Hydrogeochemical modeling of water injection into an oil and gas well under high-pressure high-temperature (HPHT) conditions

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ABSTRACT:

Approximately 80% of water extracted from oil and gas deposits in Poland is disposed of by injection into the rock matrix. The aim of the model research was to predict both the hydrochemical reactions of water injected into wells for its disposal and the hydrogeochemical processes in the reservoir formation. The purpose of hydrogeochemical modeling of the hydrocarbon formation was also to determine the potential of formation waters, injection waters, and their mixtures to precipitate and form mineral sediments, and to determine the corrosion risk to the well. In order to evaluate saturation indices and corrosion ratios, the geochemical programs PHREEQC and DownHole SAT were used. The results of hydrogeochemical modeling indicate the possible occurrence of clogging in the well and the near-well zone caused mainly by the precipitation of iron compounds (iron hydroxide Fe(OH)₃ and siderite FeCO₃) from the formation water due to the presence of high pressures and temperatures (HPHT). There is also a high certainty of the precipitation of carbonate sediments (calcite CaCO₃, strontianite SrCO₃, magnesite MgCO₃, siderite FeCO₃) from the injection water within the whole range of tested pressures and temperatures. The model simulations show that temperature increase has a much greater impact on the potential for precipitation of mineral phases than pressure increase.

Key words: Water injection; Well; Hydrogeochemical modeling; Zechstein Main Dolomite; Poland.

INTRODUCTION

On a global scale, it is estimated that approximately 35 million m³ of water per day is extracted during hydrocarbon production (SPE 2011; Ulriasz-Misiak and Chruszcz-Lipska 2017). Formation waters, mostly with high mineral content, are reused in the petroleum industry to intensify mining and improve drilling technical conditions, and otherwise are disposed of by injection (Morrow et al. 1998; McGuire et al. 2005; Lager et al. 2008; Ahmadun et al. 2009; Rychlicki et al. 2011; Robinson 2013; Ampomah et al. 2017; Salehi et al. 2017; USEPA 2018). Much of the water used for drilling in the petroleum industry is injected into the rock mass for its disposal. In the USA, more than 90% of the extracted water is injected, of which approximately 60% is used for water flooding (Meng et al. 2016; Railroad Commission of Texas 2018).

In Poland, approximately 80% of formation water extracted from crude oil and natural gas reservoirs is injected into wells located on depleted or active hydrocarbon fields for its disposal as a waste (Ulriasz-Misiak and Chruszcz-Lipska 2017). If a drill hole
does not meet the economic criteria, it is abandoned, but if the result of injection tests is positive, the well is used for formation water injection.

The aim of this paper is to predict by hydrogeochemical modeling the reactions of formation and injected waters in both the reservoir rock and the injection wells, as well as the possibility of the occurrence of hydrogeochemical processes. The results of model simulations allow the taking of actions to minimize the negative environmental effects of water injection, involving the technical protection of drilling operations and the prediction of chemical changes in formation waters. Hydrogeochemical modeling is quite valuable for the development of a range of pretreatment processes of waters prior to injection, for making decisions on the use and selection of inhibitors, anticorrosion coatings, and other protectants, and for developing a policy of the monitoring of injection wells and the preparation of legal regulations regarding the possibilities of disposal of formation water by water injection.

LOCATION OF INJECTION WELLS IN POLAND

In Poland, over 270 natural gas fields and over 80 crude oil fields have been identified (Państwowy Instytut Geologiczny 2018; Text-fig. 1). The natural gas resources are more than 140 billion m³, and the crude oil resources over 23 million tons. In 2017, the natural gas production in Poland was 4.37 billion m³ (166 PJ), remaining constant for more than a decade, while the crude oil production was 996,000 tons and has not changed significantly since 2013 ( Główny Urząd Statystyczny 2018).

According to the regulations of the Federal International Union of Railways (UIC), since 2010 injection wells are categorized into six classes defined by the type and depth of the injection activity, and the potential for that injection activity to result in endangerment of groundwater intakes (SPE 2011). According to the above mentioned classification, class II represents injection wells used for injecting liquids that originate from hydrocarbon extraction.
Class II is subdivided into two subgroups: subgroup 1 including wells used for injecting liquids to intensify hydrocarbon extraction, and subgroup 2 including wells used for injecting crude oil for its storage and for water disposal. Currently, there are about 144,000 class II wells in the USA, of which approximately 20% belong to subgroup 2 – mainly injection wells for brine disposal (Ampomah et al. 2017). In Poland, based on the same classification, most of the wells are categorized into class II, subgroup 2, because they are non-productive wells used for injecting formation waters for their disposal.

