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A Novel Quantitative and Predictive Reservoir-Souring Approach to Assess Reservoir Souring During Planned-Waterflood Development Plan

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Abstract

Souring potentials of fields during planned-waterflood development need to be investigated to enable the selection of the injection-water source and facility-design options. This paper presents the application of a novel reservoir-souring approach to assess the souring potential of a Middle-East field that is associated with three potential injection-water sources in terms of souring, to recommend ways to prevent or reduce H_2S production, and to determine the optimum solution for injection water.

The novel approach includes fluid sampling and analysis, a desktop study, a dynamic-reservoir simulation, and a surface-facility evaluation. In the desktop study, a qualitative assessment of souring associated with the three potential injection-water sources (shallow-aquifer water, produced water, and mixtures of produced and shallow water) and mitigation strategies to limit future H_2S concentrations were carried out. Subsequently, a compositional non-isothermal dynamic model that includes 3 phases, 18 components, and 18 reactions was developed to quantitatively predict the most-likely and the worst-case H_2S levels over the field's life. Several sensitivity runs were performed to assess the impact of the key uncertain parameters on the H_2S level.

The results indicate that re-injection of produced water (deep aquifer) with a salinity of 173,000 mg/l not only has a very low souring risk, but also offers the most manageable conditions in terms of scaling and corrosion control for both the reservoir and the facilities. For this water, the simulated earliest H_2S-breakthrough time is year 2038 and the H_2S concentration in the gas phase will not exceed 1000 ppmv until 2074. On the other hand, injection of the shallow-aquifer water with a salinity of 11,000 mg/l has a high risk of souring. The simulated earliest H_2S-breakthrough time is 2025 and after breakthrough within one year the gas-phase H_2S concentration reaches 1,500 ppmv at ambient conditions. When mixtures of produced and shallow-aquifer water are used, the risk of souring depends on the mixture salinity; if it would be higher than 150,000 mg/l, the souring risk would still be very low, otherwise the souring risk would be moderate to high.

In terms of mitigations, nitrate injection is very effective in significantly reducing the high souring risk of injecting the shallow-aquifer water. Stripping out the dissolved H_2S in the shallow-aquifer water can delay the H_2S-breakthrough time by 11 years and can reduce the max H_2S concentration by 50%.

Introduction

The AA field has started producing since 2016. Oil has been produced under primary depletion. The field is currently undergoing field development planning (FDP) using waterflooding. For the full-field waterflood, injection water will be derived from either (1) produced water re-injection from the reservoir, (2) a shallow aquifer, or (3) a mixed injection water of the two previously mentioned sources. The current facilities are not sour safe because no produced H_2S was assumed. Therefore, the risk of water-induced reservoir souring from H_2S production during water injection is a major concern for facilities corrosion and HSE.

This study aims to evaluate the souring risk associated with each injection-water source and the duration until H_2S breakthrough at production wells, if applicable. Particularly, the shallow aquifer is of interest because it is a new potential water source that needs to be understood. Furthermore, we present mitigation strategies to limit future H_2S levels during waterflooding, but we also qualitatively assess the potentially significant impacts of scaling and corrosion on operations.

The paper is organized as follows. First, we discuss our reservoir-souring workflow. Then, we give a general overview about the available water-injection sources. Afterward, we discuss a qualitative prediction of H_2S levels in the field (desktop study). After that, we elucidate the steps taken to develop a compositional dynamic box model. Next, we use the compositional dynamic box model to run different souring-forecast scenarios. We perform a number of sensitivity runs to assess the impact of the key uncertain input parameters on the souring level. Subsequently, we investigate nitrate injection as a mitigation option. Finally, we summarize the conclusions and recommendations of the key findings of this study.

Reservoir-Souring Workflow

In this Chapter, we present a reservoir-souring workflow that is based on our experience of carrying out several reservoir-souring projects. Fig. 1 illustrates our reservoir-souring workflow.
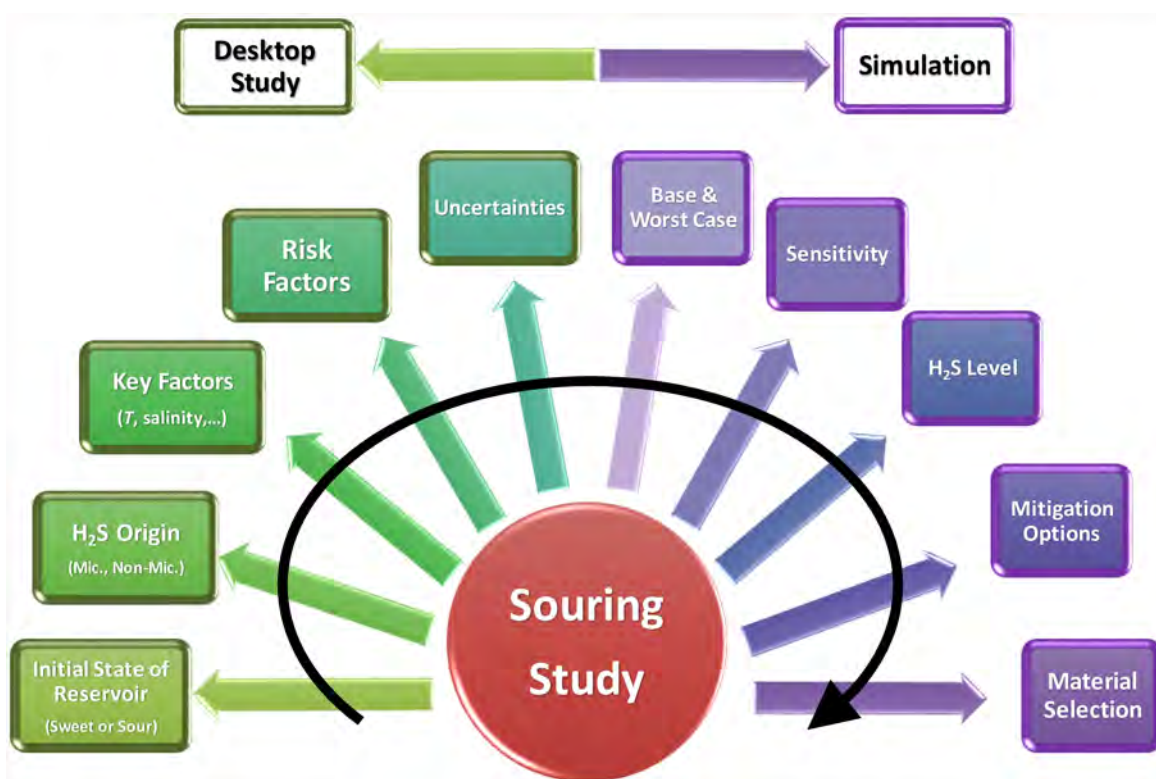

Figure 1—PanTerra workflow for reservoir-souring studies.

The reservoir-souring workflow shown in Fig. 1 consists of a desktop study, a well sampling and analysis, and a modeling study to address all objectives of a reservoir-souring-assessment study.

Desktop Study

The desktop study involves data gathering and analysis thereof to qualitatively assess possible souring principles and processes. Data of the field is analyzed. The biogenic and non-biogenic factors that may have an impact on souring in the field under consideration are inventoried and associated reactions are defined providing input for the modeling phase. The results of the desktop study will be integrated in the well sampling-and-analysis and used in the modeling as well.

Study the Possible Souring Principles and Processes. In this stage, we study the possible souring principles and processes to determine the origin(s) of the produced H_2S (see Fig. 2). To achieve this goal, we

- map out the H_2S occurrence in the field block and over time. We determine the water injection, volumes, injection water and H_2S occurrence during the field history;
- make inventory of all major chemical and physical processes that will influence degree of biogenic or non-biological souring in the reservoir: geophysical elements, bacterial nutrients (fatty acids, oil components, sulfate, oxygen, others, including added production chemicals) content in injection and reservoir waters per production scenario, temperature, phase partitioning, adsorption and mineral scavenging;
- identify the most probable cause (source) of the souring in the reservoir by studying available reservoir data. Check possibility of apparent souring due to partitioning;
- parameterize the souring processes e.g., temperature, pressure, water and rock composition and nutrient concentrations, H_2S-PVT data, mineral-scavenging capacity;
- Define simulation inputs.
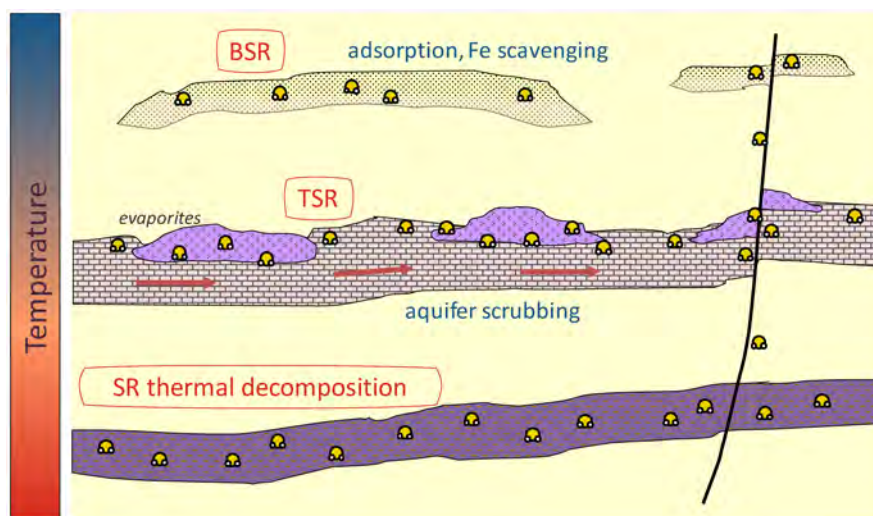
Figure 2—Different H_2S origins (sources). BSR (bacterial-sulfate reduction) origin is microbial whereas TSR (thermo-chemical sulfate reduction) and thermal decomposition are non-microbial origins.

Well Sampling and Analysis

For reservoir-souring assessments, analyses of the produced- and proposed injected water are necessary. The goals of well sampling are to

- determine the actual H_2S levels in the gas phase at the wellhead;

- determine the actual H_2S levels in the vapor liberated from crude;

- determine dissolved H_2S concentration in injected water;

- determine sulfur isotope ($\delta^{34}S$) of dissolved sulfate in produced and injected water;

- precipitate dissolved H_2S in water for $\delta^{34}S$ measurement;

- collect dead oil at well heads for $\delta^{34}S$ measurement;

- collect water at wellheads and production and/or water treatment facilities to be analyzed for presence of sulphate reducing bacteria (SRB), volatile-fatty acid (VFA), BTEX (benzene, toluene, ethyl-benzene, and xylene), nitrate, ions etc.

