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Published in: Geothermics

Link to article, DOI: 10.1016/j.geothermics.2021.102179

Publication date: 2021

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Injection of Ca-depleted formation water in the Lower Triassic Bunter Sandstone Formation for seasonal heat storage in geothermal sandstone reservoirs: Effects on reservoir quality

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ARTICLE INFO

Keywords:
High temperature aquifer thermal energy storage
Deep aquifer thermal energy storage
Reactive transport modelling
Flooding experiments
Bunter Sandstone Formation
Dolomitisation

ABSTRACT

Optimisation of the use of commonly available energy sources through seasonal storage of excess heat in hot deep aquifers is considered. The chemical effects of heating the Bunter Sandstone Formation to up to 150 °C are investigated by laboratory core flooding experiments at reservoir conditions, petrographic analysis and geochemical modelling. Experiments are performed with a Ca-depleted synthetic formation water in order to avoid loss of injectivity by calcium carbonate scaling at elevated temperatures. The synthetic formation water is injected into a Bunter Sandstone Formation sample at 25 °C, 75 °C (reservoir temperature), 100 °C and 150 °C with a velocity of 0.05 PV/h. Results show a significant increase in the aqueous concentration of calcium, silicon and barium upon heating, while the concentration of magnesium decreases. The main chemical processes taking place upon heating of the reservoir to up to 150 °C is dolomitisation, the replacement of plagioclase with albite, the dissolution of quartz and barite and the precipitation of mica. A significant portion of the cementing calcite dissolved during the experiment, and consequently the tested Bunter Sandstone sample disintegrated after the experiment, indicating that injection of heated calcium depleted Bunter brine into the Bunter Sandstone Formation may damage the reservoir. The results highlight the importance of investigating the effects that removal of selected ions may have on the reservoir properties, since the injection of modified formation water may cause new problems in the reservoir.

1. Introduction

Typically, a temporal incongruity exists between the supply and the demand for heat. Excess heat is for example produced from waste incineration during the summer, while the demand for energy peaks in the winter. This mismatch between the supply and the demand for heat may be managed by seasonal storage of the surplus heat in the subsurface. Thus, in seasonal heat storage, formation water is extracted from the aquifer during the summer and heated using the available surplus energy prior to reinjection into the reservoir. In the winter, the heated formation water stored in the reservoir is extracted and used for e.g., district heating.

In Denmark, seasonal storage of excess heat in deep sandstone aquifers with temperatures up to 75 °C is considered, as some of these aquifers are already being used for geothermal energy for district heating. The advantage of storing heat in these deep hot aquifers is that the relatively high in situ temperature may minimise the heat loss during the storage. Also, the utilisation of geothermal energy may benefit from the heat storage, as the injection of heated formation water may increase the heat potential in the aquifers and possibly prolong the lifetime of the geothermal aquifer (Kabus et al., 2005; Reveillére et al., 2013).

The increase in the reservoir temperature caused by the heat storage will disturb the initial thermodynamic equilibria in the reservoir and will potentially trigger geochemical reactions that may affect the reservoir properties. Both the extent and rate of chemical reactions between the reservoir minerals and the formation water is affected by changes in the temperature. In general, chemical reaction rates increase with increasing temperatures, and mineral solubility generally increases, but may decrease when a gas phase is involved in the equilibria. As is the case for carbonates (Dove and Crerar, 1990; Brons et al., 1991; Griffioen and Appelo, 1993; Hoyer et al., 1994; Appelo and Postma, 2005; Gruber et al., 2016), the effects of heating become more

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https://doi.org/10.1016/j.geothermics.2021.102179
Received 12 June 2020; Received in revised form 16 June 2021; Accepted 20 June 2021
Available online 22 July 2021
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pronounced at higher temperature differences due to the exponential dependence of reaction rates on temperature (Palandri and Kharaka, 2004; Appelo and Postma, 2005). A major concern regarding heat storage in the hot deep aquifers is that the heat may permanently damage the aquifer making the extraction of further geothermal energy unfeasible. For example, the dissolution of the cementing material in the aquifer may reduce the mechanical strength of the aquifer and the heat or the associated dissolution/precipitation processes in the aquifer may affect the permeability of the aquifer by changing the pore connectivity and the pore space geometry (Moore et al., 1983; Tenthorey et al., 1998; Schembre and Kovscek, 2005).

In many countries, aquifer thermal energy storage systems are already operating successfully in shallow aquifers by injecting water with a temperature of up to approximately 20 °C and small temperature differences (ΔT < 15 °C) (Reveillere et al., 2013; Bonne et al., 2014; Possemiers et al., 2014). Experiences with higher operational temperatures of up to 150 °C are less frequently reported (Perlinger et al., 1987; Griffioen and Appelo, 1993; Hoyer et al., 1994; Vetter et al., 2012). Laboratory (Azaroual and Fouillac, 1997; Schembre and Kovscek, 2005; Fu et al., 2009; Gong et al., 2013; Holmlykke et al., 2017) and field (Perlinger et al., 1987; Hoyer et al., 1994) tests reveal that at elevated temperatures, the release of silicium increases sharply due to the dissolution of quartz and feldspars, while the precipitation of several secondary minerals, including kaolinite, boehmite, gibbsite, and smectite has been observed. The precipitation of calcium carbonate due to heating of the ambient ground water is, however, found to be the most critical water chemistry problem in field tests of heat storage at temperatures up to 150 °C in a confined shallow sandstone aquifer (Perlinger et al., 1987; Hoyer et al., 1994). Thus, for a successful operation of the heat storage, the calcium concentration was reduced to prevent scaling in the heat exchanger and storage well. Alternatively, addition of CO₂ has recently been proposed as a means of preventing calcite precipitation (Wasch et al., 2019). This could, however, induce other problems such as corrosion in the geothermal installations.