In Poland, natural gas and crude oil deposits are the main commodities mined in the Rotliegend and Zechstein Permian Basin (66% of proven natural gas resources). The major oil-bearing formation is the Zechstein Main Dolomite, one of the most important formations in Europe, in which several tons of crude oil deposits and numerous gas deposits have been discovered (Karnkowski 2007). The Rotliegend sandstones and Zechstein Limestone (basal) deposits are also proven and productive reservoirs. The geologic formation, into which the formation water is pumped, is composed of two hydrodynamically linked formations: (1) the Zechstein Limestone which is the main top part of the injection formation, and (2) the Rotliegend sandstones which rest at the formation base (Piesik-Buś 2011). The layers immediately sealing the injection formation from the top are the successively overlying impermeable series of Zechstein deposits: anhydrite, salt, salt clay and claystones (Gąsiński and Poszytek 2013). The total thickness of the Zechstein impermeable complex is c. 260 m. The wells were drilled to various depths ranging from approximately 1,000 to more than 2,500 m. The other area of natural gas and crude oil production in Poland is the Carpathians and Subcarpathians. In the Carpathian Foredeep, hydrocarbon extraction occurs from various Eocene sandstone horizons (30% of proven deposits). In the Carpathians, which is the oldest Polish oil and gas region, hydrocarbon deposits occur in the Carpathian flysch belt (0.9% of proven deposits) in the Cretaceous to Oligocene formations. The deposits are sealed by the Carpathian-Stebnik overthrust zone and Sarmatian clay deposits (Cisek and Czernicki 1988; Myśliwiec 2004; Karnkowski 2007). Wells were drilled to various depths ranging from about 1,000 to over 4,500 m (average 1,700 m), and the total thickness of the overburden seal is variable.

The quantity of injected water in Poland is monitored in the individual deposits; however, there are no data on the total volume of injected formation waters for their disposal. Assuming the average water content (determined by the water contained in a cubic meter of the gas deposit) is 5 mL/m³, it can be estimated that more than 20,000 m³ of water can be obtained from about 4 billion m³ of natural gas per year.

**POLICIES AND REGULATORY ASPECT OF THE WATER INJECTION PROCEDURE**

The injection of formation water into the rock mass into wells is subject to legal regulations in many countries, mainly in the areas of protection of water intended for consumption. In 1974 the USA Safe Drinking Water Act (SDWA) was passed and the Environmental Protection Agency regulates the injection of all waste into the rock mass. Since then, the Underground Injection Control (UIC) program was modified to introduce stricter rules. The wells that were drilled before the establishment of the UIC could continue to be operated without authorization for a period of 5 years. After this period, the operator had to submit an application for permission for further use or had to cease operations. All new wells were allowed if they met the minimum requirements set out in the UIC regulations (Wilson and Holland 1984; Visocky et al. 1985; Meyer 1990; SPE 2011).

In Poland, formation water injection into the rock mass is possible if certain geological and environmental conditions are fulfilled. The Water Framework Directive (2000), which regulates water protection in Europe, and the Water Law principles in Poland, which were implemented from this directive (Water Law 2017), rigorously impose strict conditions for the protection of the amounts and levels of groundwater to prevent its contamination.

**METHODS AND MODELING**

**Hydrogeochemical characterization of formation waters**

The physical and chemical properties of formation waters extracted during hydrocarbon exploitation vary considerably depending on the geological formation from which the hydrocarbons are withdrawn, the depth of the deposit, the hydrodynamic conditions of the water inflow, the type of sealing layers, and the type of final hydrocarbon product. These waters have a high salt content (often expressed as salinity, conductivity, or mineralization). Physicochemical analyses of formation waters are usually carried out to identify technical drilling
problems or due to legal requirements. These results are, however, not sufficient as input data for hydrogeochemical modeling (Stober and Bucher 2012; Krogulec et al. 2018).