In terms of analysis, we typically need the following to be measured for the produced and injected fluids:

- Cations and Anions;

- Sulfate content;

- Total dissolved sulfide (if any)

- VFA content

- pH

- Density

- Nitrate

- Salinity

- Sulfur isotope ratio of sulfate in the water

- Sulfur isotope ratio of dissolved H_2S in the water if any

- Sulfate reducing bacteria and total bacteria content

- TOC and BTEX in water

For the gas, we need the following to be measured:

- Sulfur isotope ratio of H_2S

- H_2S concentration (free gas and dissolved gas)

For the oil, we need the following to be measured:

- HC composition up to C36+

- Sulfur isotope ratio of sulfur in oil

Reservoir-Souring Dynamic Simulation
The aim of this phase is to build a reservoir-sour model that can simulate different reservoir-souring processes. We develop a sour model such that it is capable to combine theoretical and empirical data to consider the effects of temperature, pressure, pH, salinity, water chemistry. We use CMG STARS for the souring modelling. Fig. 3 shows the features of our reservoir-souring dynamic model.
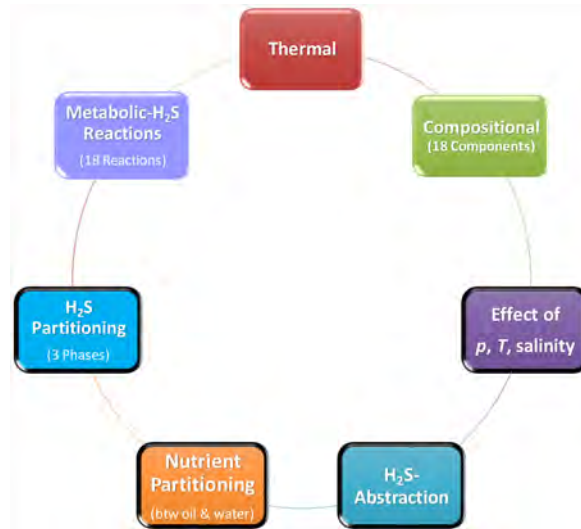
Figure 3—Reservoir-souring dynamic-model features.

The simulation phase includes the following items:

1. Verify existing static and dynamic models in terms of geological features and the quality of the history matching of the production data (oil rate, GOR, water cut, and pressures);
2. Build a base-case sour model in CMG-STARS;
3. Build and implement EOS/k values for partitioning components;
4. Define and then set up chemical reactions in CMG-STARS to model production of H_2S souring that approximate souring processes in the reservoir;
5. Implement the effects of temperature, pressure, PH, salinity, and water chemistry;
    a. By implementing the effects of temperature in the model, the model will be thermal so that the effects of cold-water regions (thermal variable shell) around injectors on souring can be modeled.
6. Calibration (history matching) of the reservoir-souring model with the historical H_2S production if applicable;
7. Sensitivity analysis to better understand the souring behavior upon variation of the main parameters;
8. Forecast (e.g., base-case run, run based on a future development plan, etc.);
9. Modeling of potential mitigation strategies (e.g., different sources of injection water, nitrate injection, etc.).

Potential Injection-Water Sources

Two main potential sources for waterflood are considered: (1) produced water from the reservoir, which would be re-injected, or (2) aquifer water supply from a shallow formation. A make-up water using both water sources is another potential candidate.

Produced Water Re-Injection

Wells AA-2 and AA-3 produced approximately 276 m³/d water in May 2017, and the trend in the field history suggests steadily rising water production. The collective PWRI production could hence adequately cover the anticipated water injection rate of one injection well, and partially two injection wells if the same injection volume of 300–600 m³/d is assumed per pattern in the waterflood-development plan.

The produced water is highly saline (total dissolved solids (TDS) of production water are 165,000 and 175,000 mg/l, respectively). Sulfate concentrations range from 268 mg/l to 295 mg/l.

In a preserved produced-water sample from well AA-2 analyzed by PanTerra, 51 mg/l total organic carbon was found. Acetate was the only VFA present in this sample (75 mg/l), with other VFA compounds below detection levels (i.e., < 10 mg/l).

Shallow-Aquifer Water
The shallow-aquifer source for water injection in the region is a formation that is partly dolomitized limestone of Paleogene age. This water will be used at least for the waterflood trial. Water supply well AAWSW-1 was already drilled in the AA field. The shallow-aquifer water in the AA field is characterized by low salinity (11,334 mg/l TDS), but remarkably high sulfate content (1,551 mg/l). Organic carbon including VFA compounds are below detection levels according to the water-analysis reports. In one analysis on the water from the aquifer, a dissolved H_2S concentration of 10 mg/l was found.

Qualitative Prediction of H_2S Levels in AA Field

H_2S readings taken in the field (approximately every two weeks according to PDO pers. commun.) and the PVT report suggest that the reservoir in the AA field does not contain detectable H_2S. The reservoir is therefore seen as naturally sweet in this field. This is an important base parameter for the desktop study, as well as a vital input to dynamic modelling. We believe that any H_2S occurring in further field life, if applicable, will be associated with waterflooding.

For the estimation of the extent of potential souring, the reservoir conditions for the viability of SRB are evaluated. In this chapter, we consider the impact of the factors for souring risk.

We cannot exclude the possibility that H_2S of deeper, non-microbial origin breaks through at the production wells due to e.g., fault activation (Al-Eid et al. 2001), but the probability of this event is low and is not further considered in this study.

Temperature
In-situ reservoir conditions in the AA field are inhibitive to microbial H_2S generation. This is partly the result of the reservoir temperature (88°C), ensuring negligible bacterial activity. However, it is assumed that any injected water, whether the PWRI water or the shallow aquifer water, will enter the reservoir at ambient surface temperature (approximately 30-45°C) and will thus reduce the temperature of the invaded zone (or at least an inner zone around the injection wellbore). Even a small localized area that saw cooling to 70°C would allow very low levels of microbial sulfate reduction. Significant souring is likely to occur close to 60°C, below which microbial activity increases towards the lowest feasible temperature, i.e., in the region of 45°C. At this temperature, this factor essentially represents no constraint on bacterial metabolism and growth.

Reservoir pressure in the range of the reservoir (17,419 kPa) only has a minor restrictive effect on the metabolic rate of most SRB and is therefore not further considered.

Salinity
The high formation-water salinity also protects the reservoir from self-souring, particularly in combination with the high reservoir temperature. For waterflooding with the PWRI water, this constraint will remain the most important factor for ensuring a low risk of souring as the minimum salinity would be 165,000 mg/l TDS. The small variation in salinity between the two existing wells suggests a relatively homogenous reservoir in terms of salinity.

Due to the low salinity of the aquifer water of approximately 11,000 mg/l TDS, waterflooding using this injection source would result in significant dilution and displacement of the high salinity in an increasingly large zone around the injection wells. In these zones, salinity will fall rapidly below 100,000 mg/l, a

commonly viewed threshold for activity of a large number of microbes, which means that salinity would no longer be a constraint to souring.

A make-up water of these two injection-water sources (PWRI and aquifer) will be of intermediate composition. Balancing the salinities from both sources, a produced water contribution of 60% would result in an injection water salinity just over 100,000 mg/l. This salinity is good enough for microbial - souring activities. However, a more desirable target would be 150,000 mg/l by using at least 90% PWRI and not more than 10% aquifer water.

Once a make-up or aquifer water breaks through at the production wells, the salinity of the produced water will obviously decrease. In this case, the fraction of the aquifer water will need to be reduced if a salinity target is to be maintained.

The choice of the water injection rate (300 – 600 m³/d) has a significant impact on the travel time of the low-salinity (and low-temperature) water front in the reservoir. The viable zone for SRB will thus develop faster, and be larger after a given injection time when injecting 600 m³/d, compared to injecting 300 m³/d. As the aquifer water is sour, the mass of H_2S injected into the reservoir after a given time will also be greater at higher injection rates, which means that the sour front (trailing the injection-water front because of scavenging, adsorption and partitioning into residual oil) will also arrive at production wells faster. On the other hand, the carbon-source compounds that are essential for BSR will be displaced and diluted more rapidly as well. The effect of an increased injection rate on this is, therefore, difficult to assess in the desktop-study part of the study, but this will be investigated in the dynamic simulations. The other implication of larger injection rates is that a purely PWRI-based waterflood can less likely be realized due to limited availability, while a mixed PWRI/aquifer injection water will have to contain a lower fraction of the high-salinity produced water. The lower resultant salinity of the mixed injection water (most likely significantly below the 100,000 mg/l TDS threshold) implies an enhanced microbial - souring tendency.

Availability of Carbon Source and Nutrients

The sulfate content of the formation (produced) water is moderate (max. 295 mg/l), but sufficient for a potentially very significant amount of microbial sulfate reduction. Excess concentrations of sulfate occur in the aquifer water (1,551 mg/l). In general, the effect of sulfate level on H_2S generation will be irrelevant as long as the system is carbon limited, which is very likely to be the case at these concentrations.

More critical for the prediction of souring is the determination of carbon source availability: In the analysis by PanTerra of the aquifer water, the level of total organic carbon (TOC), serving as a proxy for the carbon source available to microbes, is 51 mg/l. The major carbon source is acetate (75 mg/l), while other VFA are below detection levels. Moderate concentrations of BTEX compounds occur in the formation water (toluene 7.4 μg/l; ethylbenzene, m-, p- and o-xylene were all <1 μg/l). However, it should be noted that the solubility of BTEX and other hydrocarbons is reduced at the very high salinity, and hence partitioning from the oil could change when this is replaced by less saline water. The concentration of benzene was found to 90 μg/l, which may be slightly high relative to toluene, and is perhaps elevated by residual oil in the sample. The concentration of individual BTEX compounds used for the dynamic simulations will be calculated based on their abundance in the crude oil and their partition coefficients.

The water analysis of the aquifer water shows no detectable TOC and VFA. Indeed, shallow aquifers are often devoid of carbon source and other nutrients because they tend to be subject to meteoric influx, which can introduce abundant microbial activity and thus consume the nutrients. Consequently, the electron donors relevant for souring are predominantly present in the formation water. Based upon the necessary dilution of the formation water (roughly at least a 1:1 mixing ratio until the salinity of the mixture falls below 100,000 mg/l), the effective concentration of acetate in a microbially viable area would be 37.5 mg/l at most. The potential for souring during waterflooding with the aquifer water will be therefore determined by the time (the number of pore volumes of injection water) after which carbon-source compounds have been displaced or consumed from the water in the near-wellbore, where conditions are viable for bacterial

growth. This nutrient stripping can be relatively effective in matrix-flooded reservoirs, whereas in the case of significant flow along fractures, BTEX and other water-soluble compounds from residual oil can migrate slowly out of the rock matrix (by a combination of diffusion and imbibition) and thus provide a sustained substrate for bacteria biofilms. As a result, the degree of reservoir heterogeneity has a potentially major impact on the nutrient availability for microbes, and hence on the extent of souring.

The aquifer water contains 16 ppb of oxygen, which is not far above acceptable concentrations for injection water (often taken to be < 10 ppb) but any excursions above the detected level could be relevant for souring because these could lead to aerobic degradation of the residual oil and produce water-soluble organic compounds (like VFA). These compounds would then be available for SRB in anaerobic zones of the reservoir. However, a base concentration of 16 ppb should not be a large concern as most oxygen will be scavenged by carbon steel piping before even reaching the reservoir. The formation water is anoxic (no oxygen detected), though it is common that processed water picks up small amounts (and occasionally not small!) of oxygen during passage through the production and re-injection facilities.