Though many potential chemical reactions caused by the injection of heated formation water into the reservoir may be anticipated from the existing knowledge, laboratory tests are crucial to determine the actual reactions expected to take place at each potential heat storage site as well as the rate, extent and coupling of these reactions. In this study, the potential for the storage of excess heat in the Lower Triassic Bunter Sandstone Formation in the Southern North Sea Basin is investigated because this formation is considered one of the most promising potential geothermal aquifers in Denmark (Nielsen et al., 2012). The formation water is calcium carbonate saturated and heating of the formation water for heat storage purposes would most likely require the removal of calcium from the water in order to avoid scaling problems due to calcium carbonate precipitation. Therefore, core flooding experiments, petrographic analysis and geochemical modelling are conducted to identify the potential geochemical reactions most likely to take place when heated (up to 150 °C) calcium depleted synthetic formation water is injected into a Bunter Sandstone Formation sample from the Tender area, Denmark.

2. Materials and methods

2.1. Geological description

The Bunter Sandstone Formation is present in the southern part of the Danish area (Fig. 1) at burial depths of 1.1–2.1 km onshore (Nielsen and Japsen, 1991). In the Tender area the Bunter Sandstone Formation has a reservoir temperature of approximately 75 °C. The Bunter Sandstone Formation was deposited during the Early Triassic where regional subsidence prevailed in the Central European Basin. The formation is enveloped by mudstones of the Lower Triassic Bunter Shale Formation below and evaporites of the Middle Triassic Röt Formation above (Michelsen and Clausen, 2002). Towards north the formation develops to the Skagerrak Formation (Weibel et al., 2017).

Onshore Denmark, the thickness of the Bunter Sandstone Formation is up to 300 m (Michelsen and Clausen, 2002), and where fully

Fig. 1. Map of Denmark showing the extent of the Bunter Sandstone Formation in red colour (to the left) and the stratigraphic scheme (to the right). The gradual change from red to yellow indicates how the Bunter Sandstone Formation gradually develops to the Skagerrak Formation in the northern part of Denmark. Modified from Weibel et al. (2017).
developed, the formation consists of four regional sandstone units. In the Tønder area, two major sandstone intervals are informally referred to as the lower and the upper Bunter sand, which have thicknesses of up to 35 and 30 m, respectively. The lower Bunter sand is dominated by aeolian sand supplied from the south during arid climatic conditions, whereas the upper Bunter sand is dominated by ephemeral river deposits supplied from the north during semi-arid climatic conditions (Olivarius et al., 2015). The sandstone units of the Bunter Sandstone Formation are separated by thick mudstone units formed in playa-lake environments (Clemmensen, 1979, 1985).

Weibel and Frits (2004) found that the sandstones of the Bunter Sandstone Formation are mainly arkoses and subarkoses. They found that the feldspars comprise K-feldspar and minor Na-rich plagioclase, and that the most common authigenic phases include carbonate cement (calcite and dolomite), anhydrite cement and clay minerals (illite, chlorite, mixed-layer illite/smectite and mixed-layer smectite/chlorite), while the presence of iron-oxide coatings gives the sandstone a red colour. Chemical analysis and petrographic studies of cores from the Bunter Sandstone Formation in the Tønder area have revealed the presence of a cementing halite, mainly in the middle and the lower part of the sandstone layers of the upper Bunter sand unit (Laier and Nielsen, 1989).

2.2. Sample description and fluid composition

A cylindrical specimen was prepared from a cored interval of the Lower Triassic Bunter Sandstone Formation in the Tønder-3 well (Fig. 1). The specimen represents the upper part of the upper Bunter sand unit at a depth of 1654.69 m below surface. Special care was taken to avoid sampling from the part of the upper Bunter sand unit containing a cementing halite (Laier and Nielsen, 1989). The length and diameter of the sample was 74.7 mm and 37.3 mm, respectively. The porosity, gas permeability and Klinkenberg permeability were measured to be 28.17%, 251 mD and 234 mD, respectively.

Backscatter electron microscopy of two polished samples from the same depth (1654.77 m) and well (Tønder-3) as the tested specimen were carried out to identify the mineralogy of the Bunter Sandstone Formation at the tested depth. Results show that the core specimen primarily consists of quartz (34%), secondarily of feldspar (25%) (albite, alkali-feldspar, pure K-feldspar and plagioclase), calcite (5%), biotite (4%) and heavy minerals (Quantification based on QEMSCAN®).

The chemical composition of the Bunter brine is modified from Laier (2008) and is shown in Table 1. Initial equilibrium calculations with PHREEQC (Parkhurst and Appelo, 2013) show that the Bunter brine was supersaturated with halite at room temperature. Consequently, the salt concentration was reduced 15% to dissolve the NaCl at room temperature, reducing the salinity from 27 wt% to 23 wt%. The silicium and aluminium concentrations were not determined by Laier (2008). The high concentration (4500 mg/L) of aqueous calcium measured in the formation water necessitate a softening of the formation water to prevent scaling problems due to calcium carbonate precipitation. To simulate a situation with softening of the water, the calcium concentration determined in the formation water was replaced by potassium in a 1:1 wt ratio. Such a low calcium concentration may not be realistic but represents a worst case scenario to maximise dissolution.

### Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (mole/L)</th>
<th>Ca-depleted brine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>5.00</td>
<td>4.35</td>
</tr>
<tr>
<td>K</td>
<td>0.04</td>
<td>0.26</td>
</tr>
<tr>
<td>Ca</td>
<td>0.11</td>
<td>0</td>
</tr>
<tr>
<td>Mg</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>Cl</td>
<td>5.62</td>
<td>4.75</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>0.002</td>
<td>0.0002</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

### 2.3. Experimental procedure

A core flooding experiment was performed with the cored specimen from the Bunter Sandstone Formation at reservoir pressure and temperatures up to 150 °C and a flow velocity of 0.05 pore volumes per hour (PV/h). Calcium depleted synthetic brine (Table 1) was used as the flooding fluid. Prior to testing, the specimen was cleaned in methanol to remove salt assumed to have precipitated from pore water during the retrieval and drying of the core. He-porosity, N₂-gas permeability and Klinkenberg permeability were determined (API, 1998) before the tests to determine the basic petrophysical data of the tested plug. Measurements of the porosity and permeability after the test were not possible as the specimen disintegrated when removed from the core holder. Prior to testing, the specimen was at vacuum (at ~1 mbar) and pressure (at 110 bar for three days) saturated in degassed formation water and the saturation state of the specimen was verified using the Archimedes test.

Upon testing, the brine saturated specimen was placed in a Viton sleeve in a hydrostatic core holder and connected to a high precision Quizix® pump assuring a constant flow with synthetic calcium depleted formation water (Table 1) at a rate of 0.05 PV/h through the specimen during the test (Fig. 2). A confining pressure of 315 bar and a pore pressure of 180 bar were applied corresponding to the in situ pressures. High corrosion-resistant Hastelloy (C-276) was used for all parts of the experimental setup in contact with the flooding brine. The experimental setup except the pumps and the back pressure regulator were placed inside an oven (Fig. 2) to allow tests at 23 °C, 75 °C (reservoir temperature), 100 °C and 150 °C with flows for at least one week at each temperature. Effluent brine for chemical analysis was collected at the experimental temperature and pressure from either of two sampling loops placed downstream the core holder. During the experiment, the flow was allowed to pass through one of the two loops. At the time of sampling, the flow was shifted to the other loop and the loop recently filled with brine was dismantled from the oven and cooled fast to ambient temperature (23±1 °C) before transferring the content of the loop to a syringe. The sampling procedure was conducted as fast as possible without compromising the quality of the determinations to minimise the risk of precipitation during the sampling. At the end of the sampling procedure, the sampled loop was placed in the oven again and re-pressurised to 180 bar by injection of distilled water. Distilled water was used as the pressurising fluid to be able to detect any mixing of the effluent brine and the pressurising fluid, since any mixing will be evident as a dilution of the Bunter brine. No dilution of the Bunter brine was observed during the experiment indicating that all of the distilled water was replaced by effluent upon sampling.

The alkalinity and pH were determined immediately after extracting the effluent from the sampling loop. The alkalinity was determined by a Gran-titration (Stumm and Morgan, 1981) and the pH was measured using a standard glass electrode containing KCl as a reference liquid. Unfortunately, due to the high salinity of the brine, the liquid–junction potential between the brine samples and the pH buffer solutions was not negligible as is the case when measuring pH in dilute samples (Knauss et al., 1990) resulting in measurement drift and slow electrode response making accurate pH measurements impossible.

Samples for analysis of the total elemental concentrations were passed through 0.22 μm cellulose-acetate syringe filter into three separate polyethylene vials. Samples for analysis for cations and silicium received 1 vol% of 7 M HNO₃ and 10 vol% of 5 M NaOH, respectively, and were kept refrigerated until Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) analysis (PerkinElmer Elan6100DRC Quadrupol) with a standard deviation of 3–15% depending on the element.
determined. Samples for anion analysis (chloride and sulphate) were frozen until undergoing ion-chromatography analysis (LC50-CD50, Dionex, CA, USA) with a quantification limit of 0.05 mg/L.

2.4. Mineralogical analysis

Mineralogical changes of the specimen during the flooding experiment were identified by thin section analysis using optical microscope and backscatter electron microscopy (Inspect S instrument from FEI) prior to and after the flooding experiment. Mineral identification was aided by Energy-dispersive X-ray spectroscopy (EDX). These mineralogical observations provide input to the geochemical modelling and help identify the major chemical reactions responsible for the observed changes in aqueous chemistry.

2.5. Geochemical modelling

To help the interpretation of the laboratory experiment and identify potential geochemical reactions upon injection of Ca-depleted Bunter brine into the Bunter Sandstone Formation, geochemical modelling using PHREEQC version 3.0 (Parkhurst and Appelo, 2013) was applied. A 1D reactive transport model including dissolution/precipitation kinetics was constructed. The thermodynamic data from the Thermodem database (Blanc et al., 2012) was applied as this database includes a large collection of relevant silica minerals along with being optimised to high temperatures. To calculate the activity coefficient of the ions in solution, the Thermodem database uses an extended Debye-Hückel model (B-dot model) theory (Atkins and de Paula, 2002), which makes the database applicable for modelling relatively concentrated solutions.

Due to the high salinity of the Bunter brine, the Pitzer approach (Pitzer, 1981; Plummer et al., 1988) to calculate the ion activity may be more appropriate. However, the Pitzer database only includes an inadequate range of aqueous species and minerals, excluding many of the silica minerals relevant for this study. The Thermodem database has successfully been used to model the experimental data in a similar study (Holmslykke et al., 2017).

A 1D transport model column, consisting of 10 cells with a length of 0.00747 m each, was constructed and flushed with synthetic calcium-depleted Bunter brine (Table 1) at 23 °C, 75 °C, 100 °C and 150 °C and at 180 bar. The model included the thermo-kinetic processes of mineral dissolution/precipitation reaction using the kinetic rate law given by (Palandri and Kharaka, 2004; Appelo and Postma, 2005):

$$r = k_{\text{exp}} A_0 \left( \frac{m}{m_0} \right)^{0.67} \left( 1 - \Theta \right)$$

(1)

where $r$ is the dissolution/precipitation rate (mol/L/sec), $k$ the overall rate constant (mol/m²/sec), $A_0$ the initial surface area (m²), $V$ the liquid volume (L), $m$ the remaining mass of mineral, $m_0$ the initial mass and $\Theta$ the mineral saturation ratio given by $\Theta = IA/P/K$, where $IA$ is the ionic activity product and $K$ the equilibrium constant. The term $(m/m_0)^{0.67}$ corrects for changes in reactive surface sites during the dissolution/precipitation process (Appelo and Postma, 2005).