The largest hydrogeochemical database is managed by the USGS Produced Waters and contains the locations and geochemical characteristics of 161,915 formation waters in the USA, of which 7,430 samples are located in California (Blondes et al. 2016; Meng et al. 2016). In Poland, no hydrogeochemical database of formation waters has been developed. The formation waters of the Carpathian Foredeep and the Carpathians are characterized by a mineralization level which is dependent on both the depth and locality of the deposit, and which ranges from a few to c. 150 g/dm3. In the Carpathians, mineralization of approximately 80% of formation waters is in the range of 10–50 g/dm3; for 16% of waters, it is 3–10 g/dm3; and for c. 5% it is more than 50 g/dm3. Mineralization over 100 g/dm3 was found in several water samples from deep-seated natural gas reservoirs. Mineralization in the range of 25–35 g/dm3 prevails in waters from a depth of 1,500 m. Waters occurring below 1,500 m have a mineralization level of 30–50 g/dm3 (Cisek and Czernicki 1988). An important factor affecting water mineralization is the regional flow of infiltration waters, which causes variation in the chemical composition of waters near the deposit (dilution) and within the deposit (isolation from the main groundwater flow) (Zubrzycki 2004).

In the Carpathian Foredeep, formation waters originating from Eocene, Miocene or flysch sediments are represented by brines with a mineralization level ranging from 8 to 32 g/dm3, which gradually increases with depth (Jabczyński et al. 1990). A characteristic feature is their considerable diversity of anionic composition. The iodine concentration remains at a level of 0.016–0.03 g/dm3 (average 0.023 g/dm3), while the amount of bromine is slightly higher (average 0.038 g/dm3, maximum 0.06 g/dm3). The average concentration of HCO3- and CO32- is 1.883 g/dm3 (ranging from 1.49 to 2.18 g/dm3). The average concentration of hydrogen ions in terms of pH is 8.35 and indicates a slightly alkaline reaction.

The formation water from oil and gas deposits located in the Rotliegend and Zechstein Permian Basin is also characterized by a variable chemical composition. The chemical characteristic of the formation water was determined according to the results of 12 archival chemical analyses from the period of 2001–2011, carried out for the needs of documentation of selected Zechstein Main Dolomite oil and gas deposits. These are highly mineralized sodium chloride brines. Their total mineralization varies between 170 and 331 g/dm3 (average 261 g/dm3). The waters are dominated by the Cl- ion (110.4–194.0 g/dm3 and above 99% meq/L of anions) and Na+ ion (43.5–110.6 g/dm3 and 50.3 to 82% meq/L of cations). Calcium is typically the second most common cation, ranging from 14.1 to 42.4% meq/L of cations. The high mineralization is accompanied by the water’s acidic pH ranging from 4.0 to 7.2, with an average value of 5.4. The value of the metamorphic index (rNa/rCl) is low (less than 0.65), which is a characteristic of relict brines occurring in the Zechstein Limestone and Rotliegend sediments, underlying the natural gas deposits in the succession.

The hydrogeochemical modeling was based on physical and chemical data from 12 analyses of formation waters (WZ) from the years 2001–2011. Detailed indication of the field study is not possible due to the rights of the mine operator, who does not consent to the publication of data such as the location, profile, depth and number of boreholes. These are considered as ‘sensitive data’ in Poland. The authors’ own extended analyses include physical and chemical properties, concentrations of dissolved inorganic and organic constituents, and the content of gases (Table 1).

**In situ** measurements in water samples include electrolytic conductivity, pH, temperature, and redox potential (multifunctional Elmetron CX-401). Other substances were measured in the accredited laboratory.

<table>
<thead>
<tr>
<th>Properties and substances</th>
<th>Physical and chemical properties</th>
<th>Ions and gases</th>
<th>Metals</th>
<th>Organic substances</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>density, temperature, electrolytic conductivity, pH, redox potential, acidity, alkalinity, suspensions</td>
<td>Br-, F-, PO43-, CO32-, HCO3-, NO3-, NO2-, NH4+, Cr(VI), SO42-, CN-, CO32-, H2S, O2</td>
<td>Al, As, B, Ba, Be, Ca, Cd, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Si, Sr, Zn</td>
<td>TOC, mineral oil index (C12,33), benzene, toluene, ethylbenzene, m-, p-xylene, o-xylene, styrene, sum of BTEX, naphthalene, acenaphthylene, acenaphthalene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, sum of WWA</td>
</tr>
</tbody>
</table>

Table 1. Range of input data for hydrogeochemical modeling.
Changes in the chemistry of formation waters during water pre-treatment before injection into the rock mass

Formation water, extracted with crude oil and natural gas, is separated in a technological process and directed during various stages to the degassing installation and preliminary purification. After separation from oil/gas, one of the treatments of the formation water is desalination, so that a lower concentration of sodium and chloride in the injection water is an effect of the technological treatment. Before injection, clog-generating suspended matter is usually removed by a process of sedimentation in natural conditions or by using coagulants and floculants. During natural sedimentation, only 80% of the suspension is removed regardless of the duration of sedimentation (Macuda et al. 2007). The processed formation water is then injected into the deposit with an efficiency dependent on the depth, deposit’s hydrodynamic conditions, and the water volume.

