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# Analysis of Temperature Influence on Precipitation of Secondary Sediments during Water Injection into an Absorptive Well

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**Abstract:** The extraction of hydrocarbons is associated with obtaining certain amounts of water, which is heavily contaminated with a wide range of chemical compounds that negatively affect the environment. At present, practically the only method of managing extracted reservoir waters is their injection into absorbing horizons. Large changes in parameters (pH, Eh, temperature, etc.) occurring during the extraction and storage of water, as well as the contact of the injected water with reservoir water and rock, may result in the precipitation of secondary sediments. The complexity of the injected water/native water/deposit rock system and the wide range of possible interactions do not always allow for correct interpretation of the processes and their impact on near-well zone permeability. One of the factors which has a decisive influence on dissolution/precipitation is temperature change. Applying analytical data of water with low (W-1) and high (W-2) mineralization, calculations were carried out with the use of PRHEEQC software. Changes in solubility index values were determined at ambient temperature (20 °C) and reservoir temperature (94 °C). The obtained results indicate that with increasing temperature, SI changes for a given chemical compound may run in different directions and take different values, depending on the composition of the injected water. The calculations indicate the possibility of a change in the direction of the reaction from dissolution to precipitation, which may lead to clogging of the near-well zone. Simulations of the injected water's contact with minerals present in the reservoir rock were also carried out. The obtained data indicate that these minerals, in the entire studied temperature range, dissolve in the injected water, but the solubility of anhydrite and dolomite decreases with increasing temperature. If the water is saturated with minerals at low temperature, after heating in the bed, sedimentation and blockage of rock pores may occur, which means there is a reduction in the efficiency of water injection.

**Keywords:** water injection; absorptive well; solubility index; PHREEQC

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## 1. Introduction

Reservoir waters, often extracted in large amounts during the exploitation of crude oil and natural gas, may contain very large loads of pollutants that adversely affect living organisms [1]. There are large amounts of various substances in reservoir waters: soluble salts—mainly chlorides, but also sulphates, bicarbonates, bromides and sulfides; metal ions—sodium, potassium, calcium, magnesium, iron and manganese; heavy metals; insoluble substances—sands, clays, metal oxides and silica; remains of drilling fluids and treatment fluids; petroleum hydrocarbons—including phenols, aromatic hydrocarbons and PAHs; and chemicals dissolved in water used in order to improve its operation—corrosion inhibitors and hydrates, foaming agents, demulsifiers, etc. Treatment of such waters is difficult and costly due to strong variations in the content of individual pollutants in subsequent parts of the extracted water. The presence of a wide variety of substances makes it difficult and economically unprofitable to apply the treatment of the excavated reservoir waters to a level that enables safe discharge into surface waters or soil.

For this reason, it is preferable to remove the extracted reservoir water from the active biosphere by pumping it to absorbent horizons in hydrocarbon reservoirs. This method enables safe and inexpensive management of brines, and can be applied to intensify extraction and increase the degree of depletion of the deposit [2–4]. An alternative solution for deposit water injection is its purification and drainage to surface waters and the soil or its industrial usage, after elimination of all contaminants according to administrative law [5–7]. The diversity and huge amount of contaminants cause serious problems with water purification to the required level. Furthermore, the management of wastes which appear during water purification increases the costs of this solution.

However, injection as a preferred method of management requires proper water preparation in terms of removing components that may damage a borehole zone and limit injection efficiency.

The preparation for injection is usually carried out by removing sediment (e.g., by filtration). However, in many cases this is insufficient due to the presence of fine particles of suspended solids that are not retained on the filters, as well as iron oxide deposits formed upon contact with air.

Due to their properties, these oxides cause difficulties in filtration (clogging of filters), and may also precipitate after filtering the water. Their colloidal nature means that, together with the injected water, they can deeply penetrate the near-well zone and cause damage which is extensive and difficult to remove.

A proper solution is a water treatment installation using appropriately selected processes to remove pollutants: removal of iron and manganese ions (by air blow oxidation, absorption on the bed in ion exchange process or masking their presence with complexing compounds), coagulation (precipitation of pollutants in a form of sediment) with flocculation (agglomeration of suspended particles and colloids) or using a ballasting agent [8–10] followed by sedimentation and/or filtration to remove solid particles from the water phase [11–14]. Due to the large variation in the content of individual components in the extracted reservoir waters, it is not possible to determine optimal doses of chemicals and parameters of individual treatments at one time. It is necessary to carry out the optimization procedure for individual stages of the preparation process and to control the effectiveness individually for each batch of formation water intended for injection (Figure 1) [15].

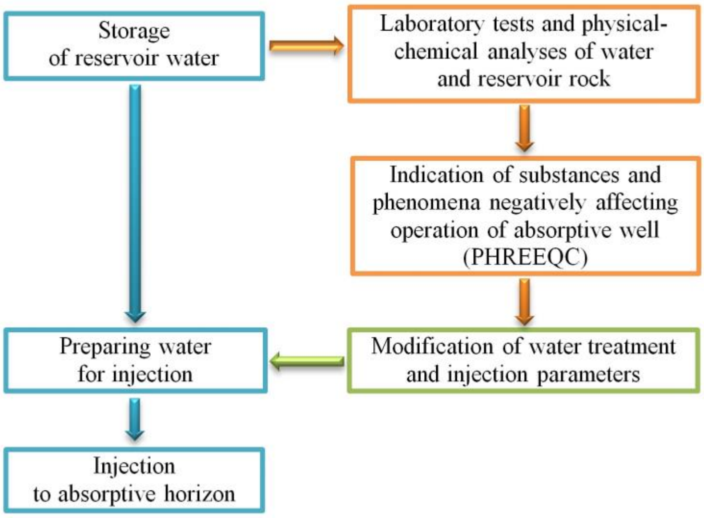


**Figure 1.** Scheme of water injection process with necessary laboratory and modelling research.

Membrane systems can also be used in water treatment to remove petroleum pollutants and to obtain water with low salinity. Research on the application of these methods is most often applied in areas suffering from water shortages [16].

However, even the correct and effective conduction of the process of water preparation for injection may not protect the absorptive well against progressive clogging. Undesirable chemical processes may occur when injected into a reservoir of water with a different chemical composition (the presence of incompatible components).

Precipitation of sediment particles and suspensions may take place during contact of the injected water with native water present in the reservoir and with the reservoir rock, as well as in the case of the successive injection of water batches containing components reacting with each other with precipitation. Sludge formation reactions can also be triggered by changing physical and chemical properties of the water (e.g., changing the pH, redox potential, temperature, etc.) [17,18].

Water in a deposit has its temperature (several dozen °C on average). It decreases during water excavation, separation, transport, storage and preparation for injection. The temperature of treated water is usually the same as the surrounding temperature. During injection into a well, flowing water has contact with zones of increasing temperature. Reaching an absorptive horizon, the water heats up to the deposit temperature. To a certain extent, water temperature can be controlled by the following treatments: limiting the time of the presence of water on a surface, thermal isolation of the installation, a change in injection speed (a decrease in speed results in higher temperature growth before the water reaches an absorptive horizon) or heating the water before injection. However, these methods cannot be technically and economically justified. The exception is a situation in which excavated water (after separation from hydrocarbons) can be injected directly into an absorptive horizon. No sediments or suspensions in the water, low hydrocarbon content, and a lack of contact with oxygen during preparation and injection are required.