Dissolved H_2S (in Injection Water)

The high dissolved H_2S in the aquifer water (10 mg/l) carries a substantial souring risk on its own, regardless of the effect of this water on production of H_2S by SRB. This injected H_2S will affect the H_2S concentration in the produced gas due to the partitioning into the oil and aqueous phase in the reservoir. In fact, H_2S from this source could appear sooner after injection-water breakthrough than would microbially generated H_2S, because there is no requirement to establish a microbial biofilm in the reservoir (requiring modification of the salinity and temperature of the near-wellbore followed by a period of microbial growth). It is, however, still subject to the effects of partitioning into residual oil, adsorption and chemical scavenging, as would also be the case with microbial H_2S, and hence, will still lag behind the waterflood front to an extent determined by the magnitude of these retarding factors.

The subsequent level of H_2S in the produced gas is a function of these retarding factors in the reservoir and operating conditions at the production wells (pressure, temperature, GOR and water cut). Given the most recent production data, there is still enough sweet gas production to dilute the H_2S exsolving from the liquid phase below harmful levels (<< 500 ppmv); however, the concentration will rise rapidly as water cut increases. This process will be simulated in the modeling phase to give a quantitative result of this effect on souring. In any case, the presence of dissolved H_2S introduces an additional souring risk that could be easily avoided by omitting this injection-water source.

H_2S Abstraction (Scavenging and Adsorption)

This is one of the largest uncertainties of this souring study. Any sour fluids in the reservoir are subject to physical adsorption (reversible) to minerals with high relative surface areas such as clay minerals and to scavenging (irreversible) by iron-bearing minerals (primarily siderite). The total surface available for adsorption and mass of scavenger in a reservoir formation can sometimes be large enough to sweep up essentially all generated H_2S. The prerequisites for this are that (a) enough quantities of clay minerals for adsorption and scavenging minerals are present and (b) that the fluids are in fact exposed to scavenging minerals. Efficient contact can be compromised by scavenging minerals being overgrown by other minerals and by fracture flow, in which case a large portion of the abstraction capacity would simply be by-passed by the fluids.

Petrographic descriptions of sidewall samples indicate absence of siderite (traces may be present but not mentioned, e.g., because they are below detection limits), the rare presence of ferroan calcite cement and of an unspecified, but probably very minor amount of clay minerals. The scavenging and adsorption potential based on these factors is likely low. The absence of robust rock composition data of the reservoir means that the abstraction capacity, one of the largest factors in souring prediction, cannot be estimated.

Compositional Dynamic Model

This section includes the reservoir-souring aspects of the compositional dynamic model and its set up. The features of the compositional dynamic model have already been mentioned earlier.

PVT

Because, the reservoir-souring dynamic model is a non-isothermal compositional model, partitioning coefficients of partitioning components and the oil viscosity at different reservoir temperatures and pressures are needed. A single PVT report that includes PVT analyses on three bottomhole samples taken from the reservoir was provided. This PVT report, however, includes PVT analyses in the black-oil format. Therefore, in order to calculate some of the required PVT properties, an equation of state (EoS) is needed to be developed. For this purpose, the PR Peneloux EoS and the corresponding-states-principle (CPS) correlation for viscosity have been used.

Subsequently, regression to experimental PVT data has been carried out to calibrate the selected EoS. The tuned EoS calculates a saturation pressure of 8,254 kPa, which leads to a relative deviation of 0.7% with respect to the measured saturation pressure 8,310 kPa. Fig. 4 shows the simulated relative volume and the oil viscosity against the corresponding experimental PVT properties at the reservoir temperature $T_R = 88°C$. Fig. 4 illustrates that the calculated PVT properties match very well the corresponding experimental PVT properties.
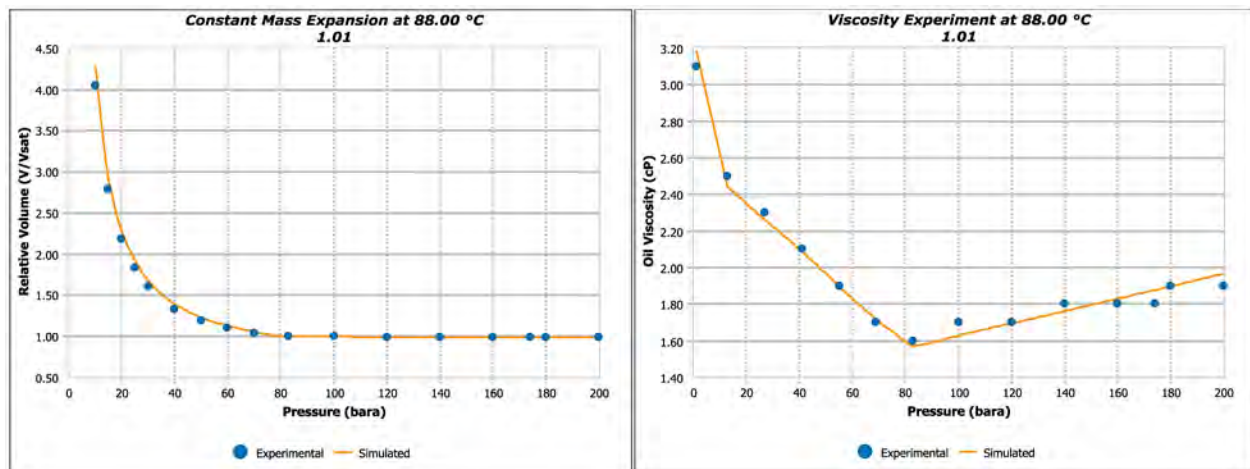

Figure 4—Simulated relative volumes and the oil viscosities against corresponding experimental PVT properties.

This tuned EoS is subsequently used for calculating the oil viscosity at different reservoir temperatures and the H_2S partitioning factors.

H_2S Partitioning. The developed EoS has been used to perform the regular 3-phase PT flash for calculating H_2S-partitioning coefficients among the three phases (aqueous, oleic, and gas). In addition to the temperature and pressure dependency, the H_2S partitioning coefficients are a function of pH and salinity.

The salinity dependency is because the salt content of water changes the aqueous-phase density and molecular weight, and, consequently, the H_2S mole fraction in the aqueous phase. For a given total H_2S, pressure, temperature, and pH, the gas/water and the oil/water H_2S partitioning coefficients increase as the salinity increases. This is because a given mass of H_2S in the aqueous phase leads to a smaller mole fraction of H_2S in the aqueous, which is in the denominator of the gas/water and the oil/water H_2S-partitioning coefficients.

The pH dependency is attributed to the reason that H_2S is dissociated in the aqueous phase. When the pH increases, more fractions of the total H_2S in the aqueous phase become in the form of HS^- due to dissociation.

Therefore, for a given total H_2S, pressure, temperature, and salinity, the gas/water and the oil/water H_2S-partitioning coefficients decrease considerably as the pH increases. This is because only the un-dissociated concentration of H_2S in the aqueous phase can partition between the gas and oleic phase; but H_2S partitioning coefficients are based on the total H_2S (i.e., un-dissociated $H_2S_{(aq)}$ + dissociated $HS^-_{(aq)}$).

During waterflood, the pH and salinity of the injected water and consequently of the produced water may change. This is because the formation water has a pH of 6 and a salinity of 173,164 mg/l, on the other hand, the shallow-aquifer water has a pH of 7.5 and a salinity of 10,874 mg/l. Consequently, the H_2S-partitioning coefficients have been computed for the formation water, the shallow-aquifer water, and for different maxing ratios of these two water sources.

Fig. 5 shows the calculated gas/water H_2S partitioning coefficients at different pH and salinity values as a function of pressure at a temperature of 40°C.
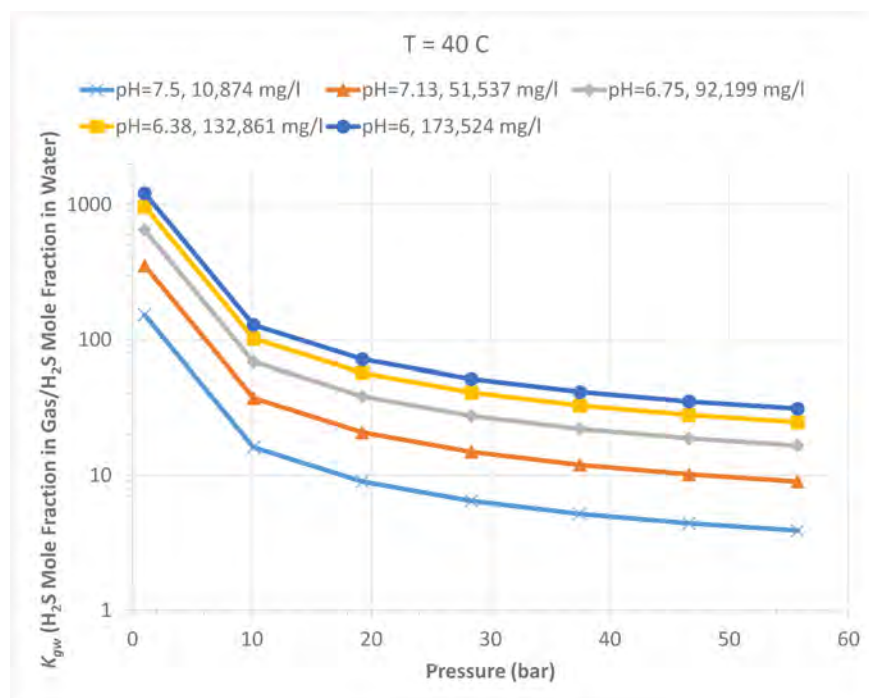

Figure 5—Calculated gas/water H₂S-partitioning coefficients for different pH and salinity as a function of pressure at T = 40°C.

Fig. 6 shows the calculated oil/water H_2S-partitioning coefficients (K_{ow}, H_2S) at different pH and salinity values as a function of pressure at a temperature of 40°C.
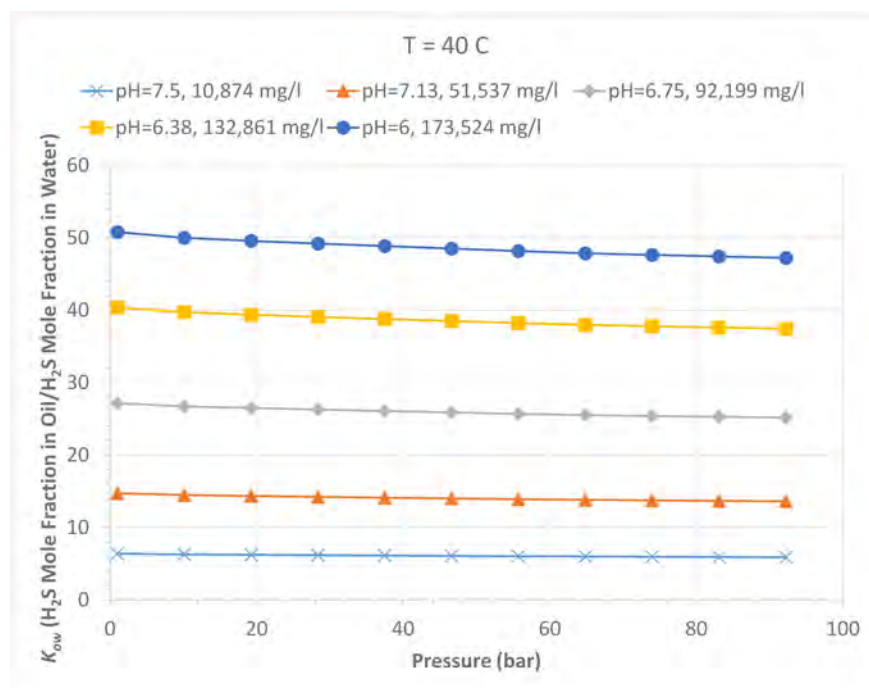
Figure 6—Calculated oil/water H₂S-partitioning coefficients for different pH and salinity as a function of pressure at *T* = 40°C.