An example of a change in the formation water (WZ) chemistry during pre-treatment is provided by the results of 2 chemical analyses of injection waters (WI) sampled in May, 2015 and April, 2018. The content of total dissolved solids is more than 10 times greater in the original formation waters and the concentrations of potassium, sodium, calcium, and chloride ions are much higher. Iron concentration displays the largest difference (up to 1,400 times) between the formation water and the injected water. There is also a significant difference in pH, which is slightly acidic in formation water and alkaline in injection water (Table 2).

The mineralization decreased to 191 g/dm³ and the pH remarkably changed from acidic to alkaline (8.7). A characteristic feature, not analyzed earlier, is high concentrations of organic carbon, lithium and strontium, reaching 7,070 mg/dm³, 29 mg/dm³, and 89.9 mg/dm³, respectively.

Modeling of processes occurring in wells during water injection

Hydrogeochemical modeling allows forecasting of both hydrogeochemical changes in the well (Macuda et al. 2007; Lewkiewicz-Małysa and Konopka 2009; Lewkiewicz-Małysa and Winid 2011; Labus and Suchodolska 2017) and the environmental impacts while injecting formation water into the rock mass for its disposal. However, little use of hydrogeochemical modeling has been made in high-pressure high-temperature (HPHT) conditions so far. Modeling results can be used in research on the selection of a method for chemical modification of injected waters in order to use injection efficiently and to minimize the negative environmental and technical effects of injection. Hydrogeochemical modeling identifies chemical processes occurring in the geological environment in the case of water mixing, and allows the simulation of possible alterations depending on the assumed boundary conditions of the model (Jia and Qu 2000; Kühn et al. 2002; Janocha and Kluk 2005; Liang et al. 2006; Merdhah and Yassin 2007; Jakubowicz 2010; Kluk 2011; Shutemov 2013; Li et al. 2014). Among the most serious technical problems during water injection into the rock mass is clogging, which can be detected by an increase in pressure. During the injection process, formation water fundamentally changes its chemical composition and physical properties, causing geochemical changes in the rock matrix, i.e., clogging and corrosion of the reservoir formation and corrosion of technical components of the well (Banaś et al. 2007). This may result from the effects of soluble and insoluble chemical compounds, during both hydrocarbon exploitation and formation water injection (Brandl et al. 2011). The most important physical and chemical factors that have a major impact on the corrosivity of the solution are the concentrations of carbon dioxide, hydrogen sulfide, total sulfides and chlorides, pH, water hardness, temperature, and the presence of microorganisms (affecting pH change

<table>
<thead>
<tr>
<th>Physical and chemical parameters</th>
<th>Units</th>
<th>Formation water (WZ)</th>
<th>Injection water (WI)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min.</td>
<td>Max.</td>
<td>Min.</td>
</tr>
<tr>
<td>Specific weight</td>
<td>[g/cm³]</td>
<td>1.1790</td>
<td>1.2489</td>
</tr>
<tr>
<td>pH</td>
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<td>3.5</td>
<td>6.88</td>
</tr>
<tr>
<td>Bromine (as Br)</td>
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</tr>
<tr>
<td>Chloride (as Cl)</td>
<td>[mg/dm³]</td>
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<td>217000.0</td>
</tr>
<tr>
<td>Bicarbonate (as HCO₃⁻)</td>
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<td>15250.0</td>
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<tr>
<td>Sulfate (as SO₄²⁻)</td>
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<tr>
<td>Calcium (as Ca)</td>
<td>[mg/dm³]</td>
<td>3910.0</td>
<td>55000.0</td>
</tr>
<tr>
<td>Iron (as Fe)</td>
<td>[mg/dm³]</td>
<td>5.6</td>
<td>1997.4</td>
</tr>
</tbody>
</table>

Table 2. Selected physical and chemical parameters of formation water (WZ) and injection water (WI).
and the presence of, for example, H₂S (Wigand et al. 2009; Gaus 2010; Lu et al. 2010; Mason et al. 2013). The presence of ions, such as carbonates, phosphates and chromates, reduces the intensity of corrosion due to the formation of protective layers and thus the metal passivation phenomenon is observed. The corrosion rate is much more rapid in highly mineralized waters (Kowal and Świderska-Bróz 2000). The most frequently formed compounds of secondary precipitation are calcium carbonate, barium sulfate, strontium sulfate, and oxides and sulfides of iron and manganese (Nešić 2007; Noga et al. 2011).