The system of injected water/reservoir water/reservoir rock is characterized by a high degree of complexity, taking into account all factors influencing changes in physical–chemical properties and a wide range of interactions between individual components. The available analytical data do not always enable correct assessment of the direction of precipitation/dissolution and determination of their impact on the stability of the system, particularly on the permeability of the near-well zone.

Computer simulations enable assessment of direction of sediment dissolution/precipitation when water is injected into the deposit [19–22].

At present, there are several specialized hydrogeochemical modeling systems available, e.g., TOUGHREACT [22–25], ChemPlugin [26], PHREEQC [27–29], and FEDLOW (piChem module) [30,31], which can be used to solve problems related to the chemistry and reactivity of water, mass and energy transport, secondary mineral precipitation, exploitation of geothermal deposits, etc. [32–36].

PHREEQC software (pH-REdox-EQuilibrium) [37–39] was selected for tests to perform simulations on highly concentrated brines. This program is widely used to study issues related to the flow of brine through porous media and accompanying phenomena [40–43], especially in the processes of deposits flooding (enhanced oil recovery) in oil mining [44–47].

This software package calculates solubility indexes (SIs) which can be used to assess precipitating/dissolving ability [18,45,48]. Moreover, it allows the determination of the effect of temperature change on the solubility of individual minerals, which may be key information for limiting damage to the near-well zone during the process of injecting water into the absorptive horizon.

PHREEQC is software with a wide range of applications. It can be used in simulations of processes and geochemical environments. However, it has several limitations which ought to be taken into account. One of the limitations of water models is a lack of inner cohesion in implemented databases. The pitzer.dat database defines the most consistent water model, but its contents of ingredients are limited. All remaining databases include sets of constant equilibrium logarithms ($\log K_s$) and enthalpies of reactions coming from the literature. There were no systematic attempts to determine which tests were performed in order to determine the assumed individual parameters of the $\log K_s$. In addition, there was no determination of whether the simulation results (obtained by application of a certain model) are compatible with original experimental data. Information included in the files of databases delivered with the software should be treated as preliminary. The precise selection of solutions' contents and thermodynamic data is in the hands of the user.

The presented research results in a decrease in contaminants emitted to the natural environment during oil and natural gas excavation. Improved methods of brine management lead to significant reductions in the use of environmental resources by the oil industry.

This article describes innovative applications of PHREEQC to determine problems associated with near-well zone colmatation. Difficulties are caused by sediments which can appear in the injection of consecutive parts of the water of diversified properties into absorptive horizons. Obtaining the above-mentioned information enables modification of the parameters of the preparation and injection of waters into an absorptive horizon. In addition, it leads to a reduction in the risk of a decrease in rock permeability by sediments. It would result in less frequent application of expensive treatments such as near-well zone decolmatation.

These benefits can encourage industry representatives to perform more advanced planning of deposit water injection. This involves selecting a proper deposit to inject with a certain type of water, performing research on the compatibility of injected waters and increasing the effectiveness of water preparation. This can result in extensions of the time of failureless work of absorptive horizons as well as decreases in the costs of management of excavated waters.

## 2. Materials and Methods

Research material consisted of W-1 and W-2 waters from wells exploiting natural gas from reservoir in Cechsztyn limestone, with highly differentiated properties (Table 1). In the tested waters, the following parameters were determined: reaction, redox potential and sodium content (pH/mV/Ion/°C/F—ION 700 m—measurement error 2%), chemical and biological oxygen demand, total organic carbon, anionic and nonionic surfactants and potassium (Hach Lange DR 3900 photometer—measurement error 4%), density (Anton Paar 35 N—measurement error 5%), content of dissolved and undissolved substances, residue after ignition at 600 °C and content of organic substances (analytical balance WAA 220/C/2—measurement error 3%), anions ($Cl^-$, $Br^-$, $CO_3^{2-}$, $HCO_3^-$, $S_2^-$, $SO_4^{2-}$), calcium and magnesium, carbonates, bicarbonates and chlorides (complexometric, acid-base and argentometric titration—analysis error 4%), sulphates, iron, manganese and selected heavy metals (UV/VIS Lambda 35 spectrophotometer—measurement error 4%).

**Table 1.** Results of physical–chemical analyses of separator water samples W-1 and W-2.

| Analysis | Unit | W-1 | W-2 |
|---|---|---|---|
| pH | | 5.9 | 4.8 |
| Eh | g/cm$^3$ | −108 | −117.8 |
| Density (20 °C) | mV | 0.997 | 1.182 |
| Total dissolved substances | mg/dm$^3$ | 551 | 306,428 |
| Residue of roasted (in 600 °C) | mg/dm$^3$ | 318 | 288,904 |
| Total suspended solids | mg/dm$^3$ | 76 | 159 |
| COD | mg $O_2$/dm$^3$ | 15,023 | 13,589 |
| BOD | mg $O_2$/dm$^3$ | 1875 | 2258 |
| TOC | mg/dm$^3$ | 1004 | 1059 |
| TPH | mg/dm$^3$ | 64 | 284 |
| Organic substances (dichloromethane extract) | mg/dm$^3$ | 91 | 1102 |
| Anionic surfactants | mg/dm$^3$ | 1.23 | 18.9 |
| Nonionic surfactants | mg/dm$^3$ | 247 | 1.73 |
| Chloride $Cl^-$ | mg/dm$^3$ | 129 | 176,615 |
| Sulphates $SO_4^{2-}$ | mg/dm$^3$ | 4.3 | 189 |
| Carbonates $CO_3^{2-}$ | mg/dm$^3$ | – | – |
| Bicarbonates $HCO_3^-$ | mg/dm$^3$ | 215 | 169 |
| Nitrates $NO_3^-$ | mg/dm$^3$ | – | – |