The rate constant $k$ as function of temperature is calculated by the Arrhenius equation:

$$k = k_{\text{exp}} \exp \left( \frac{-E_a}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right)$$

(2)

where $E_a$ is the activation energy (J/mol), $k_{\text{exp}}$ the rate constant at 25 °C, $R$ the gas constant (J/mol/K) and $T$ the temperature (K). In addition to dissolution in pure water (neutral mechanism), the dissolution and precipitation of alumino-silicates may be controlled by $\text{H}^+$ (acid mechanism) and $\text{OH}^-$ (alkaline mechanism). The overall rate constant is thus given by (Palandri and Kharaka, 2004):

$$k = k_{\text{exp}} \exp \left( \frac{-E_a}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right) \theta^{n\theta}$$

$$+ k_{\text{exp}} \exp \left( \frac{-E_a}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right) \theta^{n\theta}$$

(3)

where the indices $N$, $A$ and $B$ refer to neutral, acid and alkaline mechanisms, respectively and $\theta$ represents the activity of the species.

For carbonates the dissolution/precipitation mechanisms depend on $\text{HCO}_3^-$ and reaction rates depend on the $\text{CO}_2$ pressure ($P_{\text{CO}_2}$) (Carbonate mechanism). The overall rate expression for carbonates is therefore:

$$r = k_{\text{exp}} A_0 \left( \frac{m}{m_0} \right)^{0.67} \left( 1 - \Theta \right)$$

(1)

where $r$ is the dissolution/precipitation rate (mol/L/sec), $k$ the overall rate constant (mol/m²/sec), $A_0$ the initial surface area (m²), $V$ the liquid volume (L), $m$ the remaining mass of mineral, $m_0$ the initial mass and $\Theta$ the mineral saturation ratio given by $\Theta = IA/P/K$, where $IA$ is the ionic activity product and $K$ the equilibrium constant. The term $(m/m_0)^{0.67}$ corrects for changes in reactive surface sites during the dissolution/precipitation process (Appelo and Postma, 2005).

The rate constant $k$ as function of temperature is calculated by the Arrhenius equation:

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(2)

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$$+ k_{\text{exp}} \exp \left( \frac{-E_a}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right) \theta^{n\theta}$$

(3)

where the indices $N$, $A$ and $B$ refer to neutral, acid and alkaline mechanisms, respectively and $\theta$ represents the activity of the species.

For carbonates the dissolution/precipitation mechanisms depend on $\text{HCO}_3^-$ and reaction rates depend on the $\text{CO}_2$ pressure ($P_{\text{CO}_2}$) (Carbonate mechanism). The overall rate expression for carbonates is therefore:
\[ k = k_{25}^N \exp \left[ \frac{-E_{aN}}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] + k_{25}^A \exp \left[ \frac{-E_{aA}}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] a_{\mathrm{in}}^{\text{AN}} + k_{25}^C \exp \left[ \frac{-E_{aC}}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] P_{\mathrm{CO}_2}^{\text{AN}} \]  

(4)

where the indices \( C \) refer to the carbonate mechanism.

For most minerals, precipitation rate data are not available and therefore the same kinetic expression is assumed for both dissolution and precipitation processes (Cantucci et al., 2009). The initial amount of the minerals \((m_0)\) was calculated from the mineral content obtained by the QEMSCAN® analysis while rate constants and the initial specific surface area of the minerals were found in the literature (André et al., 2007; Cantucci et al., 2009). The specific surface area was used to fit the model to the observed data. The specific reactive surface area is difficult to measure or calculate since only part of the mineral surface is involved in the reaction (Azaroual and Fouillac, 1997; Cantucci et al., 2009).

3. Results

3.1. Composition of the effluent from the core flooding experiment

The aqueous concentration of selected elements in the effluent of the core flooding experiment injecting synthetic calcium-depleted Bunter brine into a Bunter Sandstone Formation sample at reservoir conditions and elevated temperatures at a flow rate of 0.05 PV/h is shown in Fig. 3. Upon a temperature increase, a clear and immediate increase in the aqueous concentration of calcium, silicium and barium is observed, suggesting that heat induced dissolution of carbonates, silicates and barium minerals takes place during the experiment. Particularly when increasing the temperature from 100 °C to 150 °C, the aqueous concentrations increase significantly. Magnesium, on the other hand, shows a different pattern with a decreasing concentration when increasing the temperature to 100 °C and particularly to 150 °C. The decrease in the magnesium concentration corresponds to the increase in the calcium

![Fig. 3. Measured and modelled calcium (top left), magnesium (top right), silicium (middle left), barium (middle right) and bicarbonate (lower left) concentrations in the effluent of a Bunter Sandstone Formation sample flushed with calcium depleted synthetic formation water (Table 1) with a flow velocity of 0.05 PV/h and at 23, 75 (reservoir temperature), 100 and 150 °C.](image-url)
concentration in a 1:1 molar ratio, suggesting that a substitution of calcite with dolomite may be responsible for the decreasing magnesium concentration.

No observable changes were identified for the concentration of chloride, sulphate, potassium, and sodium. Aluminium remains below detection limit (0.03 mg/L) throughout the experiments (data not shown).