Clogging occurs due to changes in oxygenation conditions, namely oxidation-reduction potential, pH, and temperature. Consequently, hardly soluble salts, such as iron and manganese oxides and hydroxides, amorphous silica, iron and manganese sulfides, carbonates, and sulfates precipitate. Clogging needs to be considered because of the precipitation of solids on installation walls and in pores and fractures of the near-well zone. The most important factors generating clogging include: high suspended solid content in the injected water, microbiological processes, swelling of clay minerals, introduction of corrosion-released solids into the deposit, precipitation of sediments from the injected water, precipitation of sediments from mixed injected and formation waters (differing in their chemistries), and changes in the pressure and temperature within the deposit due to the injection process (Witherspoon et al. 1962; Wright and Chilingarian 1989; Bradley 1992; Tomaszewska 2008; Waligóra et al. 2016).

Hydrogeochemical modeling can be used to assess the corrosion or clogging of the deposit and the well. Forecasting of the occurrence of these processes is possible by performing computational simulations depicting the size of precipitation indicators (Vetter et al. 1982; Sobie and Macky 2000; Mackay and Jordan 2005; Nešić 2007; Amiri and Moghadasi 2013; Khormali et al. 2016).

A prerequisite for the reliable development of hydrogeochemical models is input data in the form of detailed chemical analyses of the injected and formation waters. The input data for hydrogeochemical models requires knowledge of the mineral composition of the rock matrix of the injection layer for a real assessment of the dissolution or precipitation of mineral phases present in the deposit. For deep wells in oil and gas fields, data on the range of temperatures and pressures existing in the reservoir formation and during injection operations are of key importance.

Determination of the activity of individual ions in a solution of saline water, such as formation water, is possible in geochemical speciation modeling using the PHREEQC program and the dedicated pitzer.dat database (Clauser and Villinger 1990; Pitzer 1991; Parkhurst and Apello 2013). Another program using the pitzer.dat database is DownHole SAT. This program was designed specifically for modeling of chemical processes in highly mineralized liquids (brines). It is frequently used by the oil and geothermal industry, specifically in high-pressure and high-temperature conditions (HPHT; DownHoleSAT Product Manual 2008).

Multistage hydrogeochemical modeling allows the determination of various precipitation indicators. Precipitation from formation waters or treatment fluids is defined by two precipitation indicators (Shutemov 2013) as follows:

- Saturation Index (SI), i.e., the ratio of ion activity products (IAP) to the equilibrium constant at a given temperature (Ksp) [SI = \log_{10}(IAP/Ksp)]. The Saturation Index depends on the thermodynamic equilibrium of the solution; the more the SI value is greater than 0, the greater is the potential of the solution to precipitate mineral deposits;

- Free Ion Momentary Excess (FIME), also called Precipitation to Equilibrium, which determines the potential quantity (in mg/dm³) of free mineral phases in the solution, precipitation of which will bring the solution to equilibrium; it depends mainly on the kinetics of the reaction and indicates the potential quantity of precipitable sediments (DownHoleSAT Product Manual 2008).

The quantitative evaluation of precipitation is possible by calculating the values of both indicators simultaneously for many mineral phases that undergo precipitation from various types of brines (Ferguson 2013). It is also possible to quantify the corrosion by counting the potential thickness of the layer of corrosively removed material per year (mm/y). Such model simulations involve the content and pressure of carbon dioxide (CO₂) and hydrogen sulfide (H₂S) in the solution (Kermani and Morshed 2003; Choi et al. 2011; Elgaddafi et al. 2016, 2017). For the qualitative assessment of the risk of precipitation and corrosion, the so-called simple chemical stability indices of liquids, describing the state of equilibrium of the solution, can also be used. The most frequently used indices in the oil and geothermal industry are based on the equilibrium of calcium carbonate solution – Langelier, Puckorius, Oddo-Tomson and Stiff-Davis indices (Puckorius and Brooke 1991; Oddo and Tomson 1994; Melidis et al. 2007). Stability indices in the solution are used to determine the possibility of dissolving and removing carbonate sediments, form-
ing a protective layer on the surface of the well walls and on injection infrastructure.

The qualitative assessment of the corrosion risk of soft steel can be performed using the Larson-Skold index. High values of this index suggest the ability of the solution to induce pitting corrosion caused by high concentrations of chloride and sulfate ions in the solution. The modified Larson index also includes the temperature of the solution, which is particularly important in simulations for deep wells (Larson and Skold 1958; Imran et al. 2005).