**Table 1.** *Cont.*

| Analysis | Unit | W-1 | W-2 |
|---|---|---|---|
| Ammonium $NH_4^+$ | mg/dm$^3$ | – | – |
| Phosphates $PO_4^{3-}$ | mg/dm$^3$ | – | – |
| Bromides $Br^-$ | mg/dm$^3$ | 4.12 | 249.3 |
| Sodium $Na^+$ | mg/dm$^3$ | 61.9 | 68,841 |
| Potassium $K^+$ | mg/dm$^3$ | 28.6 | 588 |
| Calcium $Ca^{2+}$ | mg/dm$^3$ | 18.6 | 35,258 |
| Magnesium $Mg^{2+}$ | mg/dm$^3$ | 12.7 | 4974 |
| Ferrous ion $Fe^{2+}$ | mg/dm$^3$ | 2.10 | 6.50 |
| Ferric ion $Fe^{3+}$ | mg/dm$^3$ | 16.00 | 56.40 |
| Manganese $Mn^{2+}$ | mg/dm$^3$ | 3.91 | 7.05 |
| Copper Cu | mg/dm$^3$ | 0.021 | 0.009 |
| Lead Pb | mg/dm$^3$ | 0.068 | 0.035 |
| Zinc Zn | mg/dm$^3$ | 0.651 | 0.358 |
| Tin Sn | mg/dm$^3$ | 0.023 | 0.51 |
| Nickel Ni | mg/dm$^3$ | 0.067 | 0.129 |
| Cobalt Co | mg/dm$^3$ | 0.009 | 0.028 |
| Cadmium Cd | mg/dm$^3$ | 0.003 | 0.048 |
| Strontium Sr | mg/dm$^3$ | 0.061 | 3012 |
| Barium Ba | mg/dm$^3$ | 0.038 | 81.0 |
| Silicon Si | mg/dm$^3$ | 3.18 | 4.26 |
| Aluminum Al | mg/dm$^3$ | 0.061 | 0.056 |

W-1 water was characterized by low mineralization at a level of 551 mg/dm$^3$ and suspension content of 76 mg/dm$^3$, while W-2 water sample was highly mineralized (306,428 mg/dm$^3$) and suspension content was 159 mg/dm$^3$.

Chemical analyses were supplemented by mineralogical analysis of core material samples from the injection well (Figure 2). The quantitative analysis of the mineral composition of the core samples was performed using the X-ray diffraction method (XRD) at the Department of Drilling Geophysics, Oil and Gas Institute—National Research Institute [49].

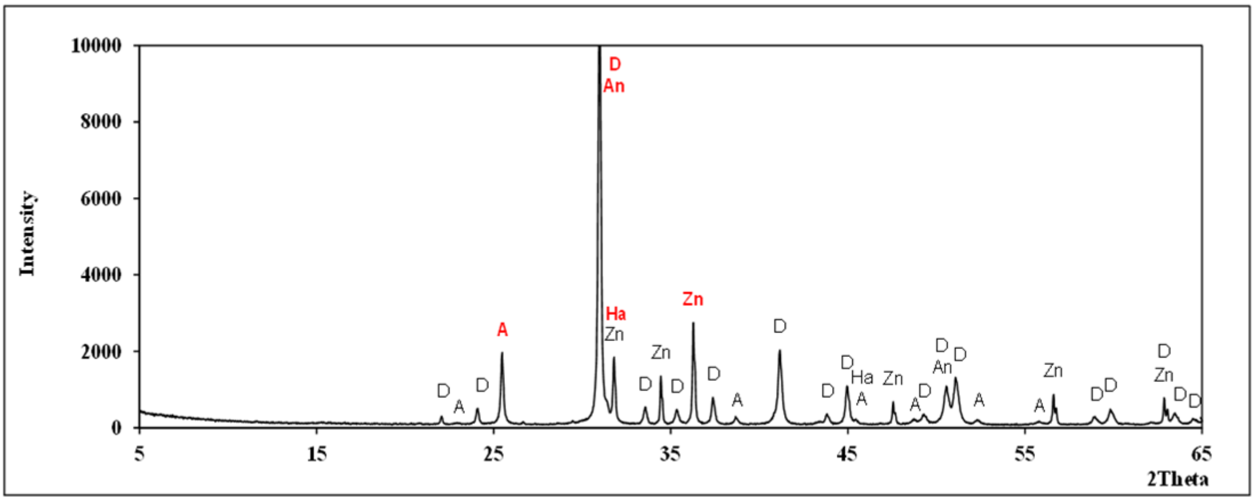


**Figure 2.** Results of mineral composition analysis of core material from injection well (D—dolomite, A—anhydrite, An—ankerite, Ha—halite, Zn—zincite—reference material).

Mineralogical analysis showed that the main component of reservoir rocks is dolomite (74.6%), whereas the other components are anhydrite (13.1%) and ankerite (11.3%), calcium and iron carbonate with the formula $CaFe(CO_3)_2$ and a slight addition of halite (1.0%).

The solubility index (SI) is an indicator suggesting the possible direction of reaction of dissolution/precipitation of minerals during mixing of water or in contact between water and a deposit rock. PHREEQC software was used to calculate the SI when considering injection of separator waters into the absorptive horizon.

The values of the solubility index calculated for individual components (minerals or chemical compounds) indicate whether it is possible to dissolve a specified component in water of a given composition (negative SI values), or whether their precipitation from the solution should be expected (positive SI values).

The assumption of a value close to "zero" by the calculated solubility index suggests the existence of an equilibrium state in which even small changes in water parameters (e.g., change in temperature, reaction or the content of one of the components) may cause a shift towards dissolution or precipitation of a defined substance.

There are three databases that can be used to calculate the solubility indexes: phreeqc.dat [50], pitzer.dat [51,52] and wateq4f.dat [53]. Reports in the literature show that the pitzer.dat database should be used to simulate highly concentrated brines, which is based on the calculation of ionic strength of the solution (Pitzer theory) [54] and not concentrations of components. This database, unfortunately, has a small number of components (about 40) for which it is possible to perform calculations. The other two databases should be used for calculations in solutions in the Debye–Hückel region. The phreeqc.dat database has 60 components, while the waeq4f.dat includes over 160 items.

In the vast majority of cases, the extracted formation water is prepared for injection in batches, the volume of which depends on the size of the storage tank in which it is collected. The entire process of separating water from hydrocarbons and its storage reduces temperature to ambient temperature. On the other hand, during the injection, water temperature rises to reservoir temperature. This can cause significant changes in solubility of individual minerals and affect permeability of the near-well zone.

The results of laboratory analyses of W-1 and W-2 water samples' composition were used to calculate solubility indexes for individual minerals (PHREEQC). In order to capture influence of temperature on solubility of individual components (minerals and chemical compounds), SI calculations were performed for two temperatures: 20 °C, assumed as the temperature of water prepared for injection, and 94 °C, the reservoir temperature of the injection well.

Taking into account the distinct influence of water temperature changes on the direction of the dissolution/precipitation, simulations of changes in solubility of minerals (forming reservoir rock) during contact with the injected water as a function of temperature were also carried out. The simulations assumed the contact of 1 kg of deposit rock with 1 kg of injected water. Due to the lack of ankerite (and other minerals with similar composition) in the databases of the PHREEQC software, this core component was not included in the calculations.

## 3. Results and Discussion

The results of the analyses show that the mere removal of sediments and suspensions from the water phase is not enough to pump the water safely into the absorptive horizon [55]. Water samples W-1 and W-2 were filtered through a filter to remove sediment and left in contact with the air for 48 h. After this time, the water was filtered again, obtaining sediments with masses of 14.35 mg/dm$^3$ (W-1) and 55.40 mg/dm$^3$ (W-2), respectively (Figure 3).