3.2. Mineralogical changes

The petrographic analyses identify possible mineralogical changes due to flooding (Fig. 4). The quartz and mica do not show any obvious signs of chemical dissolution or precipitation. Amongst the feldspars, detrital pure K-feldspar seems unaffected, detrital plagioclase and the Na-rich part of perthitic intergrown alkalifeldspar show signs of dissolution in a sample near the inlet (Fig. 4.2, dashed ring), whereas neomorphic albite is found in all flooded samples (Figs. 4.2 – 4.4, rings) and not in unflooded sample (Fig. 4.1). This pure albite thus apparently has grown during flooding. Calcite occurs as detrital grains and as cement in unflooded samples and to a minor extent in a sample close to the outlet (Fig. 4.4), but is largely absent close to the inlet and in a central part of a sample (Figs. 4.2 – 4.3). This indicates the dissolution of calcite as a consequence of flooding. Dolomite was only noted in flooded samples and can have formed during flooding as neomorphic crystals.

3.3. Geochemical modelling

3.3.1. Modelling of the core flooding experiment

Based on the petrographic analysis, kinetically controlled dissolution/precipitation of the minerals calcite, dolomite and albite were included in the reactive transport model. Kinetically controlled dissolution of quartz was also included as several studies have shown that the dissolution of quartz increases sharply at elevated temperatures (Perlinger et al., 1987; Azaroual and Fouillac, 1997; Gong et al., 2012; Holmslykke et al., 2017). Stability diagrams for K-feldspar and its weathering products (Appelo and Postma, 2005) show that muscovite may be the stable weathering product in the experiment due to the high potassium concentration in the modified Bunter brine, and therefore muscovite is also included in the model. Also, equilibrium with barite is imposed in the model. The feldspar mineral group includes three end members: K-feldspar (KAlSi₃O₈), albite (NaAlSi₃O₈), as well as anorthite (CaAl₂Si₂O₈)(Fig. 5) and continuous solid solutions exist between albite and anorthite (plagioclase) and at high temperatures between K-feldspar and albite (alkali feldspars). Depending on the composition, alkali feldspars exsolve into perthite by cooling so perthite indicates that a feldspar is of a high temperature (igneous) origin (Fig. 5). Because the results of the petrographic analysis indicate that only Na-rich or Ca-rich feldspar dissolves during the flooding experiment and because the flooding fluid is depleted in calcium and thus subsaturated with respect to any mineral containing Ca, we chose to include a solid solution of 70% albite and 30% anorthite (Na₀.7Ca₀.15AlSi₃O₈) in the model. The dissolution of plagioclase was subsequently validated by equilibrium calculations (Section 3.3.2).

An overview of the minerals included in the reactive transport model and the kinetic parameters applied is shown in Table 2. Generally, the kinetic parameters applied comply with the data found in the literature (Brantley and Mellott, 2000; Cantucci et al., 2009). A strong coupling between calcite dissolution and dolomite precipitation is observed as changes in the dolomite precipitation rate affect the modelled calcium and magnesium concentrations. The rate of dolomite precipitation is therefore constrained by both the calcium and magnesium concentrations. The best fit of the model to the observed data was obtained when applying a specific surface area for dolomite of 1•10⁻⁵ m²/g, which corresponds to a crystal radius of 10 cm. Such a low specific surface area may not be realistic but may instead reflect a lower precipitation rate than applied in Eq. (1). The applied kinetic expression for the dolomite dissolution/precipitation is given by:

\[
d \frac{d}{dt}N_{Dol} = \frac{K_{Dol} a_{Ca} a_{Mg} - K_{Dol} a_{Ca} a_{Mg}}{a_{Ca} a_{Mg}}
\]

where \(N_{Dol}\) is the molar concentration of dolomite, \(K_{Dol}\) is the solubility constant for dolomite, and \(a_{Ca}\) and \(a_{Mg}\) are the activities of calcium and magnesium, respectively. The applied kinetic expression for the dolomite dissolution/precipitation is given by:

\[
d \frac{d}{dt}N_{Dol} = \frac{K_{Dol} a_{Ca} a_{Mg} - K_{Dol} a_{Ca} a_{Mg}}{a_{Ca} a_{Mg}}
\]

where \(N_{Dol}\) is the molar concentration of dolomite, \(K_{Dol}\) is the solubility constant for dolomite, and \(a_{Ca}\) and \(a_{Mg}\) are the activities of calcium and magnesium, respectively.
precipitation is identical to the dissolution rate obtained in the temperature range 0 - 65 °C (Busenberg and Plummer, 1982), and may therefore not adequately describe the precipitation of dolomite at temperatures up to 150 °C. For example, the dolomite precipitation rate is shown to be directly proportional to the induction time (Kaczmarek and Sibley, 2011), a parameter that is not included in the kinetic expression for the dissolution rate. Also for the plagioclase, the best fit of the model was obtained by applying a specific surface area that corresponds to an unrealistically large crystal size (0.3 cm), probably due to the uncertainty of the actual mineral dissolving and the amount of the mineral present.

![Composition range of common feldspars. Modified from (Nesse, 2009). The red cross marks the chosen composition of the dissolving feldspar in the model and the arrow indicates the direction of the mineral transformation during the core flooding experiment.](image)

**Fig. 5.** Composition range of common feldspars. Modified from (Nesse, 2009). The red cross marks the chosen composition of the dissolving feldspar in the model and the arrow indicates the direction of the mineral transformation during the core flooding experiment.

**Table 2**

Specific surface area (SSA), initial mass of mineral \( (m_0) \) and kinetic parameters for the reactive transport model. Kinetic parameters are from (Palandri and Kharaka, 2004).