It is noted that the H_2S partitioning coefficients between the gas and oleic phase are not dependent on pH and salinity because pH and salinity are only relevant to the aqueous phase.

Overall, it can be concluded that the H_2S partitioning can play an important role in determining the actual level of reservoir souring. For example at P = 100 kPa and T = 40°C (e.g., surface conditions), 10 mg/l H_2S in the formation (produced) water would be in equilibrium with 6,594 ppmv H_2S in the gas phase; on the other hand, 10 mg/l H_2S in the shallow-aquifer water would be in equilibrium with 822 ppmv H_2S in the gas phase.

Components Names and Types

Based on the metabolic reactions for H_2S generation and mitigation, 18 components are defined and included in the dynamic model. The types of components are determined according to their mother phase. The mother phase is referred to a phase in which either components are initially generated or are mainly partitioned to. Out of 18 components, 13 components are aqueous-like components and 5 components are oleic-like components. These 18 components are

- Aqueous-like (13 components): H_2O, H_2S, CO_2, H_2CO_3, N_2, SO_4^{2-}, salt (to incorporate the salinity), nitrate, nitrite, VFA (i.e., formate, acetate, propionate, and butyrate).
- Oilec-like (5 components): BTEX (i.e., benzene, toluene, and xylene), solution gas, and dead oil.
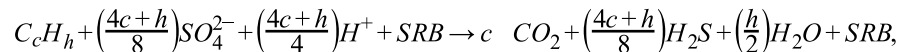
Metabolic Reactions

Once the conditions (e.g., temperature, salinity, and nutrient availability) are suitable for SRB growth, it takes SRBs several days to a week or two—according to laboratory tests—to stablish a large population (Coombe et al. 2010). This bacterial-growth phase is short relative to the timescale required for nutrients to invade one grid cell. Therefore, based on the time and length scales of the field application, a model simplification is used wherein the growth phase of the bacterial species responding to changes in nutrient levels is ignored. This simplification does not cause restrictions in the model capabilities and significantly reduces the number of field matching parameters (Coombe et al. 2010). Implementing the growth phase

in the model adds huge additional complication that increases precision without having much impact on accuracy.

Due to this simplification, bacterial metabolic reactions are merely based on the energy reactions. The energy reactions for the major electron donors (i.e., BTEX and VFA) are presented below.

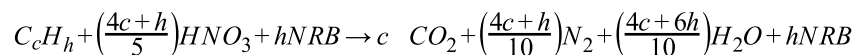The reaction for sulfate reduction with SRB and BTEX is

$$C_cH_h + \left(\frac{4c+h}{8}\right)SO_4^{2-} + \left(\frac{4c+h}{4}\right)H^+ + SRB \rightarrow c\ CO_2 + \left(\frac{4c+h}{8}\right)H_2S + \left(\frac{h}{2}\right)H_2O + SRB,$$

where Table 1 shows the stoichiometric coefficients of BTEX reactions with sulfate and SRB.

Table 1—stoichiometric coefficients of BTEX reactions with sulfate and SRB.

BTEX	Formula	SO_4^{2-}	H^+	CO_2	H_2S	H_2O
Benzene	C_6H_6	3.75	7.5	6	3.75	3
Toluene	C_7H_8	4.5	9	7	4.5	4
Xylene	C_8H_{10}	5.25	10.5	8	5.25	5

The reaction for nitrate reduction with hNRB (Heterotrophic nitrate-reducing bacteria) and BTEX is

$$C_cH_h + \left(\frac{4c+h}{5}\right)HNO_3 + hNRB \rightarrow c\ CO_2 + \left(\frac{4c+h}{10}\right)N_2 + \left(\frac{4c+6h}{10}\right)H_2O + hNRB$$

The reactions for sulfate reduction with SRB and 4 VFA components (formate, acetate, propionate, and butyrate) are

$$4\ HCOO^- + SO_4^{2-} + H^+ + SRB \rightarrow 4HCO_3^- + HS^- + SRB$$
$$CH_3COO^- + SO_4^{2-} + SRB \rightarrow 2\ HCO_3^- + HS^- + SRB$$
$$4\ CH_3CH_2COO^- + 3\ SO_4^{2-} + SRB \rightarrow 4\ CH_3COO^- + 3\ HS^- + 4\ HCO_3^- + H^+ + SRB$$
$$2\ CH_3CH_2CH_2COO^- + SO_4^{2-} + SRB \rightarrow 4\ CH_3COO^- + HS^- + H^+ + SRB$$
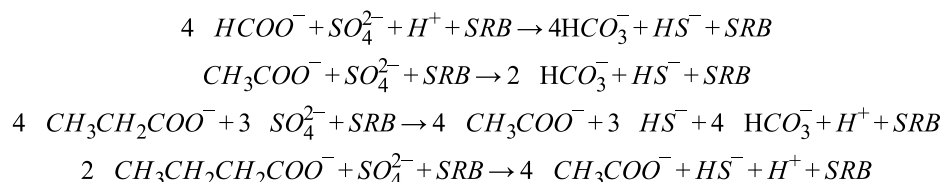
The below reactions are for nitrate reduction with hNRB and VFA. These reactions are more favorable than the sulfate-reduction reactions from the thermodynamic point of view.

$$5\ HCOO^- + 2NO_3^- + 7\ H^+ + hNRB \rightarrow 5\ CO_2 + N_2 + 6H_2O + hNRB$$
$$5\ CH_3COO^- + 8\ NO_3^- + 13\ H^+ + hNRB \rightarrow 10\ CO_2 + 4\ N_2 + 14\ H_2O + hNRB$$
$$5CH_3CH_2COO^- + 14\ NO_3^- + 19\ H^+ + hNRB \rightarrow 15\ CO_2 + 7\ N_2 + 22\ H_2O + hNRB$$
$$5CH_3CH_2COO^- + 6\ NO_3^- + 6\ H^+ + hNRB \rightarrow 5\ CH_3COO^- + 3\ N_2 + 5\ CO_2 + 8\ H_2O + hNRB$$
$$5CH_3CH_2CH_2COO^- + 20\ NO_3^- + 25\ H^+ + hNRB \rightarrow 20\ CO_2 + 10\ N_2 + 30\ H_2O + hNRB$$
$$5CH_3CH_2CH_2COO^- + 4\ NO_3^- + hNRB \rightarrow 10\ CH_3COO^- + 2\ N_2 + 2\ H_2O + H^+ + hNRB$$
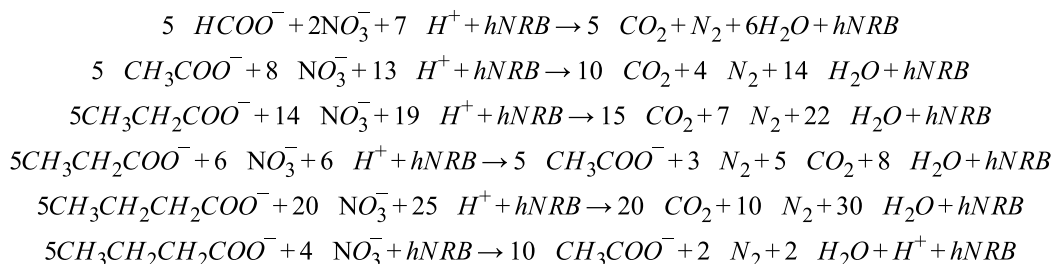
Two possible reactions exist for propionate and butyrate. It is important to note that the second reactions result in the generation of acetate. Increased acetate concentration in combination with decreased H_2S, in the presence of the sulfate in the produced water, is a sign of success in a nitrate treatment.

The reaction for nitrate reduction with NR-SOB is

$$1.6\ HNO_3 + H_2S + NR-SOB \rightarrow H_2SO_4 + 0.8\ N_2 + 0.8\ H_2O + NR-SOB$$
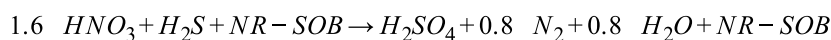
This reaction consumes the H_2S produced by the sulfate reduction-with-SRB reactions or may already be present from non-microbial origins.

The above-mentioned reactions—in a form of $aA + bB \rightarrow cC + dD$—are implemented in CMG STARS as follows:

$$\text{Reaction Rate} = \text{Reaction-rate constant}(\text{salinity, } p) \times \exp\left(\frac{-E_a}{RT}\right)C_A^a C_B^b,$$

E_a is the activation energy, R is the universal gas constant, T is temperature, and C_A and C_B are the concentrations of reactive components A and B, respectively. The dependencies of the reaction rate to temperature, water salinity, and pressure are incorporated in the simulation model.

H$_2$S Abstraction Modeling

CMG STARS treats scavenging and adsorption (chemical reactions, physical, and mechanical) in the same way using the Langmuir isotherm. STARS has options to make Langmuir completely irreversible or completely reversible or a combination of both. Therefore, in the compositional dynamic model, part of the abstraction that is related to scavenging is considered irreversible and the adsorption part of the abstraction is treated reversible. In this way, both scavenging and adsorption effects can be studied by the compositional dynamic model.

In the AA field, according to the findings of the desktop-study part, the scavenging and adsorption potential is likely low because of the absence of siderite (traces may be present but not mentioned because they are below detection limits) and very minor amount of clay minerals.

In the dynamic model, an abstraction of 1 mg H$_2$S/kg rock has been considered as the base-case value. Moreover, it is assumed that the contribution of scavenging and adsorption is the same to the total abstraction. As a result, an abstraction of 1 mg H$_2$S/kg corresponds to 0.0007 wt% siderite and 0.5 mg H$_2$S/kg rock adsorption. Later, other values of abstraction are used for sensitivity analysis.

Reservoir-Souring Dynamic-Simulation Results

According to the conclusions of the desktop-study part, water injection using re-injection of produced reservoir water (PWRI) has a very low souring risk, but the injection of the sour water from the shallow aquifer in the AA field has a high risk of souring. Therefore, the case that uses the produced water is defined as the base-case scenario. On the other hand, the case that utilizes the shallow-aquifer water is called the worst-case scenario in this study. For both scenarios, water injection started in Jan 2018.

It is recalled that changes to the total (overall) H$_2$S concentration in produced fluids is called reservoir souring. However, H$_2$S concentrations in the produced gas phase are typically measured. Therefore, in this context, both the total H$_2$S-production rate and the H$_2$S concentration (mole fraction) in the produced gas phase are plotted to illustrate both the level of souring and the expected H$_2$S trend in the produced gas phase. A surface pressure of 101 kPa and a surface temperature of 40°C are used to calculate the H$_2$S mole fraction (volume fraction) in the produced gas phase.