In the tested water samples, iron ions were present. These ions are relatively easily oxidized with oxygen from the air, which resulted in gradual precipitation of sediments in the filtered water. An increase in the Eh of the water can occur not only through contact with the air, but also through degassing the water from hydrocarbons (methane) dissolved in it under high pressure, as well as by mixing with water with oxidizing properties. This proves that in the case of increases in the electrochemical potential of the water, clogging of the near-well zone may occur due to sediment formation during the water's injection, and even after injection into the reservoir.

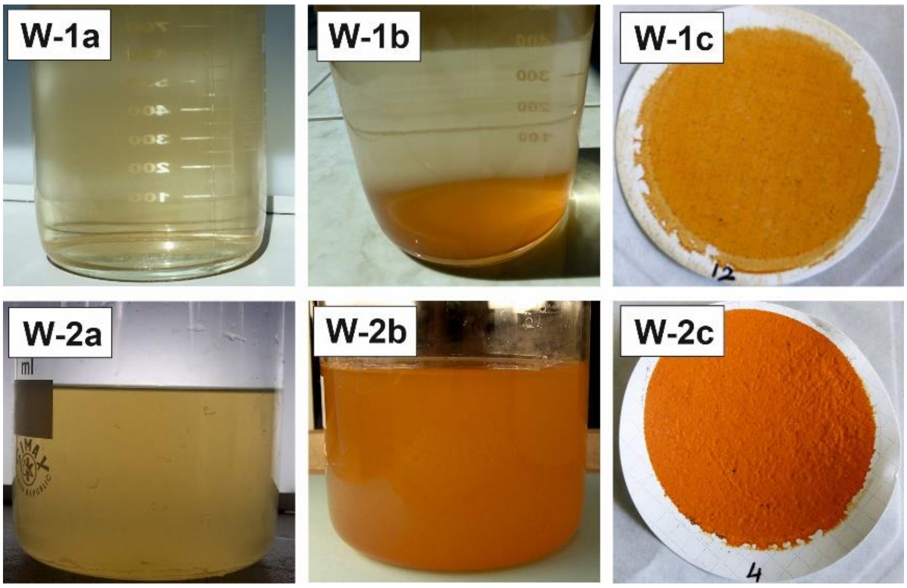


**Figure 3.** Effect of water aeration (water samples W-1 and W-2: a—raw water without air contact, b—after aeration, c—filter cake).

Therefore, using analytical data from the W-1 and W-2 samples' water composition, calculations of solubility indexes were carried out using PHREEQC in order to determine the possibility of precipitation of sediments from the water during injection into the absorptive horizon. This program is widely used to simulate the course of reactions and processes occurring in a porous medium such as a hydrocarbon deposit (Table 2).

**Table 2.** Major findings from the literature (last 2 years) concerning phenomena accompanying the injection of water.

| No. | Main Issues | Reference |
|---|---|---|
| 1 | Interactions between brine and rock minerals in static and dynamic system. | [40] |
| 2 | Study of hydrochemical simulations of a dual-layer geothermal reservoir to the long-term impact of barite scale formation on well injectivity. | [41] |
| 3 | Description of mechanistic model constructed for low-salinity water injection to consider geochemical reaction issues in low-salinity flooding among surface sites and aqueous solution. | [18] |
| 4 | Integrated open-source simulator to model hydrogeochemical processes at various scales of interest including pore-scale and reservoir-scale. | [42] |
| 5 | Modeling (with PHREEQC software) of mineral precipitation and deposition in the porous media controlled by deep bed filtration model. | [44] |
| 6 | Study of fine particle migration in the rock causing formation damage and permeability impairment. | [43] |
| 7 | Investigation of the carbonate/brine interactions, using geochemical modeling, during low-salinity water injection for enhanced oil recovery (EOR). | [45] |
| 8 | Modeling of different geochemical effects such as multivalent cation exchange and mineral dissolution during flow and transport in low-salinity waterflooding. | [46] |
| 9 | Comparison of thermodynamic data files from PHREEQC software package and influence of TDF choice on modeling results. | [47] |
| 10 | Studies of influence of anhydrite on wettability of calcite rock during low-salinity water flooding. | [56] |

### 3.1. Temperature Impact on Water Injection Process

Temperature change is a very important parameter that influences the processes of dissolution/precipitation of minerals accompanying injection of water into the reservoir. Calculations of the solubility indexes (SIs) were performed for two temperatures, 20 °C and 94 °C, with the use of all three databases, in order to maximize the obtained information on the behavior of minerals and chemical compounds. The calculation results for the water intended for injection are shown in the figures below (Figures 4–6).