<table>
<thead>
<tr>
<th>Acid mechanisms</th>
<th>Neutral mechanism</th>
<th>Carbonate mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSA m²/g</td>
<td>( m_0 ) mol</td>
<td>( \log(k_{25}) ) (mol/m²/s)</td>
</tr>
<tr>
<td>Calcite</td>
<td>0.034</td>
<td>3.46</td>
</tr>
<tr>
<td>Dolomite  ↑</td>
<td>0.12</td>
<td>3.19</td>
</tr>
<tr>
<td>Plagioclase,  ↑ (An30)</td>
<td>3.48e-4</td>
<td>1.08</td>
</tr>
<tr>
<td>Plagioclase,  ↑ (An30)</td>
<td>3.48e-4</td>
<td>1.08</td>
</tr>
<tr>
<td>Quartz(alpha)  ↑</td>
<td>0.022</td>
<td>38.02</td>
</tr>
<tr>
<td>Albite</td>
<td>0.115  ↑</td>
<td>3.09</td>
</tr>
<tr>
<td>Muscovite(dis)</td>
<td>0.106  ↑</td>
<td>0.15</td>
</tr>
</tbody>
</table>

* Cantucci et al. (2009).

* Data for disordered dolomite.

* Adjusted in the optimized model.

* Data for plagioclase.

* Brantley and Mellott (2000).
concentrations determined, the model predicts the aqueous aluminium concentration to be close to the detection limit (0.03 mg/L; data not shown). The modelled pH decreases from c. 9 to 7 during the experiment (data not shown).

The processes including the carbonates (calcite dissolution and dolomite precipitation) were also attempted modelled using the Pitzer database (Appelo et al., 2014). Excluding the silicate reactions in the model calculations does not affect the model results for the calcium and magnesium concentrations when using the Thermomodem database. However, when using the Pitzer database, the model clearly understimates the calcium concentration and overestimates the magnesium concentrations at the higher temperatures. Thus, it was not possible to fit the model to the experimental data when using the Pitzer database indicating that the Thermomodem database is more suitable for modelling reactions at higher temperatures. This difference is caused by a lower pH (approximately 0.5 pH unit) when using the Pitzer database and this difference in the pH affects both the reactions rates and the solubility of calcite and magnesium.

3.3.2. Validation of plagioclase dissolution

To validate the dissolution of plagioclase in the laboratory experiment, chemical equilibrium calculations were performed calculating the mineral saturation index (SI) at each sampling point of the core flooding experiment. The equilibrium calculations focus on the equilibrium state of the selected feldspar and were carried out using the measured chemical composition of the effluent from the core flooding experiment, the experimental temperature, the modelled pH and a pressure of 180 bar.

In order to evaluate the saturation state of plagioclase and alkali feldspars, two new phases were included in the applied database. The phases were composed of 70% albite and the rest being either anorthite or microcline (Table 3). Applying general thermodynamics for solid solutions and assuming that the properties of the solid solution approach those of an ideal solid solution, the equilibrium constant $K_{ss}$ of the solid solution can be calculated by the values reported for the end members by the relation (Tardy and Fritz, 1981):

$$\log(K_{ss}) = x_{e1} \cdot \log(K_{e1}) + x_{e2} \cdot \log(K_{e2})$$ (1)

where $x_{e1}$ and $x_{e2}$ are the mole fractions of end member 1 and end member 2 in the solid solution, respectively, and $K_{e1}$ and $K_{e2}$ are the corresponding equilibrium constants. The calculated equilibrium constants for the plagioclase and alkali feldspars studied are given in Table 3. The $\Delta$H and the analytical expression for the temperature dependence of log K for the sodium free end members were applied.

The aqueous composition determined for the effluent of the core flooding experiment is used to calculate the mineral saturation index (SI) of selected alkali feldspars and plagioclase at each sampling point of the core flooding experiment and is shown in Fig. 6. To account for the uncertainties in the chemical analysis and the thermodynamic equilibrium constants on mineral phases in saline systems, a thermodynamic saturation band of $-0.3 \leq SI \leq 0.3$ is assumed for the minerals (Castillo et al., 2015). As the aluminium concentration determined is below the detection limit (0.03 mg/L), the aluminium concentration is set to 0.03 mg/L in the calculations.

The effluent from the core flooding experiment is generally in equilibrium with albite and microcline and supersaturated with respect to any solid solution in between, represented by a solid solution composed of 70% albite and 30% microcline in Fig. 6. Thus, the dissolution of any of the alkali-feldspars is not likely to take place during the flooding experiment. In contrast, the effluent is subsaturated with respect to anorthite and any of the plagioclase, represented by a plagioclase containing 70% albite and 30% anorthite in Fig. 6. Thus, the model is in accordance with the observation that plagioclase dissolves during the experiment.

4. Discussion

4.1. Potential geochemical reactions

4.1.1. Carbonates

The model predicts the increase in the calcium concentration and the decrease in the magnesium concentration reasonably well (Fig. 3). The calcium concentration is controlled by equilibrium with calcite (CaCO$_3$), while the magnesium concentration is kinetically controlled by

Fig. 6. Saturation state of the Bunter brine with respect to selected alkali feldspar (top) and plagioclase (bottom) in the effluent of the core flooding experiment calculated with PHREEQC at the experimental temperature and 180 bar pressure assuming an aluminium concentration of 0.03 mg/L. The assumption that a mineral is in thermodynamic equilibrium with the solution if $-0.3 \leq SI \leq 0.3$ is illustrated by a grey band.