Fig. 7 shows the distributions of the reservoir temperature, the concentration of the dissolved H$_2$S, the concentration of sulfate, and the concentration of acetate (VFA) in the water phase in years 2022, 2030, and 2045 for the worst-case scenario. Fig. 7 demonstrates that the thermal front propagates uniformly in the reservoir because of the high thermal-diffusion coefficient and the heat capacity of the reservoir rock. On the other hand, the concentration distributions of H$_2$S, sulfate, and acetate in year 2022 clearly reveal a water under-riding effect due to the density difference between the aqueous and oleic phase.
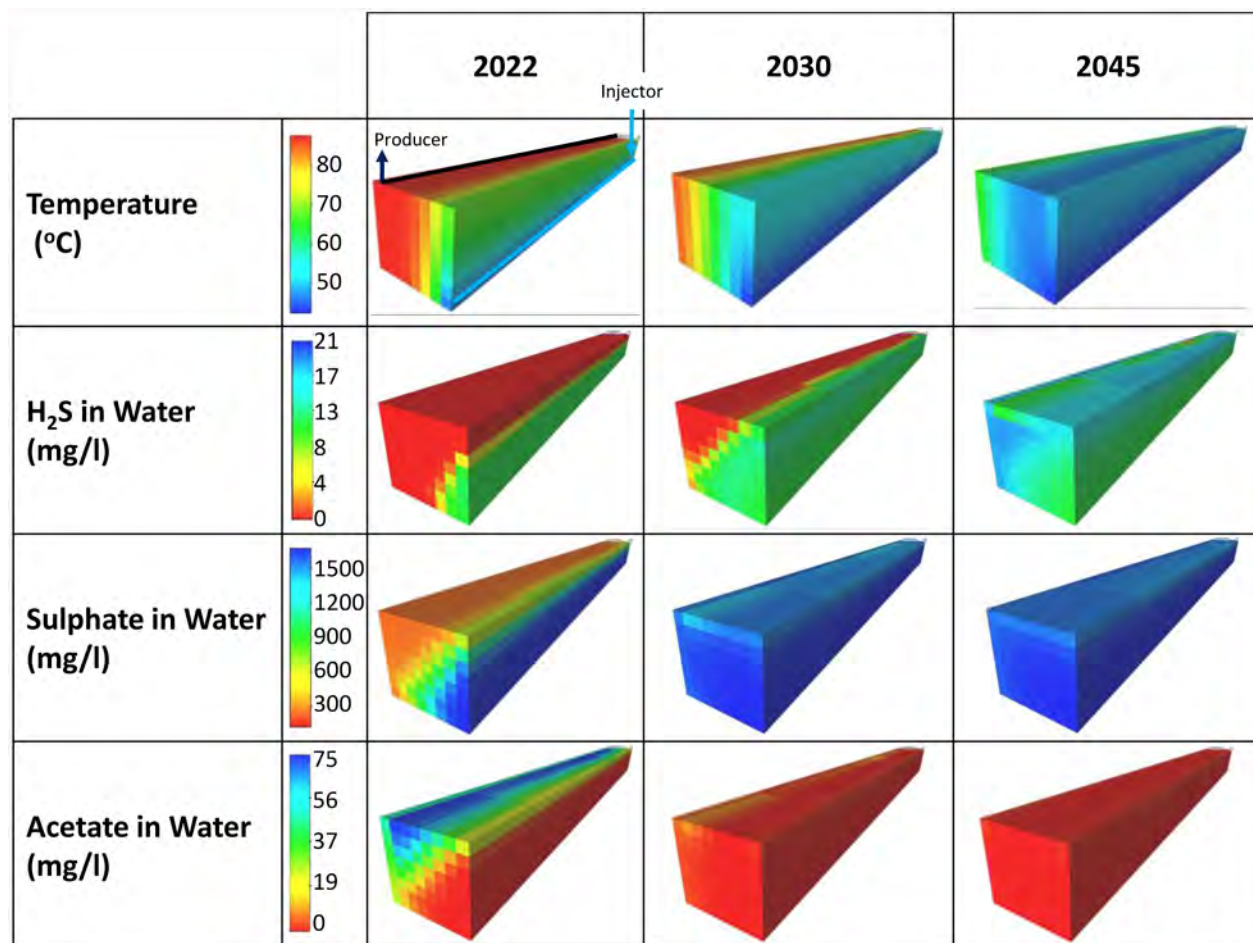
Figure 7—Temperature, H₂S-, sulfate-, and acetate-concentration distribution in different years for shallow-aquifer-water injection.

Fig. 7 illustrates that wherever the low-temperature has reached, all acetate has reacted (consumed) and consequently H_2S has formed. The sulfate concentration has not decreased in the microbial-reaction region —despite being consumed in the reaction—because the injected water constantly feeds the system with a high sulfate concentration. The front of acetate and sulfate are ahead of the front of H_2S because the front of H_2S gets retarded by the H_2S abstraction.

Because some model parameters are still unknown and/or associated with some degree of uncertainty, the impacts of those uncertain parameters on the level of reservoir souring are investigated. For this purpose, a number of sensitivity runs in terms of different water-injection rates, different abstraction capacities, and different mixing ratios of the produced water/the shallow-aquifer water. In each sensitivity run, one input parameter is varied from its base-case (or worst-case) value.

Mixed-Water Injection

Here, the injected water is varied according to different mixing ratios of the shallow-aquifer water/produced water. For this purpose, percentages of the produced water are mixed with the shallow-aquifer water for injection. In this context, whenever "%PWRI" is mentioned, it means a mixture of the produced water and the shallow-aquifer water is injected. For example, case 100%PWRI uses the total produced water for injection, but because the targeted water-injection rate is equal to the liquid-production rate and the fact that the water cut is not 100%, case 100%PWRI uses little shallow-aquifer water. However, case "Deep" uses purely the produced water, implying that the reservoir aquifer is used. Case 0%PWRI corresponds to the shallow-aquifer-water injection (worst-case scenario).

Fig. 8 shows the simulated total H_2S-production rates for various water-mixing ratios of the PWRI and the shallow-aquifer water versus time. Fig. 8 reveals that as soon as the injected water partially includes the shallow-aquifer water (> 20 vol% results in a salinity lower than 150,000 mg/l), the H_2S breakthrough happens at least 7 years earlier than purely produced-water injection. Furthermore, the H_2S-breakthrough times and the H_2S-production trends are not a monotonic function of the water-mixing ratio. In other words, when the percentage of the PWRI decreases from 100% up to 80%, the H_2S-breakthrough time consistently shifts to an earlier time. On the other hand, the H_2S-breakthrough time of case 70%PWRI is approximately identical to that of case 80%PWRI. Then from 70%PWRI until 50%PWRI, the trend of the H_2S-breakthrough becomes reverse, meaning that by decreasing the percentage of the PWRI, the H_2S breakthrough occurs later. Finally, from 50%PWRI until 0%PWRI, the H_2S-bearkthrough time shortens as the percentage of the PWRI decreases.
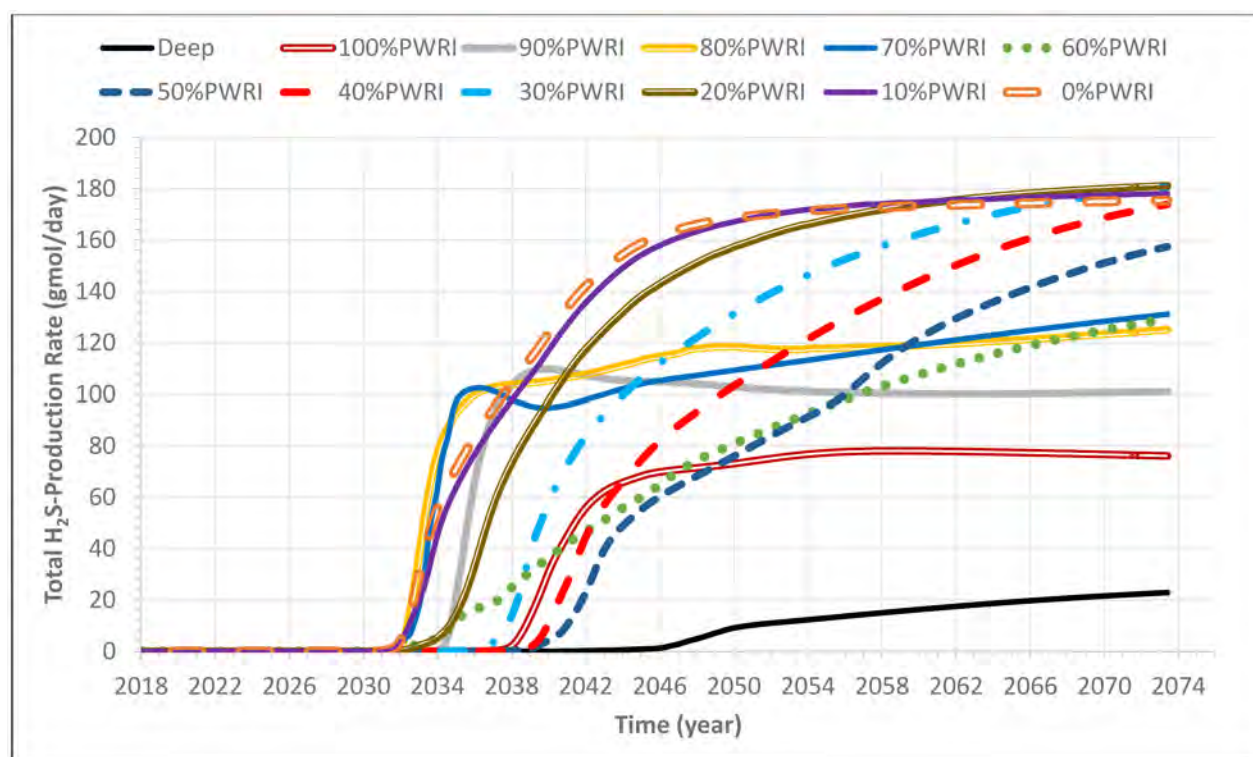

Figure 8—Simulated total H_2S-production rates for various mixing ratios of PWRI and shallow-aquifer water.

In terms of the final H_2S level (i.e., in year 2074), Fig. 8 illustrates that as the percentage of the PWRI decreases until 80%PWRI, the H_2S level increases. After that, until 60%PWRI, the H_2S level remains approximately constant. Then from 60%PWRI until 40%PWRI, the H_2S level increases. Finally, the H_2S levels of 30%PWRI, 20%PWRI, 10%PWRI, and 0%PWRI are approximately the same.

The complex (unexpected) features shown in Fig. 8 are attributed to the following reasons. Reason 1: almost shallow-aquifer-water/total-water ratio of 10%—20% brings the salinity of the mixed injection water below 150,000 mg/l. Reason 2: the shallow-aquifer water includes 10 mg/l dissolved H_2S. Reason 3: some mixing ratios of the produced water and shallow-aquifer water would be ideal for the microbial reactions because the produced water brings acetate and the shallow-aquifer water brings sulfate and low salinity. Reason 4: when the produced-water is mixed with some shallow-aquifer water for injection, the compositions of the produced water change with time and they deviate further from the formation water until they reach a steady-state situation.