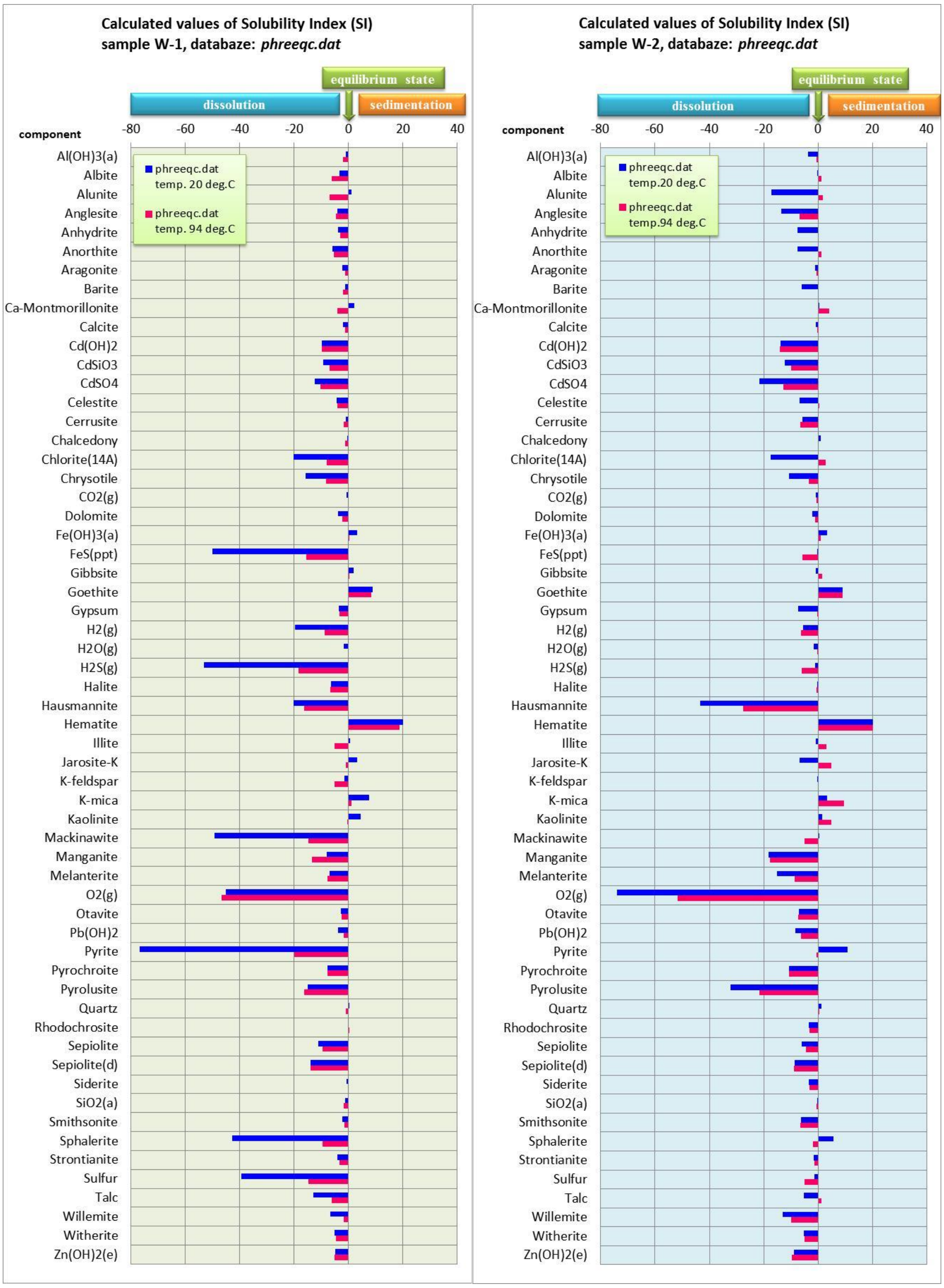


**Figure 4.** Comparison of SI calculated for W-1 and W-2 water samples using phreeqc.dat database at 20 °C (ambient) and 94 °C (deposit) temperatures.

Considering the values of the solubility index (SI) calculated with the application of the phreeqc.dat database (calculations by ionic strength of solutions, taking into account high salt concentrations), it can be seen that the dissolution/precipitation potentials of individual minerals are very different (Figure 4). For most substances, the equilibrium in the tested water solutions is shifted in the direction of dissolution. In the direction of precipitation, the balance is shifted mainly for iron-containing minerals (goethite, hematite or pyrite) and for aluminosilicates (montmorillonite, mica or kaolinite). In the case of manganese, which is usually indicated with iron, as a product easily precipitating from the solution in the form of oxide and hydroxide deposits, the calculations showed high negative SI values. This indicates an equilibrium shifted strongly towards dissolution of manganese-containing compounds and no risk of precipitation.

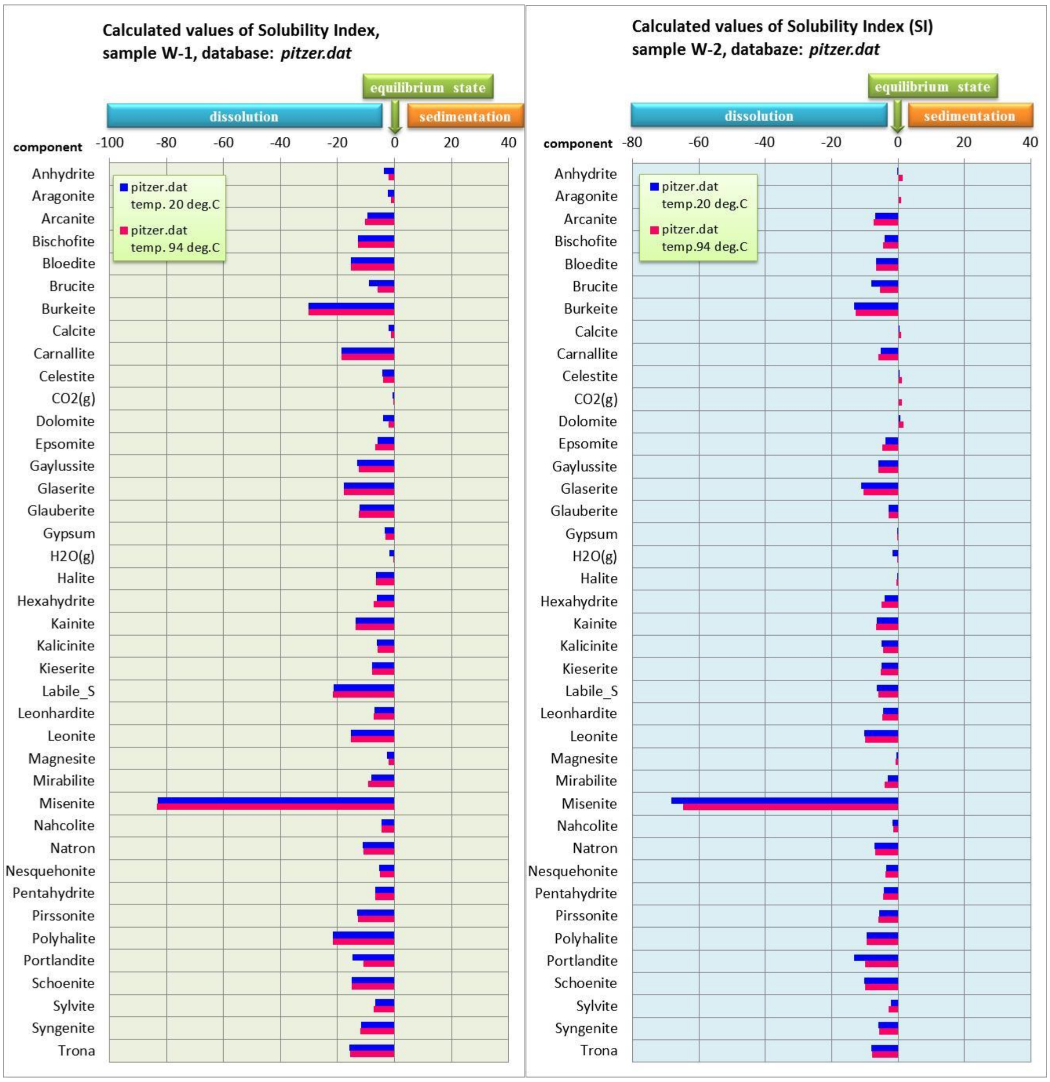
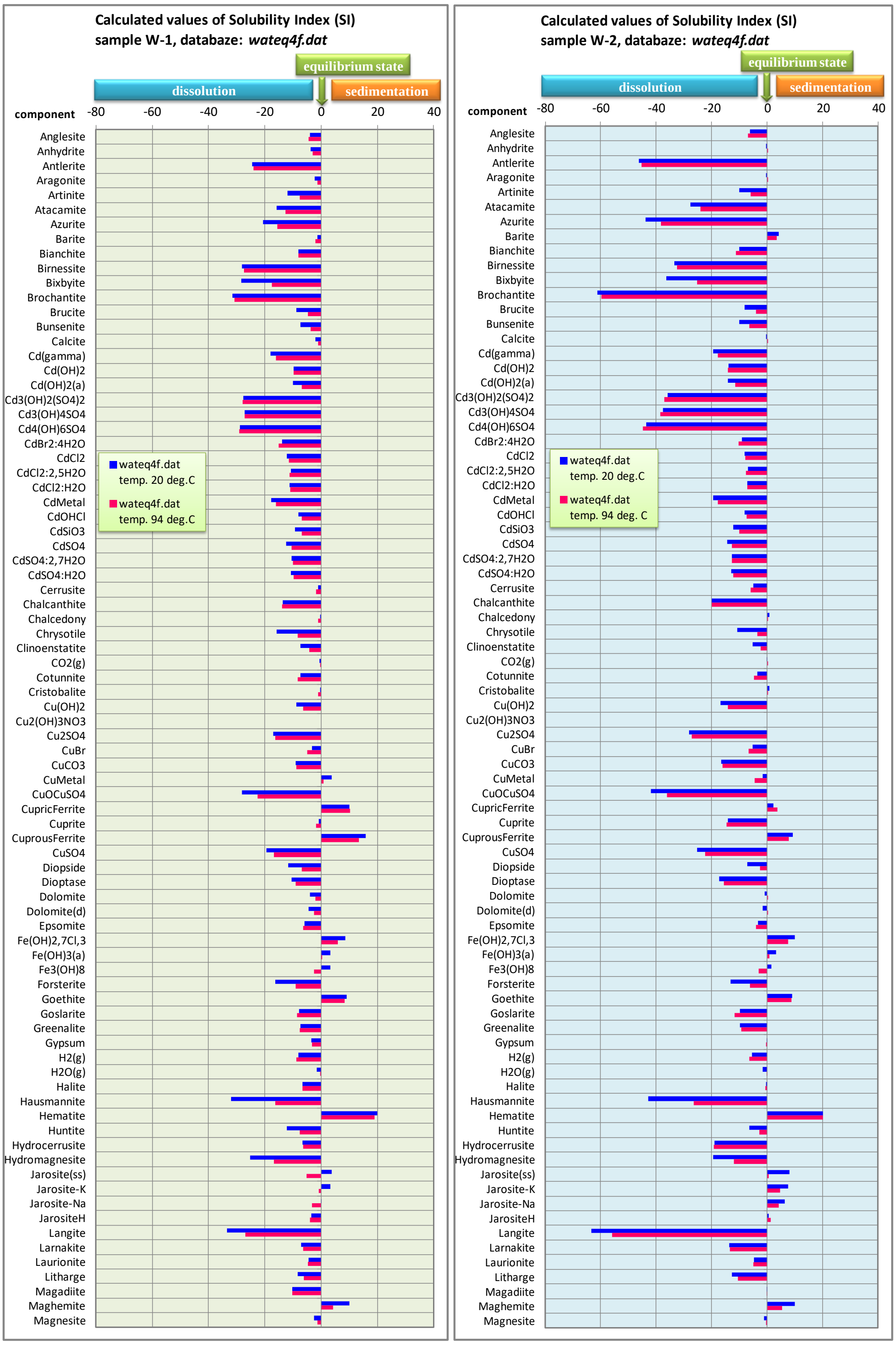