RESULTS OF MODEL SIMULATIONS AND DISCUSSION

The potential of injected water to precipitate and form mineral deposits and the risk of corrosion should be considered individually for each reservoir and selected boreholes. This potential depends directly on the chemical composition of the water and is temperature- and pressure-dependent.

Hydrogeochemical modeling was carried out for a well located in the Rotliegend and Zechstein Permian basin. The results have not been compared with other studies due to the lack of published data in a range similar to the performed model simulations. Detailed physical and chemical analyses of formation waters were carried out, and data on the gas-bearing horizon rocks and water injection conditions were used. The formation waters are extracted together with natural gas and crude oil from carbonate deposits of the Main Dolomite (Zechstein) from a depth of approximately 3,200 m and a total thickness up to 50 m. The Main Dolomite is also the injection layer, into which the formation waters are injected after pre-treatment.

The Main Dolomite deposits within the selected hydrocarbon deposit represent the margin between the platform slope and the bay plain. The location at the foot of the carbonate platform causes a significant diversity of sediments in vertical profile and between individual boreholes. Generally, the sediments consist of sublittoral, redeposited carbonate sands developed as a result of the activity of traction currents below wave base, as well as slurry currents and gravitational runoffs deeper into the bay plain. Significant microfacies variations were observed, ranging from mudstones, through bioclastic wackestones, oncoid-intraclastic packstones, to bandstones, biosedimentation laminated structures and low microbial structures (unpublished data). The main minerals observed in SEM, XRF, and optical microscopy studies include: dolomite (50–90%), calcite (5–20%), anhydrite (0–20%), clay minerals (1–7%), and accessory minerals such as quartz, halite, zeolite, apatite, and fluorite. Reservoir parameters were estimated from laboratory and geophysical tests. The permeability coefficient varies from 0.001 mD to 135 mD, its average value is around 5 mD. Effective porosity was evaluated in the range of 0.91–33%, with an average value of 8.99%. Total porosity ranges from 5 to 35%, with an average value of 18%.

Neither corrosion inhibitors nor precipitates are added to the injection waters. Hydrogeochemical modeling was carried out using the DownHole SAT program (DownHoleSAT Product Manual 2008).

For the considered deposit, the model simulations used a temperature of 127.3°C and an initial pressure of 43 MPa indicative of a depth of 3,224 m b.g.l. Before being injected into the rock mass, injection waters are stored at atmospheric pressure and a temperature of 40°C. Ranges of temperature (T) from 40°C to 127.3°C and pressure (P) from 0 to 430 atm were used in the hydrochemical modeling. Thus, the hydrogeochemical modeling may be considered to have been performed for HPHT conditions.

This paper presents the results of modeling for six mineral phases: calcite (CaCO₃), strontianite (SrCO₃), magnesite (MgCO₃), siderite (FeCO₃), barite (BaSO₄), and iron hydroxide (Fe(OH)₃). These phases are the most characteristic of highly concentrated sodium chloride brines that occur in reservoir carbonates, and they represent chemical compounds that are likely to cause clogging. The mineral phases selected for presentation below have been the most frequently analyzed in global studies of reservoir waters accompanying oil and gas (Ramstad et al. 2005; Frennier and Ziauddin 2010; Kan and Tomson 2012; Aregbue 2014; Haghtalab 2014; Olajire 2015; Li et al. 2017).

The model results show that the formation water (WZ) at the bottom-hole at a temperature of 127.3°C is strongly supersaturated with iron compounds. It is characterized by a high level of saturation predominantly of iron hydroxide (SI for Fe(OH)₃ = 2.43) and siderites (SI for FeCO₃ = 0.67) (Text-fig. 2A). The simulation of temperature-dependent saturation variation shows that the SI of iron hydroxide (Fe(OH)₃) increases with increasing temperature, whereas the SI gradually decreases for siderite (FeCO₃). This is, however, accompanied by small FIME values (maximum values do not exceed 0.02 mg/dm³ for FeCO₃), which reduces the possibility of formation of sediments of this type.

Among the remaining carbonate deposits, there is little potential for precipitation of calcium carbonate
due to low SI value, i.e., calcite (CaCO$_3$), but only up to a temperature of around 95ºC. At higher temperatures, SI is <0 and the solution becomes undersaturated relative to calcite. Thus, at the bottom-hole, in the reservoir rock it is theoretically possible to precipitate only small amounts of sediments consisting of iron hydroxides or iron carbonates (Text-fig. 2A).