Fig. 9 shows the simulated H_2S concentrations in the produced gas for the various mixing ratios of the produced water and the shallow-aquifer water versus time. Fig. 9 reveals that the trends of the H_2S concentrations in the produced gas are different from the trends of the total H_2S-production rate shown in Fig. 8. This is because of the H_2S-partitioning effects. The gas/water H_2S partitioning coefficient is much higher at higher salinity and lower pH. It is noted that the formation water (i.e., produced water) has these properties (high salinity and low pH). Because of this characteristic, cases with lower total-H_2S levels (i.e., 100%PWRI, 90%PWRI, 80%PWRI, and 70%PWRI) result into higher H_2S concentrations in the produced gas than cases with higher total-H_2S levels (40%PWRI, 30%PWRI, 20%PWRI, 10%PWRI, and 0%PWRI).
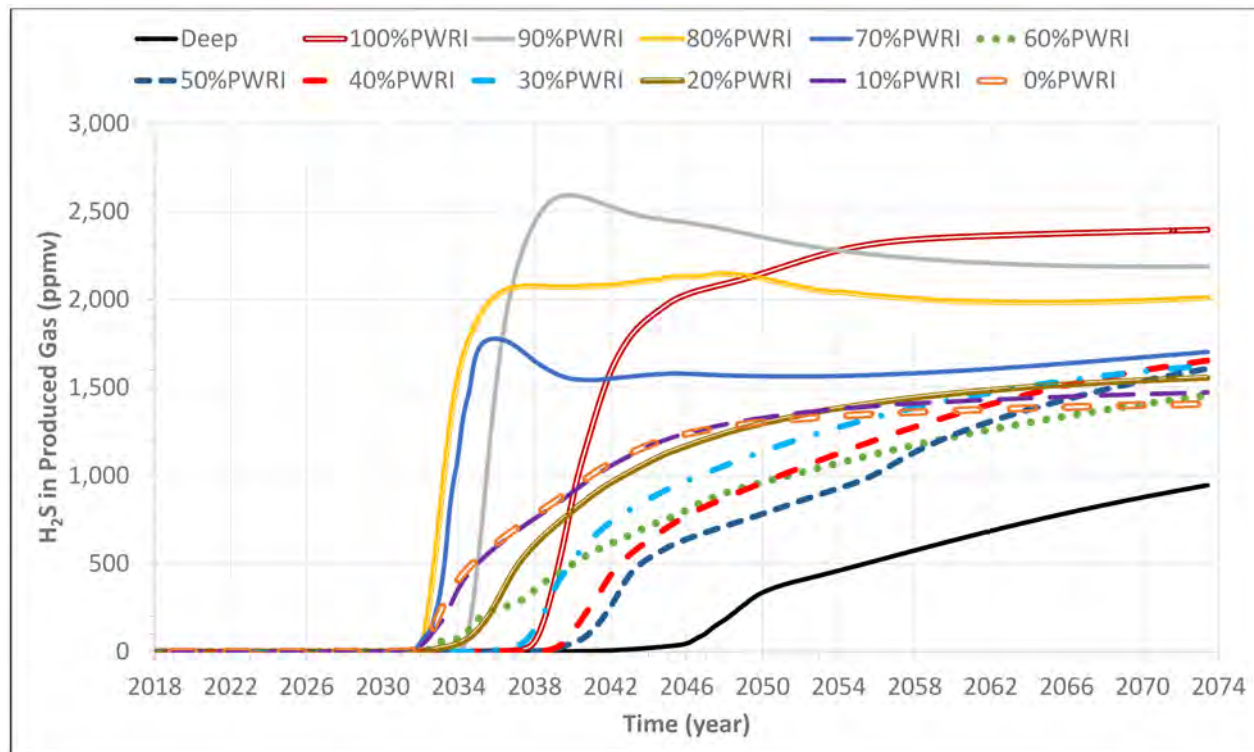

Figure 9—Simulated H₂S concentrations in produced gas for various mixing ratios of deep-(PWRI)- and shallow-aquifer water.

Once again, the definition of reservoir souring is based on the total H_2S level and the H_2S concentration in the produced gas does not always define reservoir souring. Based on this definition, as the contribution of the shallow-aquifer water to the total volume of injection water increases, the level of souring also increases.

Abstraction Capacity
Here, the effect of the rock-abstraction capacity on the souring level is assessed. For this objective, the abstraction capacity is varied from 0.25 mg H_2S/kg rock to 4 mg H_2S/kg rock. It is noted that for the base-case and the worst-case scenario, the abstraction capacity has been set at 1 mg H_2S/kg rock. For all abstraction values, the contribution of the scavenging to the total abstraction is 50%, meaning that the mineral adsorption also contributes 50% to the total abstraction capacity. Furthermore, for all these abstraction capacities, three cases in terms of the injected-water composition (viz., pure produced water, 80%PWRI, and pure shallow-aquifer water) have been used to define the abstraction-sensitivity cases. Nonetheless, only the results of the 80%PWRI cases are shown here. Case 80%PWRI has been selected because it leads to the highest H_2S concentration in the produced gas in the earliest time (see Fig. 9). The water-injection rate is 300 m³/d.

Fig. 10 shows the simulated total H_2S-production rates versus time for the various abstraction capacities using 80%PWRI and the shallow-aquifer make-up water. Fig. 10 reveals that the abstraction capacity

significantly affects the souring level. Indeed, reducing the abstraction capacity from 1 mg H_2S/kg rock (base-case value) to 0.25 mg H_2S/kg rock shifts the H_2S-breakthrough time from year 2032 to year 2027 (5 years earlier). On the other hand, increasing the abstraction capacity from 1 mg H_2S/kg rock to 2 mg H_2S/kg rock delays the H_2S-breakthrough time by 12 years.
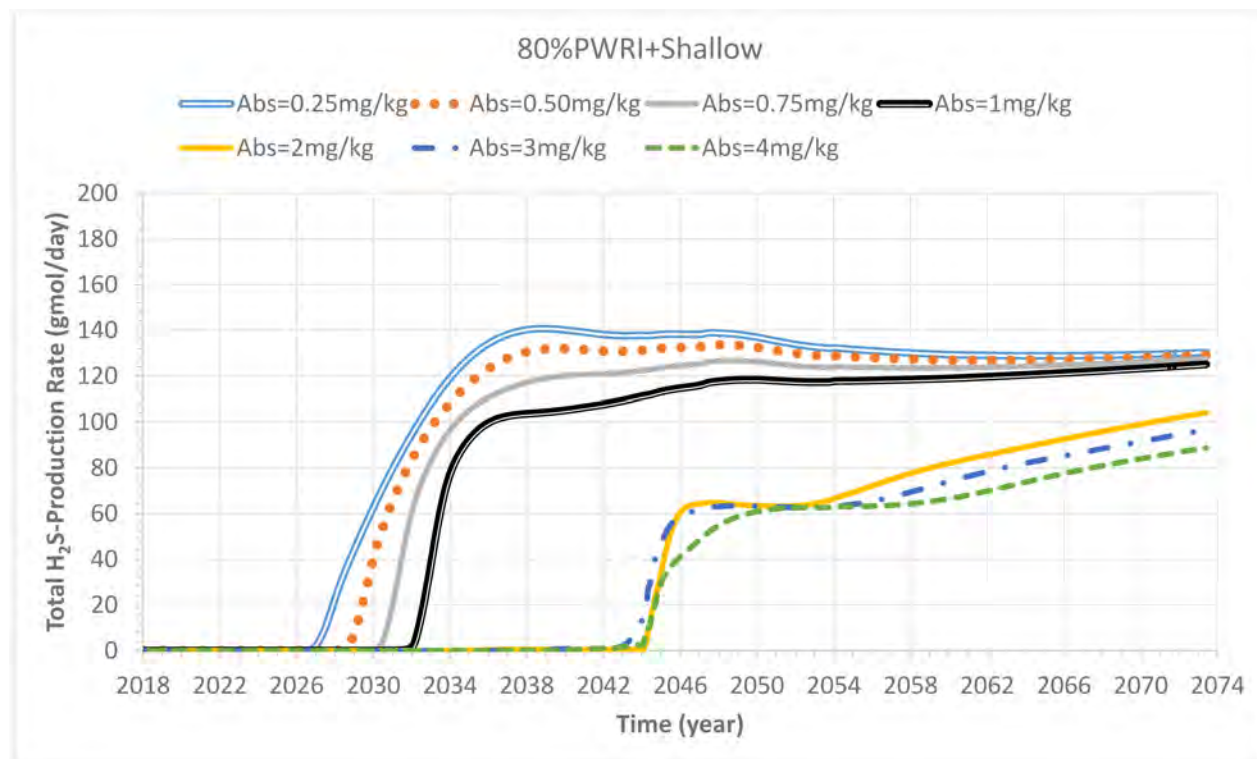

Figure 10—Simulated total H₂S-production rates for various abstraction capacities using 80%PWRI and shallow-aquifer water.

Fig. 11 demonstrates the simulated H_2S concentrations in the produced gas versus time for the various abstraction capacities using 80%PWRI and the shallow-aquifer make-up water. Fig. 11 shows the same trends as those in Fig. 10 in terms of the abstraction-capacity impact on the souring level.
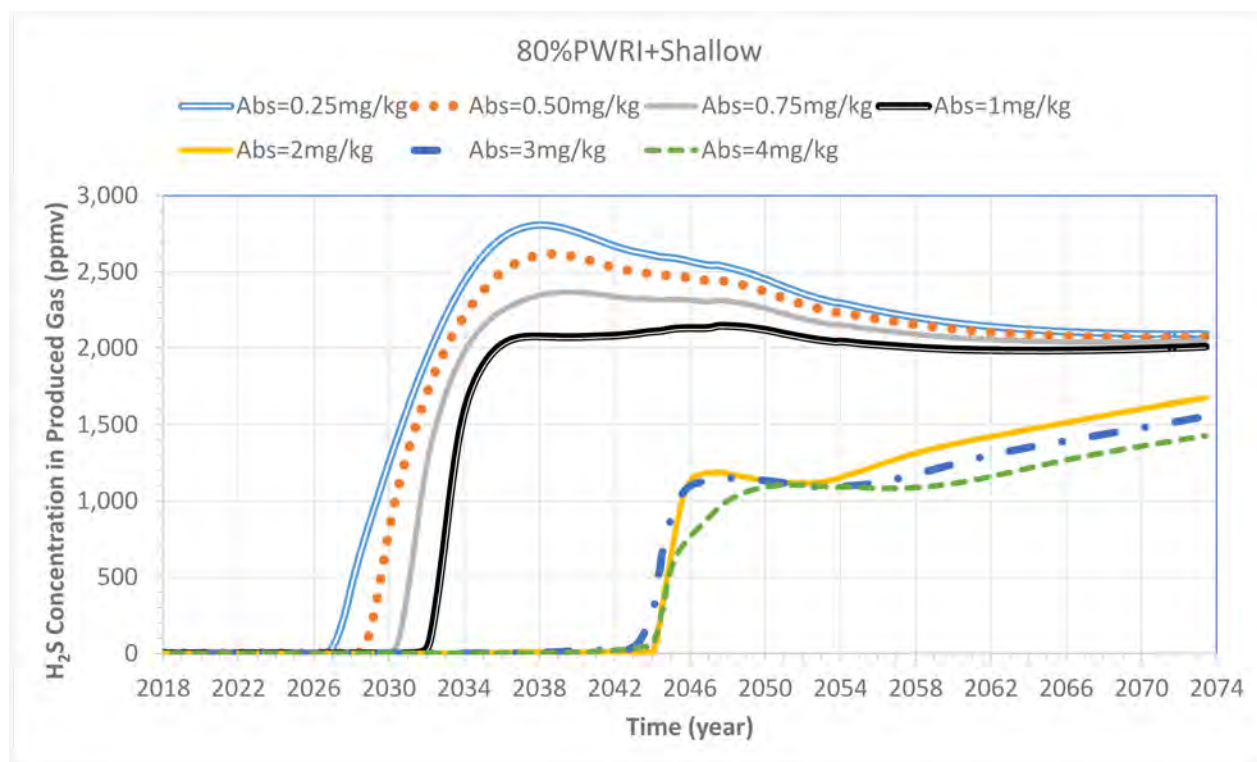
**Figure 11—Simulated H₂S concentrations in produced gas for various
abstraction capacities using 80%PWRI and shallow-aquifer water.**