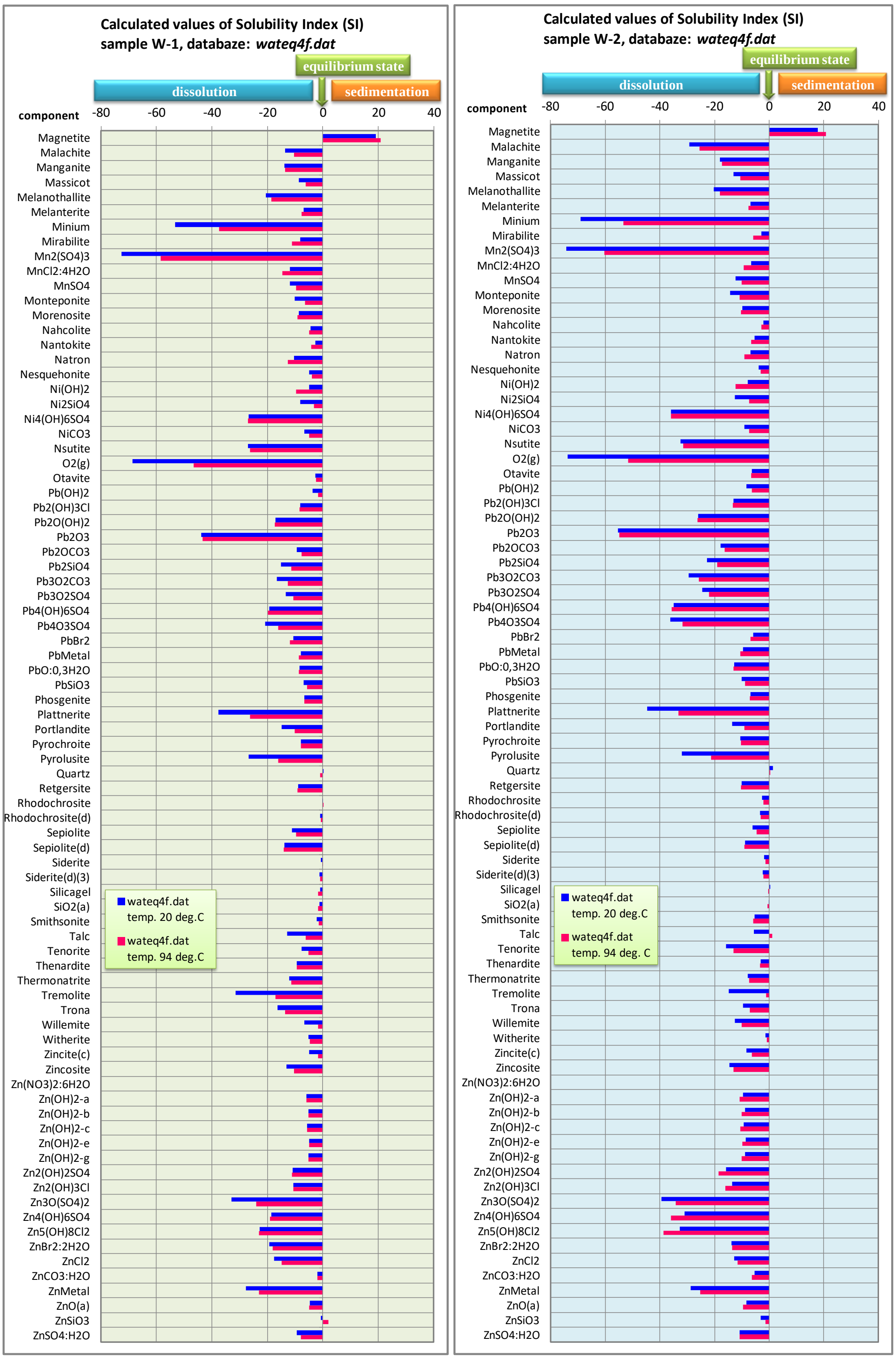
**Figure 5.** Comparison of SI calculated for W-1 and W-2 water samples using pitzer.dat database at 20 °C (ambient) and 94 °C (deposit) temperatures.