Table 3

<table>
<thead>
<tr>
<th>Solid solution</th>
<th>Mineral composition</th>
<th>Albite content (%)</th>
<th>Anorthite content (%)</th>
<th>Microcline content (%)</th>
<th>Log($K_{ss}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali feldspar (Ab30)</td>
<td>Na$_8$K$_3$Al$_2$Si$<em>4$O$</em>{10}$</td>
<td>70</td>
<td>-</td>
<td>30</td>
<td>9.319</td>
</tr>
<tr>
<td>Plagioclase (An30)</td>
<td>Na$<em>{6.3}$Ca$</em>{0.7}$Al$<em>{1.8}$Si$</em>{2.2}$O$_{10}$</td>
<td>70</td>
<td>30</td>
<td>-</td>
<td>9.1502</td>
</tr>
</tbody>
</table>
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precipitation of dolomite (CaMg(CO$_3$)$_2$) (Fig. 7). Despite supersaturation with respect to dolomite of SI = 1.6 at temperatures up to 75 °C, no or only unmeasurable amounts of dolomite precipitate, and dolomite precipitation only takes place at temperatures ≥100 °C. The lack of dolomite formation at low temperatures in solutions that were supersaturated with respect to dolomite (Sibley et al., 1994; Land, 1998) and also in recent and geologically relatively young marine carbonate environments (Machel, 2004) is typically explained by a long induction time during the dolomite formation process.

At temperatures ≥100 °C the heating induces dolomitisation i.e. the concomitant dissolution of calcite and precipitation of dolomite. Dolomitisation where calcite dissolution and dolomite precipitation take place in a 1:1 molar ratio as indicated by the experimental data, can be illustrated by the following equation:

$$2\text{CaCO}_3(s) + \text{Mg}^{2+}_{(aq)} \rightarrow \text{CaMg(CO}_3)_2(s) + \text{Ca}^{2+}_{(aq)}$$

(1)

where the subindices s and aq represent solid and aqueous phases, respectively.

The dolomitisation reaction has been divided into a three step process (Sibley et al., 1994). In the first step a nucleation of very high Mg-calcite (35–40 mol% MgCO$_3$) or nonstoichiometric dolomite is followed by the nucleation of more stoichiometric dolomite. The second step is a long induction period, where nucleation takes place, but most of this period is post-nucleation growth of the very high Mg-calcite, nonstoichiometric and stoichiometric dolomite nuclei. In the third and final step, termed the replacement period, the very high Mg-calcite and nonstoichiometric dolomite is replaced by a stoichiometric dolomite.

Dolomitisation depends on specific conditions which include a supply of an aqueous solution with high Mg$^{2+}$/Ca$^{2+}$ ratio; elevated temperature and high degree of supersaturation (Banerjee, 2016); all of which are fulfilled in the present study. The dolomite precipitation rate found in this study increases from 10$^{-6}$ moles/l/h at 25 °C to 10$^{-4}$ moles/l/h at 150 °C. The strong dependence of dolomite precipitation rate on temperature (Wilson et al., 1990; Sibley et al., 1994; Arvidson and Mackenzie, 1999; Chen et al., 2004; Jones and Xiao, 2005; Merino and Canals, 2011; Al-Helal et al., 2012) is due to the high activation energies found for very High-Mg Calcite and dolomite (48 and 49–50 kcal/mol, respectively (Katz and Matthews, 1977)) compared to the approximately 10 kcal/mol activation energy for calcium carbonate precipitation (Arvidson and Mackenzie, 1999). The dolomite precipitation rates in this study are higher than previously reported values (Arvidson and Mackenzie, 1999; Pokrovsky and Schott, 2001). Besides temperature, several other parameters have been shown to affect the rate of dolomitisation, including the alkalinity (Morrow and Ricketts, 1988; Arvidson and Mackenzie, 1997, 1999) fluid to rock ratios (Land, 1967), solution pH (Sibley et al., 1987; Sibley, 1990), surface area (Katz and Matthews, 1977), solubility of the reactants (Land, 1967; Baker and Kastner, 1981; Sibley et al., 1987) and the fluid Mg/Ca ratio (Land, 1967; Katz and Matthews, 1977). Higher fluid Mg/Ca ratios shorten the induction period and thereby increase reaction rates. Given the high Mg/Ca ratio in this study it is not unlikely that this may be a contributing factor to the high dolomitisation rate found in this study.

4.1.2. Silicates

The model reproduces the measured silicium concentration reasonably well (Fig. 3) and both the modelled and measured aluminium concentrations are below the detection limit. The concentration level of the silicium is determined by a strong coupling with the kinetically controlled dissolution and precipitation of silica minerals. Thus, at reservoir conditions (75 °C) the silicium concentration is controlled by the dissolution of small amounts of albite and precipitation of small amounts of mica. The precipitation of mica may very well be facilitated by the increased potassium concentration in the injected modified brine leading to a fluid supersaturated with respect to mica as plagioclase dissolves. Upon a temperature increase to 100 °C, the dissolution of quartz along with the conversion of small amounts of plagioclase to albite is observed while the precipitation of mica continues. At 150 °C both the dissolution of quartz and the albition increase (Fig. 8).

Albitisation of plagioclase is a common reaction known to take place over a wide range of P-T conditions (e.g. Gold, 1987; Sagal et al., 1988; Lee and Lee, 1998; Leichmann et al., 2003; Clark et al., 2005). The results of isotopic analysis and kinetic experiments suggest that the replacement of plagioclase with albite proceeds through the dissolution of the plagioclase and reprecipitation of albite (Moody et al., 1985; Perez and Boles, 2005), rather than solid diffusion. Perez and Boles (2005) concluded that time, surface area, fluid composition and primarily temperature are the most important parameters controlling the albition reaction. Thus, the process is thermodynamically constrained by the pore fluid chemistry. The reaction onset, however, is kinetically controlled and proceeds at an appreciable rate after a critical activation energy is reached, presumably at temperatures higher than 70 °C. For example, the transformation of detrital plagioclase in Mesozoic rocks to albite is shown to take place at temperatures above 75 °C. Also, in our experiment, albitionisation only takes place at temperatures above 75 °C (Fig. 8).