Therefore, the abstraction capacity has a significant impact on the souring level when a mixture of the produced water and the shallow-aquifer water is used for water injection. As a result, it is strongly recommended to measure the abstraction capacity of the formation of the AA field such that the uncertainty associated with the abstraction capacity can be reduced.

Water-Injection Rate
In this section, the impact of the water-injection rate on the souring level is studied. For this purpose, the water-injection rate is varied from 200 m³/d to 400 m³/day. All the other input parameters remain constant. It is noted that the base-case water-injection rate is 300 m³/d. Similar to the abstraction-capacity effect, three different scenarios in terms of injection-water sources are considered, viz., the pure produced water, 80%PWRI plus the shallow-aquifer make-up water, and the pure shallow-aquifer water. Nonetheless, we only illustrate the results of the worst-case sensitivity scenarios because the effect of the water-injection rate on the H₂S level is the highest for this case. In order to be able to inject water without violating the max bottomhole injection pressure and to have the same surface water-injection rate in the reservoir, the liquid-production rate is changed accordingly for each run. For instance, when the injection rate is set at 200 m³/d (or 400 m³/d), the liquid-production rate is also put at 200 m³/d (or 400 m³/d).

Fig. 12 shows the simulated total H₂S-production rates versus time for the various injection rates when the shallow-aquifer water is injected. Fig. 13 demonstrates the simulated H₂S concentrations in the produced gas versus time for the various injection rates when the shallow-aquifer water is injected. Fig. 12 and Fig. 13 reveal that higher injection rates lead to earlier H₂S breakthrough.
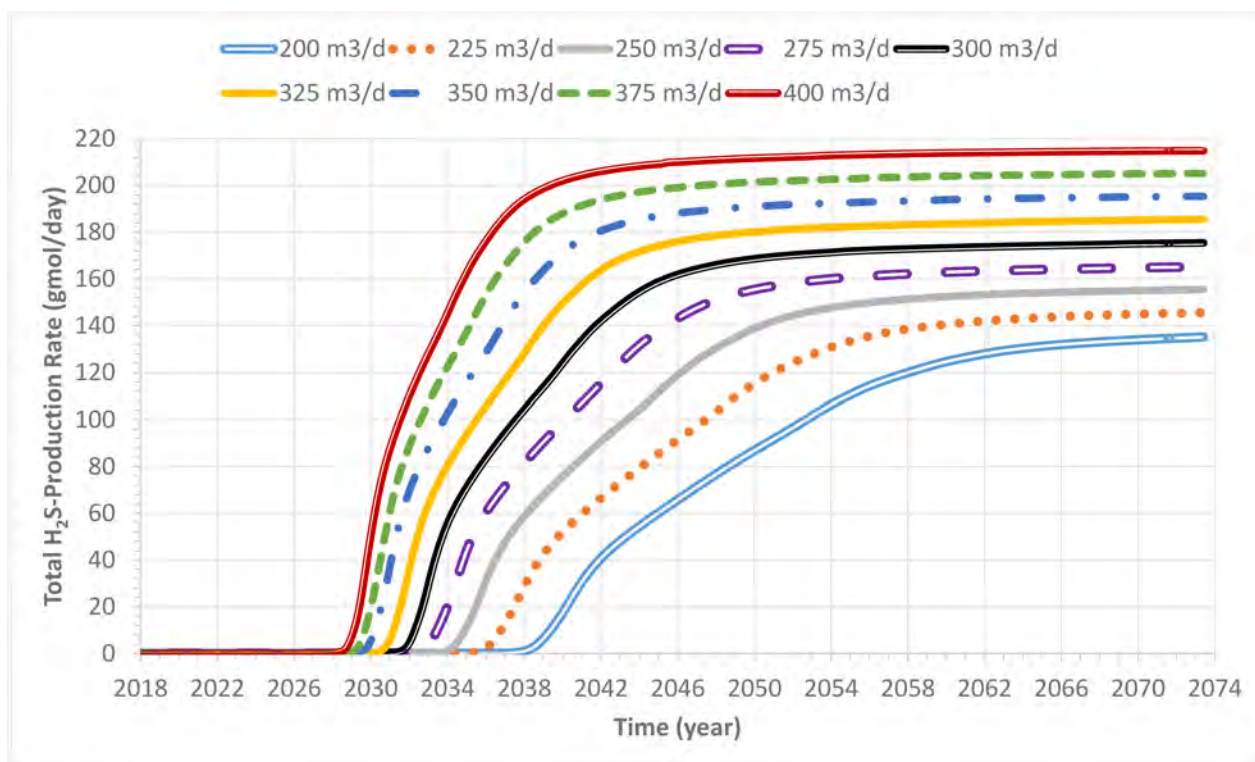
Figure 12—Simulated total H₂S-production rates for various injection rates using shallow-aquifer water.
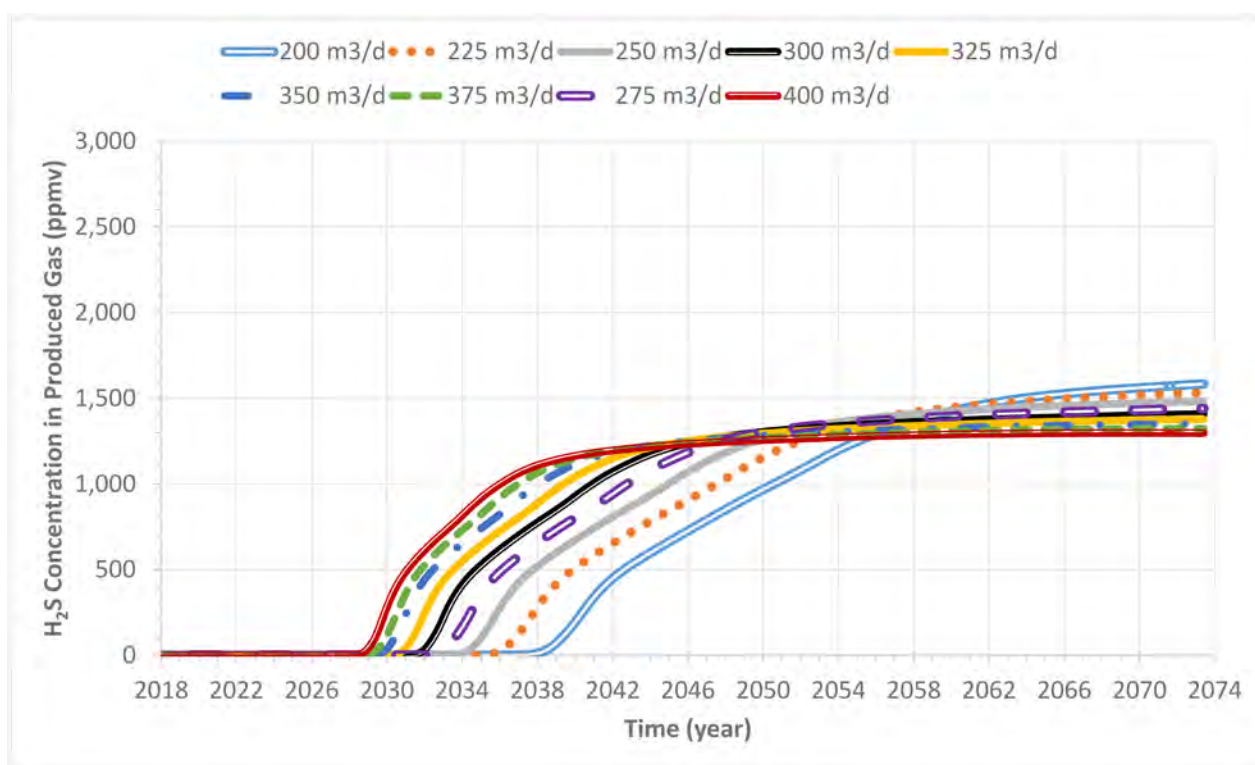

Figure 13—Simulated H₂S concentrations in produced gas for various injection rates using shallow-aquifer water.

Fig. 12 implies that even the souring level (souring risk) associated with the injection of the shallow - aquifer water can significantly be reduced by lowering the injection rate. For example, when the injection

rate decreases from 300 m³/d to 200 m³/d, the H_2S breakthrough occurs 6—7 years later and the H_2S concentration in the produced gas remains below 500 ppmv until year 2042 instead of year 2035.

Nitrate Injection

In this Chapter, the effects of nitrate injection as a microbial-souring-mitigation option are investigated. The energetic preference of nitrate reduction over sulfate reduction in anaerobe bacteria favors the use of nitrate as the electron acceptor and results in the formation of nitrite (NO_2^-), elemental nitrogen (N_2) or ammonium (NH_4^+), rather than H_2S. Therefore, nitrate injection can effectively inhibit further H_2S generation in fields that already contain active SRB colonies (e.g., McInerney et al. 1993; Sunde et al. 2004). Moreover, nitrate reduction can contribute to biological scavenging of H_2S (both microbial and non-microbial): this is achieved by nitrate-reducing sulfide-oxidizing bacteria (NR-SOB) activity, which uses H_2S as electron donor instead of fatty acids or another carbon source.

The effectiveness of nitrate injection depends largely on the ratio between the nutrient content of the ambient water (formation water or a mixture of injection and formation water) and the applied dosing of nitrate. Nitrate-reducing bacteria (NRB) activity generally outcompetes SRB activity for nutrients; however, the higher the carbon-source loading, the higher must be the nitrate dose, otherwise the nitrate will be used up and, if the conditions are still favorable, SRB will subsequently utilize any remaini ng sulfate to oxidize the residual nutrients. In reservoirs with high nutrient content and significant available sulfate, nitrate injection will only partly reduce H_2S generation (da Silva et al. 2014) for practicable dose rates. In these cases, the required doses of nitrate to significantly reduce H_2S concentrations may be less cost-effective than other mitigation options, as well as less cost-effective than H_2S-removal facilities at "end of pipe".

