the utilization of less favorable salt formations, including inhomogeneous salt structures with larger proportions of insolubles like anhydrite layers (Schneider and Crotogino, 2010). Drilling operations and/or workover operations may lead to bacterial contamination of hydrocarbon reservoirs, or SRB populations may pre-exist in such reservoirs (Kleinitz and Böhling, 2005). The optimal growth temperature for SRB is 38 °C (Bernardez et al., 2013) at near-neutral pH conditions (Cord-Ruwisch et al., 1987). However, SRB also occur in more acidic environments of pH 3 (Tuttle et al., 1969) and pH 4 (Church et al., 2007).

Furthermore, BSR is observed in saline environments where high rates of sulfate reduction are measured (Kjeldsen et al., 2007). The activity of most SRB decreases if the Na^+/Cl^- concentrations are above 50–100 g/L (Cord-Ruwisch et al., 1987; Postgate, 1984; ZoBell, 1958) but activity of SRB is even found in salt lakes and brines near "salt saturation" (ZoBell, 1958). Even if these conditions are not the optimum for SRB growth, a few SRB tolerate the high salt (NaCl) concentrations and live near salt saturation (Cord-Ruwisch et al., 1987).

Additionally, $H_2S_{(g)}$ is detected in underground storage systems of town gas (Crotogino, 2016) and in underground gas storage in porous media (Kleinitz and Böhling, 2005). Furthermore, the activity of sulfate-reducing bacteria is observed in salt caverns filled by hydrogen gas. There, the SRB live in the sump and in the brine, generating biofilms at the cavern walls (Panfilov, 2016).

This study focuses on H_2S generation by bacterial sulfate reduction in a salt cavern that is described by one- and three-dimensional hydrogeochemical reactive transport models. It is based on thermodynamic equilibrium reactions for gas-water-rock interactions and kinetic reactions for sulfate reduction. The aims of this study are (1) to draw the attention of the possible risk of $H_2S_{(g)}$ pollution in salt caverns, (2) to clarify and quantify time-dependent $H_2S_{(g)}$ generation processes in salt caverns filled with natural gas, (3) to analyze the limiting factors for $H_2S_{(g)}$ generation and release in salt caverns, and (4) to identify technical methods to decrease or inhibit $H_2S_{(g)}$ generation and release.

2. Methodology

2.1. Modelling tools

The one- and three-dimensional reactive mass transport models are based on chemical-thermodynamically principles, the reaction kinetics of BSR and the principles of diffusive mass transport.

The modelling tool for the 1-D model in this study is the computer program PHREEQC version 3 provided by the U.S. Geological Survey. PHREEQC is based on an ion-association aqueous model and can simulate batch-reaction, speciation, inverse geochemical and one-dimensional transport calculations (Parkhurst and Appelo, 2013). The calculations are based on mass action laws including all species and their corresponding equilibrium constants. The activity coefficients of species are calculated by the Debye-Hückel equation. The equilibrium phases, mass-action equations, and equilibrium constants used in the model are shown in Table 1.

The computer program PHAST (version 3.3.7–11094), provided by the U.S. Geological Survey, is the modelling tool for the 3-D model. Using PHAST, multicomponent geochemical reactions, solute transport and groundwater flow can be simulated (Parkhurst and Charlton, 2010). The geochemical reactions in PHAST are simulated with PHREEQC and the flow and transport calculations are based on HST3D; both programs are embedded in PHAST (Parkhurst and Charlton, 2010). The results are visualized using the software Model Viewer (Hsieh and Winston, 2002). The combined application of PHREEQC/PHAST and the Model Viewer software enables the visualization of the temporal and spatial development of H_2S generation in salt cavern gas storages. Detailed information about PHREEQC and PHAST are given in Parkhurst and Appelo (2013) and Parkhurst and Charlton (2010).

The thermodynamic database; which includes all elements used in the model with their species (aq, s, g), mass-action equations, and equilibrium constants; is essential for modelling with PHREEQC and PHAST. The database used for 1-D and 3-D modelling is phreeqc.dat. A more suitable database for the high Na^+ and Cl^- concentrations and the high ionic strength in the model could be the Pitzer database (pitzer.dat), but pitzer.dat does not include Si-containing aqueous species, Al^{3+}, and silicate minerals, which are important factors when modelling H_2S generation in salt caverns. To validate that PHREEQC (using phreeqc.dat) produces correct results, even under high Na^+ and Cl^- concentrations and high ionic strength, the salt solubility in PHREEQC (using phreeqc.dat) is compared with salt solubility data from literature. In Zimmermann et al. (1986), the solubility of Na^+/Cl^- is given in dependence of the

Table 1
Equilibrium phases, mass-action equations, and equilibrium constants (log K, at 25 °C and 1 bar). Data are from phreeqc.dat, except for $CH_{4(g)}$, $H_2S_{(g)}$, $N_{2(g)}$ which are from llnl.dat (Parkhurst and Appelo, 2013).

Equilibrium phase	Equilibrium reaction	log K
Halite	$NaCl = Cl^- + Na^+$	1.570
Anhydrite	$CaSO_4 = Ca^{2+} + SO_4^{2-}$	−4.39
Siderite	$FeCO_3 = Fe^{2+} + CO_3^{2-}$	−10.89
Quartz	$SiO_2 + 2H_2O = H_4SiO_4$	−3.98
Barite	$BaSO_4 = Ba^{2+} + SO_4^{2-}$	−9.97
Pyrite	$FeS_2 + 2H^+ + 2e^- = Fe^{2+} + 2HS^-$	−18.479
Dolomite	$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	−17.09
Mackinawite	$FeS + H^+ = Fe^{2+} + HS^-$	−4.648
Sulfur[a]	$S + 2H^+ + 2e^- = H_2S$	4.882
Calcite	$CaCO_3 = CO_3^{2-} + Ca^{2+}$	−8.48
$CH_{4(g)}$	$CH_4 = CH_4$	−2.8502
$CO_{2(g)}$	$CO_2 = CO_2$	−1.468
$H_2S_{(g)}$	$H_2S = H^+ + HS^-$	−7.9759
$N_{2(g)}$	$N_2 = N_2$	−3.1864

[a] Sulfur = elemental sulfur.