The modeling performed for varying pressure shows that the saturation levels for almost all carbonate mineral phases decrease slightly with increasing pressure (Text-fig. 2B). The solution is most supersaturated relative to iron hydroxide Fe(OH)$_3$, and in this case an increase in saturation is observed at high pressures. Therefore, it should be emphasized that iron compounds have a theoretical potential to form sediments at high pressures and high temperatures, i.e., at the bottom-hole and in the near-well zone.

Because of the different chemical composition and differences in the temperature and pressure conditions of injection water (WI), the obtained values of precipitation indices are clearly different in relation to those of the formation waters. Before being injected into the rock mass, i.e., at a pressure of 0 atm and a temperature of 40ºC, the mineral phases, which have the highest degree of supersaturation in the solution, are represented mainly by carbonates: calcite (SI for CaCO$_3$ = 3.07), magnesite (SI for MgCO$_3$ = 2.45), strontianite (SI for SrCO$_3$ = 2.41) and siderite (SI for FeCO$_3$ = 2.16) (Text-fig. 2). Their SI values can be higher than in the formation waters. Barite (SI for BaSO$_4$ = 0.85) also shows much greater potential for precipitation (Text-fig. 3A).

The saturation index level is accompanied by very high FIME values, demonstrating the real potential for sediment formation. The maximum FIME values are recorded at 40ºC: for CaCO$_3$ = 270.9 mg/dm$^3$, MgCO$_3$ = 227.3 mg/dm$^3$, and SrCO$_3$ = 257.2 mg/dm$^3$. It should be noted, however, that siderite (FeCO$_3$) has a saturation level decreasing rapidly with increasing temperature, and the FIME value is negligible in

Text-fig. 2. Variation in the Saturation Index (SI) of formation water: A – temperature-dependent; B – pressure-dependent.
comparison with those of other carbonates (ranging from 0.001 to 0.14 mg/dm$^3$). For barite ($\text{BaSO}_4$), the theoretical possibility of precipitation occurs at the temperature of c. 110ºC; at higher temperatures this mineral phase can dissolve (SI<0, FIME<0).

The model simulation of SI shows overall slightly decreasing values for all mineral phases (Text-fig. 3A). For injection waters, at the highest pressure of 430 atm, there were positive values of both precipitation indices (SI and FIME) for all mineral phases except for Fe(OH)$_3$, and very low FIME values for FeCO$_3$ (0.14 mg/dm$^3$).

Compared to formation waters, the main differences are the lack of the possibility of creating sediments with the presence of iron, and the high potential for precipitating carbonate sediments in the entire tested range of pressures and temperatures, and therefore both at the surface (storage before injection) and at the bottom-hole. Supersaturation of the solution with respect to these mineral phases may cause clogging. It is worth emphasizing that temperature increase has a much greater influence on the potential for precipitating mineral phases than the pressure increase, which results in much lower SI variability.

Saturation indices were also determined for different mixing ratios (from 0% to 100%) between the injection water and the formation water (Text-fig. 4). The resulting solution is characterized by supersaturation with respect to all the previously mentioned carbonate mineral phases. An SI increase correlates with the increased proportion of injection water in the mixture. It is worth paying attention to the very high SI and FIME values for siderite (FeCO$_3$), which were not recorded at such a level for the separate components before mixing. The greatest potential for precipitation of this type of sediment occurs at an 80–85% share of injection water. The solution becomes undersaturated with respect to Fe(OH)$_3$ already at c. 10% share of injection water in the mixture.
A quantitative assessment of the ability of the described solutions to induce corrosion was carried out. Model simulations were performed for the temperature range of 40–127.3ºC for formation water (WZ), injection water (WI), and their mixture (MIX) in the proportion of 50:50.

Injection water has the least potential for corrosion than the other two presented. At a temperature of 40–55ºC, formation waters are theoretically able to corrode even more than 30 mm of material per year, but this potential drops rapidly at higher temperature intervals (Text-fig. 5). The corrosive strength of all these solutions gradually increases with temperature. Very high corrosive properties of formation waters are reduced after their mixing with injection waters. The maximum corrosivity of the resulting mixture is 0.65 mm/y.