On the other hand, when considering the impact of temperature change on the ability of the injected water to dissolve individual minerals, significant differences should be noted, both in the size and the direction of changes in the calculated solubility indexes. In individual waters, the values of the SI calculated for the same minerals/chemical compounds may not only change their value, but also assume different directions of changes. For example, in the case of FeS, a significant decrease in solubility (IS from −76.75 to −19.98) was noted for the W-1 sample, while for the W-2 sample there was an increase in solubility (IS from +10.86 to −0.66). The increase in temperature may also change the direction of the dissolution/precipitation. In the case of alunite for the W-1 water, a change in the index indication from a slight tendency to precipitation to a fairly strong tendency to dissolve was observed, while for the W-2 stream, a change in the SI value from clearly negative (−17.12), i.e., from dissolving at 20 °C to precipitate alunite (SI = +1.68) at 94 °C was observed. Such dependencies are practically impossible to capture without computer simulations, and may in some cases have a decisive impact on the course and efficiency of water injection.



(**a**)

**Figure 6.** *Cont.*



(**b**)

**Figure 6.** (**a**) Comparison of SI calculated for W-1 and W-2 water samples using wateq4f.dat database at 20 °C (ambient) and 94 °C (deposit) temperatures. (**b**) Comparison of SI calculated for W-1 and W-2 water samples using wateq4f.dat database at 20 °C (ambient) and 94 °C (deposit) temperatures.

Similar calculations for the tested water samples intended for injection into the deposit were made with the use of pitzer.dat (Figure 5).

There is a relatively small number of components in this database and due to the lack of iron-containing minerals, its application in modeling the processes is significantly limited. Considering the obtained results, it should be stated that for both W-1 water with low mineralization and W-2 with high mineralization, almost all components included in the calculations are in a state of unsaturation in the solution and their equilibrium is shifted towards dissolution. Usually, large differences in mineralization and the content of individual dissolved substances in water do not cause a greater variation in the calculated mineral solubility indexes. Only in the case of a few substances (anhydrite, aragonite, calcite, celestite, dolomite and carbon dioxide) was there a slight shift of the equilibrium towards precipitation (or gas phase separation for $CO_2$).

A significant change in temperature from 20 °C to 94 °C in the performed simulations usually did not cause significant changes in the values of the solubility indexes. In the case of the W-2 water sample only, for the components showing a slight tendency to precipitate at 20 °C, a slight increase in the SI value (enhancement of the tendency to precipitate) was noted for the temperature of 94 °C.

Considering the results from the wateq4f.dat database, it was noted that water–mineral balance, for both W-1 (low-mineralization) and W-2 (high-mineralization) water, is usually shifted towards dissolving the minerals. The calculated solubility indexes indicated that precipitation of iron-containing minerals (hematite, goethite, magnetite and other iron compounds) should be expected for both analyzed samples of water, as well as, to a small extent, barite and quartz for W-2 high-mineralized water (Figure 6a,b).

An increase in water temperature from 20 °C to 94 °C, for most of the substances in the dissolution area, indicated a decrease in solubility. For only some compounds was there a slight increase in solubility, while for substances in the area of precipitation, the calculated SI values showed a decrease in the tendency to precipitate.

In the cases of only two iron-containing components, $Fe_3(OH)_8$ for both tested waters and jarosite for W-1 water, a change in the course of the reaction was found from precipitation at a temperature of 20 °C to dissolution at a temperature of 94 °C.

Attention should also be paid to a strong tendency to dissolve (absorb) oxygen in the tested waters, indicated in the phreeqc.dat and wateq4f.dat databases. In the case of contact with the air, the water is oxygenated quickly, which results in the precipitation of iron oxides and hydroxides.

The algorithm used in the wateq4f.dat database does not enable taking into account the influence of higher ion concentrations on the calculated solubility indexes. Nevertheless, the presence of a much larger number of chemical compounds in this database may lead to obtaining useful information. The calculation results from wateq4f.dat are generally more similar to the pitzer.dat database (despite the existing differences in the calculated SI values) than phreeqc.dat; however, due to the small number of common minerals found in all databases, it is difficult to determine existing similarities and differences.

### 3.2. Temperature Influence on Solubility of Rock Matrix Materials in Injected Water

Considering the influence of temperature changes on the solubility of minerals that build the reservoir rock of the absorbent horizon in contact with the W-1 water (Figure 7), it should be noted that both anhydrite and dolomite obtain maximum solubility at low temperatures (20 °C) at levels of 4.66 g/kg and 0.45 g/kg of water, respectively. The amount of halite dissolved from the deposit rock for this system is constant at 9.93 g/kg of water, regardless of temperature.

With the temperature increase, dolomite solubility decreased to the level of 0.23 g/kg (48.89%) of water for temperature of 94 °C. On the other hand, for anhydrite up to a temperature of about 30 °C, a slight decrease in solubility was noted, and at higher temperatures, there was an increase in the slope of the curve and a greater decrease in the solubility of the mineral to the level of 1.77 g/kg of water (reduction by 62.02% by weight).

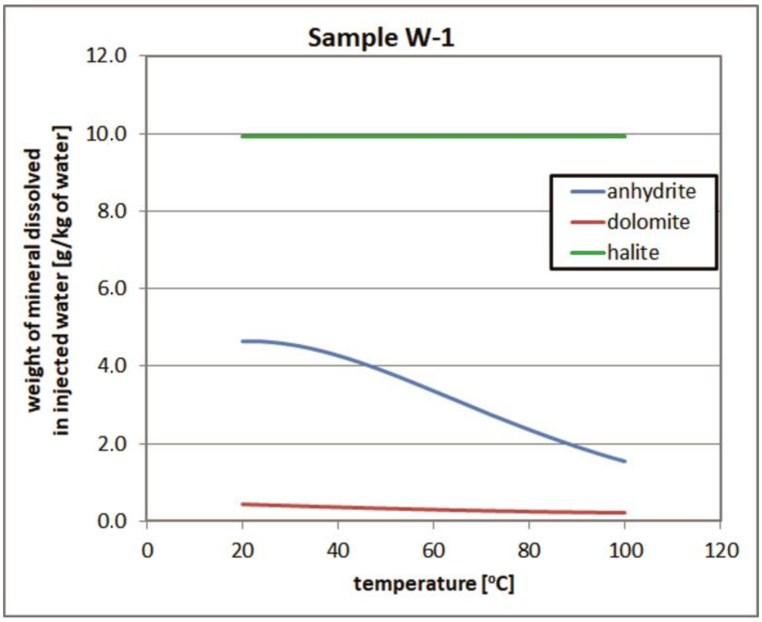


**Figure 7.** Changes in solubility of rock matrix minerals in W-1 injected water as function of temperature.

Assuming that chemical equilibrium is established, i.e., reaching the mineral saturation point for a given temperature, heating the injected water results in lower solubility for anhydrite and dolomite and a gradual precipitation of these minerals. For a continuous flow of water processes, this involves the leaching of minerals near the injection point and their precipitation at an increasing distance as a phenomenon of heating of the injected water.

On one hand, this seems to be beneficial, because the water washes away the minerals which build the reservoir rock and reduces the effects of clogging of the near-well zone by sediments injected with the water. On the other hand, in a longer period of time and assuming cyclical injection of water into the deposit, one can expect the rock pores to overgrow at a certain distance from the borehole zone by precipitating anhydrite and dolomite deposits, which may result in a reduction of permeability.