Care needs to be taken to ensure good corrosion monitoring while nitrate is injected due to potential production of corrosive by-products as a result of nitrate reduction, including nitrite, elemental sulfur, and polysulfides (Gieg et al. 2011).

Nitrate is normally injected as a 45% m/m $Ca(NO_3)_2$ solution in water. Typical rates are 50–100 ppm of this solution. Injecting this amount of nitrate salt is equivalent to injecting 38–76 ppm of nitrate. To investigate the effect of nitrate on H_2S production from the AA field, nitrate is added to the shallow-aquifer water at four concentrations (viz., 25, 50, 75 and 100 mg/l). The shallow-aquifer water is only considered here because it has the highest risk of souring.

Fig. 14 shows the simulated total H_2S-production rates for the various injected nitrate concentrations in the shallow-aquifer water. Fig. 14 reveals that by adding 25 mg/l nitrate into the shallow-aquifer water, the ultimate total H_2S-production rate is significantly reduced from 175 gmol/d to 102 gmol/d (42% reduction). The total H_2S-production rate is reduced furthermore by adding more nitrate to the shallow-aquifer water. Indeed, Fig. 14 indicates that the total H_2S-production rate decreases by 72%, 85%, and 90% by injecting, respectively, 50, 75, and 100 mg/l of nitrate.
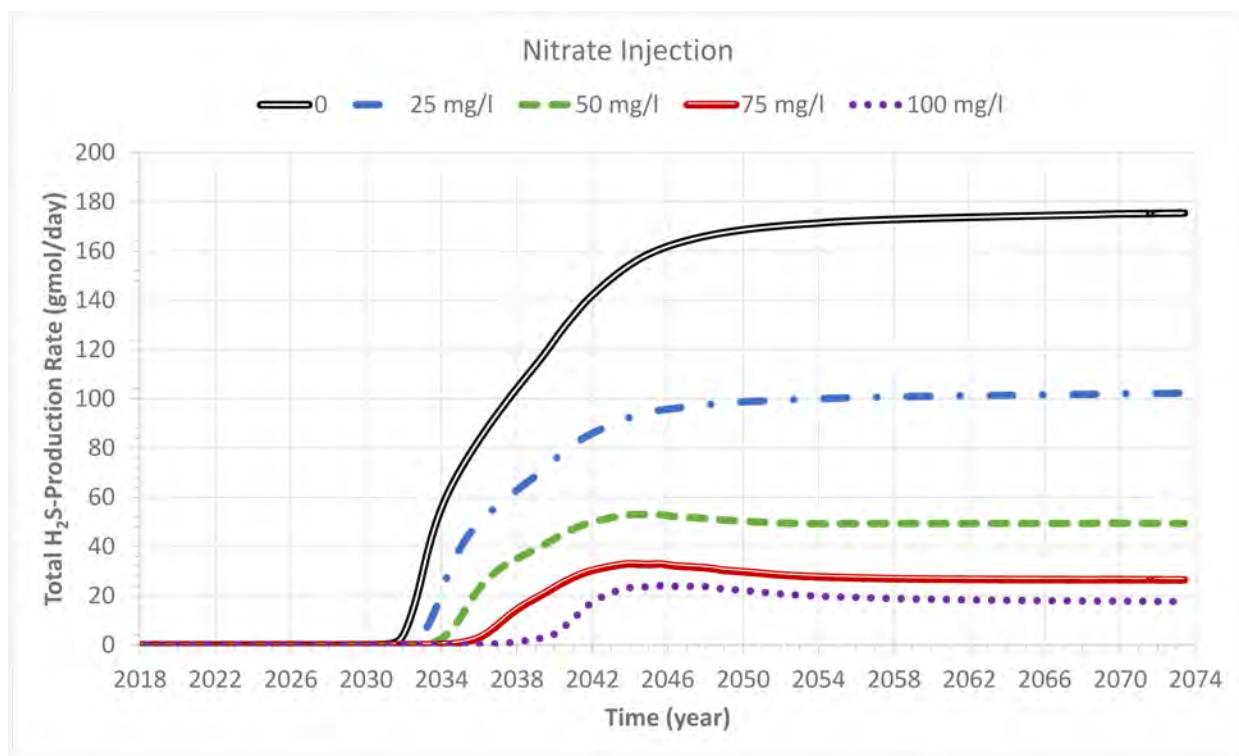
Figure 14—Simulated total H$_2$S-production rates for different injected nitrate concentrations in shallow-aquifer water.

Moreover, Fig. 14 demonstrates that the H$_2$S-breakthrough time is delayed by nitrate injection. The H$_2$S-breakthrough time occurs 1, 2, 4, and 7 years later for a nitrate-injection concentration of 25, 50, 75, and 100 mg/l, respectively.

Fig. 15 illustrates the effect of nitrate injection on the H$_2$S concentration in the produced gas. Fig. 15 shows that when 50 mg/l nitrate is added to the shallow-aquifer water, the H$_2$S concentration in the produced gas remains below 500 ppmv over the entire reservoir lifetime.
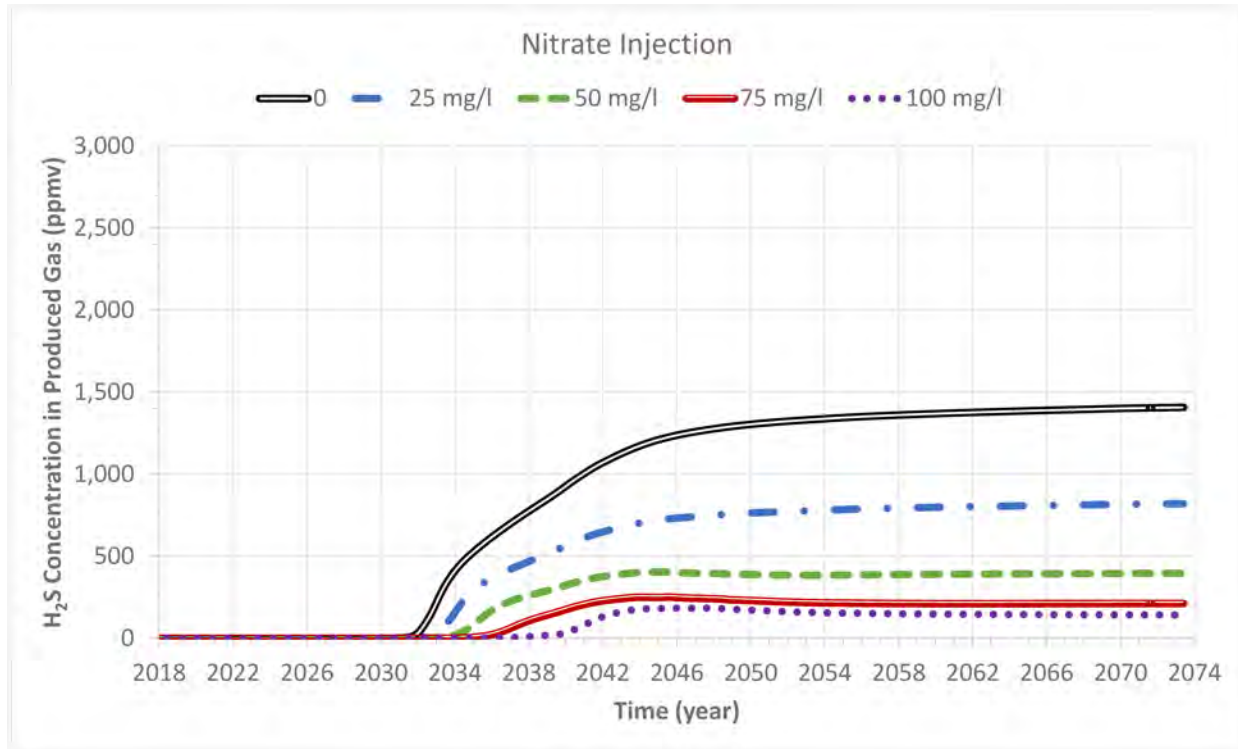
**Figure 15—Simulated H$_2$S concentrations in produced gas for
different injected nitrate concentrations in shallow-aquifer water.**

Conclusions and Recommendations

The presented reservoir-souring-assessment workflow can serve a robust risk assessment for HSE and surface-facilities selection.

The key findings of the application of the reservoir-souring-assessment workflow to the AA field are summarized here.

- Using the deep-aquifer water for water injection has a very low risk of souring. The produced fluids in the base-case scenario that uses this water remain sweep until year 2045. Moreover, the H$_2$S concentration in the produced gas remains below 500 ppmv until year 2056, and it will not reach 1,000 ppmv until year 2074.
- Using the shallow-aquifer water for water injection has a moderate to high rick of souring. The produced fluids in the worst-case scenario that utilizes this water remain sweep until year 2031. The H$_2$S concentration in the produced gas reaches 500 ppmv and 1,000 ppmv in year 2034 and 2040, respectively. The max H$_2$S concentration in the produced gas would reach 1,400 ppmv until the end of the simulation (year 2074).

  o 50% of the souring level is attributed to the dissolved H$_2$S in the shallow-aquifer water.

- Using a mixture of the produced water and the shallow-aquifer water depends significantly on the mixing ratio. If the mixing ratio would be such that the resulted salinity would still be above 150,000 mg/l (i.e., the mixture is dominated by the produced water), then the risk of souring would be very low and the souring level would be similar to the pure produced-water injection. On the other hand, if the salinity of the water mixture would be lower than 150,000 mg/l, the risk of souring would become moderate to high.

  o For mixtures with a salinity below 150,000 mg/l, the level of souring is not a monotonic function of the mixing ratio, i.e., the souring level does not necessarily increase by using more volumes of the shallow-aquifer water. This is because of the H_2S partitioning effects and the nutrient content in the water mixture.

The sensitivity runs have shown that

- The water-injection rate significantly influences the souring level irrespective of the water-injection source.
- However, the rock-abstraction capacity can significantly affect the souring level only if the shallow-aquifer water or a considerable volume of the shallow-aquifer water is injected.

  o Therefore, in case of injecting considerable volumes of the shallow-aquifer water, the abstraction capacity of the reservoir needs to be constrained through a core analysis program that involves representative XRD measurements and adsorption tests.

Nitrate injection is very effective in significantly reducing the high souring risk of injecting the shallow-aquifer water.

Stripping out the dissolved H_2S in the shallow-aquifer water can delay the H_2S-breakthrough time by 11 years and can reduce the max H_2S level by 50%.

It is strongly recommended to

- Use the produced water for injection;

- In case of injecting considerable volumes of the shallow-aquifer water such that the salinity of the injected water would become lower than 150,000 mg/l,

  o Start injecting nitrate with a concentration of 50 mg/l or higher;

  o Perform a core-analysis program that involves representative XRD measurements and adsorption tests to determine the abstraction capacity of the reservoir;

  o If possible, use a low water-injection rate (e.g., 200 m^3/d) to delay the H_2S front to the late time of the reservoir lifetime;

  o Strip out the dissolved H_2S in the shallow-aquifer water.

Acknowledgements

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