Other chemical stability indices were used in describing the carbonate equilibrium of the solution (Text-fig. 6). Values of the Langelier, Oddo-Tomson and Stiff-Davis indices < -2 are indicative of corrosive properties (Stiff Jr. and Davis 1952; Müller-Steinhagen and Branch 1988; Oddo and Tomson 1994; Melidis et al. 2007). The Ryznar and Puckoris indices indicate a higher corrosive potential of a liquid increasing when the value is greater than 6 (Puckorius and Brooke 1991; Melidis et al. 2007). None of the above indices calculated for the studied waters exceeded the limit value, but the modified Larson index (LRM) value stood out clearly. The index involves the effect of high concentrations of chloride and sulfate ions on the corrosive capacity of liquids (Larson and Skold 1958; Melidis et al. 2007). It also considers the temperature of the solution and broadens the scope of its applicability (Imran et al. 2005). It is assumed that the higher the value of the index, the greater is the risk of local pitting corrosion. Very high values of the modified Larson index were observed for formation waters (WZ) (LRM = 306.1). The pitting corrosion potential decreased after these waters were mixed with injection waters (LRM = 217.2; Text-fig. 6). Injection waters (WI) with a clearly positive value
of the modified Skold index (LRM = 9.1) indicate the possible occurrence of pitting corrosion within the well and its pumping infrastructure.

The procedure of disposing of formation water by injecting it into the reservoir layer in the presence of water with a different chemical composition may lead to a series of co-occurring geochemical alterations of the deposit that affect the well infrastructure and the near-well zone. The results of model simulations carried out for HPHT conditions indicate a high risk of precipitation and formation of carbonate and sulfate sediments together with Fe(OH)₃. This may lead to both clogging and a decrease in injectivity, but it may also protect the well and its infrastructure against corrosion, thus creating a protective passivation layer composed of these precipitates on its walls (Nešić 2007; Han et al. 2009, 2011).

The modeling results show that the performance of the injection well needs to include not only the implementation of treatments that protect against clogging and corrosion by using appropriate inhibitors in the injected water, but also strict in situ monitoring of the chemical composition of formation waters and the effectiveness of their treatment (purification).

CONCLUSIONS

1. Hydrogeochemical modeling is a tool for assessing the expected impact of injected waters on the
technical condition of the well and possible geochemical changes in the reservoir formation and groundwater environment. Model simulations allow for the assessment of predicted hydrogeochemical changes, and consequently for making decisions, primarily in the field of environmental impact and technological planning of the injection process. On the basis of the results of hydrogeochemical model calculations, it is possible to plan the scope of pre-treatment of formation waters in order to minimize the precipitation of some phases in the deposit during injection. In order to evaluate saturation indices and corrosion ratios, the geochemical programs PHREEQC and DownHole SAT were used. As the modeling results show, relatively low-cost processes of pre-treatment of formation waters before their injection reduce the risk of clogging, especially caused by iron compounds (Fe(OH)₃ and FeCO₃).

2. The main purpose of hydrogeochemical modeling of the hydrocarbon deposit in the Rotliegend and Zechstein Permian Basin was to determine the potential of formation waters, injection waters, and their mixtures to precipitate and form mineral sediments, and to determine the corrosion risk to the well. The results of hydrochemical modeling of formation waters (WZ), injection waters (WI) and their mixture (Mix) showed significant differences in the potential to precipitate sediments from various mineral phases. Injection water has the least potential for corrosion, much lower than that of formation water. At a temperature of 40–55°C, formation waters are theoretically able to corrode even more than 30 mm of material per year, but this potential drops rapidly at higher temperature intervals.

3. The research was carried out to evaluate the possibility of clogging of both the well and the near-well zone. Clogging is caused mainly by the following factors: (1) precipitation of iron compounds from formation water at high pressures and temperatures, (2) high potential of injection water to precipitate carbonate sediments in the entire range of tested pressures and high temperatures, (3) supersaturation of the solution in relation to all carbonate mineral phases in the mixture of formation and injection waters from c. 42% share of injection water, and (4) very high SI and FIME values for siderite (FeCO₃), which were not recorded at this level for separate components (with a maximum at 60–80% share of injection water).

4. The simulations enabled the assessment of the corrosion potential in the components and the mixture of formation and injection waters. The calculated indices (Ryznar, Langelier, Puckoris, Oddo-Tomson, Stiff-Davis) are low and do not indicate corrosion risk, and only the high values of the Larson-Skold index for injection waters point to a risk of pitting corrosion and possible damage to the well and infrastructure. The very high value of this index for formation waters may indicate corrosion hazard to the storage infrastructure and the equipment for the pretreatment of formation water before injection.

5. The brines are subjected to rapid changes in temperature and pressure on the way through the installations. The presented results can be used to select the methods and scope of research needed to conduct preliminary analyses and assessments of the risk of costly damages to the infrastructure and the near-well zone caused by geochemical changes of solutions in the conditions of the HPHT and mixing with solutions of a different composition.

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