A simulation carried out for the W-2 sample shows a relatively low solubility of minerals forming the deposit rock in the injected water with a high content of dissolved salts (Figure 8).

As in the case of the W-1 water sample presented above, for the W-2 sample, the solubility of dolomite slightly decreases from 0.18 g/kg of water at 20 °C to 0.13 g/kg at 94 °C. In the case of anhydrite, a slightly higher solubility of the mineral at low temperatures was observed (maximum solubility at 28 °C is 0.491 g/kg of water), which decreases to 0.15 g/kg of water when heating the water to the deposit temperature (this is similar to the level calculated for dolomite). At temperatures above 94 °C, the solubility of anhydrite continues to decrease, reaching values below dolomite solubility.

Simulations of the contact of tested waters (intended for injection) with the deposit rock indicate different responses of the systems. For both water samples injected into the deposit, contact with the deposit rock dissolves the minerals that build the rock matrix, halite in particular. In the case of water sample W-2 with high mineralization, the mass of minerals that can be dissolved is much lower than in the case of water with low mineralization. All tested minerals are found throughout the temperature range in the dissolution area. However, it should be noted that the solubility of minerals decreases significantly with increasing temperature. For W-2 water, the calculated maximum dolomite solubility decreased 2.5 times, whereas for anhydrite it decreased 9.5 times. If the reservoir water is saturated with a given mineral at a low temperature, its increase may result in sedimentation and blocking of rock pores. In the case of halite, its solubility increases all the time with increasing temperature.

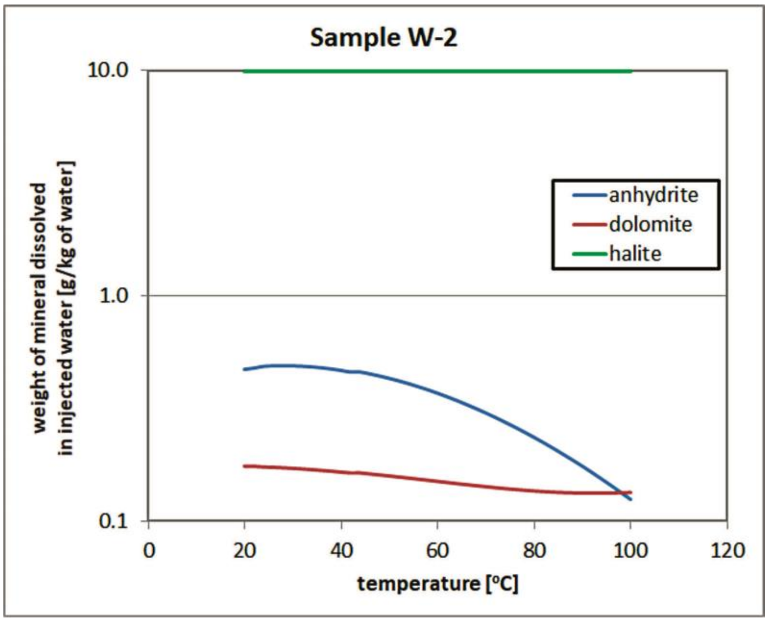


**Figure 8.** Changes in solubility of rock matrix minerals in W-2 injected water as function of temperature.

Obtaining information on possible undesirable processes taking place in deposit water injection into a certain horizon could lead to a decision about water injection into a different reservoir or have an impact on more advanced preparations of water for injection by the elimination of untypical contents. The elimination of problems related to decreases in near-well zone permeability by developed sediments will result in avoidance or reduction in frequency of expensive and not always effective treatments of rinsing and/or acidification of a well. As a result, there will be a significant decrease in the costs of deposit water management.

One of the important issues related to the production of hydrocarbons is the carbon footprint, which shows the impact of this human activity on the environment. At present, there is no unitary methodology which could determine a carbon trace and the entire life cycle of a product for the energetics sector, including for hydrocarbon extraction. Several main phases can be observed in the life cycle of natural gas and oil. These are searching for deposits, extraction, processing (treatment/purification), transport, storage, distribution and usage [57–61].

The management of extracted waters through their injection into a deposit enables a decrease in carbon traces. It is an effect of the reduction of the number of pollutants (including hydrocarbons) emitted to the active biosphere. Moreover, low usage of materials and energy in water injection (in comparison to complete purification of brine and waste management) should be taken into consideration. The proper preparation of water for injection leads to a reduction in carbon traces according to the long-term failure-free work of a borehole. This process results in a decrease in the frequency of decolmatation of a near-well zone, which means there is usage of a significant amount of equipment as well as chemicals in order to prepare treatment liquids, and the necessity of after-treatment liquid management.

The research, owing to the possibility of a reduction in the costs of brine management as well as its possible usage in order to increase a level of deposit exploitation (flooding), could result in mitigation of the energy crisis.

## 4. Conclusions

Considering the obtained values of the solubility indexes (SI) calculated with the application of databases available in PHREEQC software, it can be seen that the dissolution/precipitation potential of individual minerals is different. For most substances, the equilibrium in the injected water solutions is shifted in the direction of dissolution. In the direction of precipitation, the balance is shifted mainly for iron-containing minerals (goethite, hematite and pyrite) and for aluminosilicates (montmorillonite, mica and kaolinite). On the other hand, manganese, usually considered together with iron as a product easily precipitating from the solution in the form of oxide and hydroxide deposits, shows equilibrium shifted strongly towards the dissolution of minerals (high negative SI values).

The increase in temperature to the temperature of the deposit causes different reactions in individual minerals and chemical compounds. Depending on the chemical composition and physical–chemical parameters of a water sample, changes in the solubility of a specific mineral may take different directions and take various values, including a transition between the areas of precipitation and dissolution.

When interpreting the results of simulations, particular attention should be paid to individual components in the sensitive zone close to the equilibrium state (SI = 0). In this area, even slight changes in the properties of the water can change the solubility and formation of sediments that can damage the permeability of the reservoir rocks.

The conducted simulations of the contact of water with the deposit rock indicate the different activities of individual systems. For the tested waters, contact with the deposit rock dissolves the minerals which build the rock matrix, especially halite. However, it should be noted that the solubility of dolomite and anhydrite decreases significantly with increasing temperature. If the reservoir water is saturated with a given mineral at a low temperature, its heating may result in sediment precipitation. In the case of halite, solubility increases all the time with increasing temperature.

The saturation of water with halite may also result in changes in the solubility of anhydrite and dolomite. A decrease in the amount of dissolving minerals is clearly visible along with an increase in the overall mineralization of the water. For brine with a high content of chlorides (W-2), the maximum solubility of dolomite decreased by 2.5 times, and the solubility of anhydrite decreased by 9.5 times compared with water with low mineralization (W-1). The changes in solubility observed in the simulations proceed in various directions, strongly dependent on the composition and physical and chemical parameters of water, and are difficult to predict without performing calculations.

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