Albitisation of plagioclase may be described by a reaction such as

![Fig. 7. Reacted amounts (top) and Saturation Index (bottom) for calcite and dolomite calculated in a PHREEQC reactive transport model where synthetic Bunter brine (Table 1) is flushed through a column in which kinetically controlled dissolution or precipitation of calcite, dolomite, plagioclase, quartz, albite and muscovite (Table 2) is allowed. “Reacted amounts” indicate the amount (in moles) of a mineral that reacts; a positive “Reacted amounts” indicates that the mineral precipitates, while a negative value indicates the dissolution of the mineral. The saturation state of the effluent is indicated by the Saturation Index; the possibility of dissolution and precipitation revealed by a negative and positive value of the saturation index, respectively.](image-url)
(Moody et al., 1985):

Plagioclase Albite
\[
Na_{0.7}Ca_{0.3}Al_{1.3}Si_{2.7}O_{8} + 0.3Na^+ + 0.3H_2SiO_4 \rightarrow NaAlSi_3O_8 + 0.3Ca^{2+} + 0.3Al^{3+} + 1.2OH^- (2)
\]

The process involves the supply of sodium and silicium, while calcium and aluminium are released to the solution. In our experiment, the supply of sodium is ensured through the injected water (Table 1), whereas the supply of silicium is facilitated by the dissolution of quartz (Fig. 8). The release of calcium due to albitisation is insignificant compared to the release of calcium due to calcite dissolution (Figs. 7 and 8). The significant release of calcium due to calcite dissolution may in fact inhibit the precipitation of albite. Even though aluminium is released into the solution by the albitisation, the aluminium concentration remains below the detection limit due to the precipitation of mica. Thus, while the silicium concentration is controlled by equilibrium with albite (Fig. 8), the plateau reached at each temperature is affected by a strong coupling between the processes of quartz dissolution, albitisation, calcite dissolution and mica precipitation.

Dissolution of quartz is quantitatively the most important process (Fig. 8). It is well known that the solubility of quartz as well as the dissolution rate increases with increasing temperature (Rimstidt and Barnes, 1980). Especially at temperatures above 100 °C, the rate of quartz dissolution increases significantly (Fig. 8) as also previously observed (Holmslykke et al., 2017). This increases the supply of silicium for the albitisation, pushing reaction (2) to the right, therefore enhancing the albitisation at 150 °C.

Trace amounts of barium are known to substitute for sodium in the plagioclase (Bindeman and Davis, 2000). Incorporation of trace amounts of barium into the plagioclase may, however, not account for the aqueous concentrations of barium determined in the effluent (Fig. 3). Instead, the barium concentration appears to be controlled by equilibrium with barite (Fig. 3). The sulphate released due to the dissolution of barite is, however, insignificant compared to the original concentration of sulphate in the brine (0.01 mol/L) and therefore no changes are observed in the sulphate concentration.

4.1.3. Implications for heat storage in the Bunter Sandstone Formation

The experimental data, the observed mineralogical changes and the model results all indicate that dolomitisation might occur during the storage of heated calcium-depleted Bunter brine in the Bunter Sandstone Formation. Assuming the exact same conditions for 6 months as in the model (Fig. 7) i.e., a continuous injection of Ca-depleted heated brine into the reservoir and a constant dissolution rate during the entire injection period, extrapolation of the model results show that within an injection period of 6 months at 100 °C approximately 50% of the calcite will dissolve, while all of the calcite will dissolve within 4 months at 150 °C. The dissolution of calcite in the reservoir may be minimised through an optimisation of the softening process to the highest possible calcium concentration to prevent calcium carbonate precipitation. However, calcite dissolution will take place as heated brine subsaturated with respect to calcite is injected into the Bunter Sandstone Formation. Although the dissolution of some minerals may increase the
permeability of the reservoir, the dissolution of significant amounts of a cementing mineral may damage the reservoir integrity and thus pose a problem for the utilization of heat storage in the Bunter Sandstone Formation in the Tender area. In our experiment the plug tested dissolved after the experiment due to dissolution of the cementing calcite and even though dolomite may have formed it appears not to be capable of maintaining the strength of the plug.

The dolomitisation process is associated with the generation of secondary porosity (Jones and Xiao, 2005; Banerjee, 2016). Due to the low concentration of calcite in the reservoir it is, however, highly questionable if the dolomitisation will result in a measurable change in the porosity and permeability. Conversely the replacement of plagioclase by albite is associated with porosity decrease, as the volume of the parent mineral dissolved is smaller than the volume reprecipitated (Perez and Bole, 2005; Engvik et al., 2008). Extrapolation of the model results shows that only 0.01% and 0.5% of the plagioclase in the reservoir will dissolve upon heat storage at 100 °C and 150 °C, respectively for 6 months. The alteration process is therefore not expected to significantly influence the properties of the reservoir adversely. Also, an insignificant fraction of the quartz is expected not to dissolve upon storage for 6 months at 100 °C and 150 °C (0.04% and 0.5%, respectively) and the dissolution of quartz is therefore not expected to deteriorate the quality of the reservoir. However, caution should be taken due to the high silicium concentration in the stored brine which may reprecipitate as “amorphous silica” upon cooling. Also, the aqueous barium may reprecipitate as barite upon cooling and may potentially cause injectivity problems.

5. Conclusions

The core flooding experiment, petrographic analysis and geochemical modelling of the chemical effects of heat storage at up to 150 °C in the Bunter Sandstone Formation show that injection of a Ca-depleted synthetic formation water may induce dolomitisation, albition, dissolution of quartz and barite as well as the precipitation of mica. Extrapolation of the model results shows that during a 6 months storage mainly the dissolution of calcite may pose a problem.

Major changes observed in the brine composition include increased calcium, silicium and barium concentrations. The increased calcium concentration is not expected to constitute a problem in the cold injection well in a duplex heat storage facility as long as the temperature is lower than the temperature in the storage well. However, to ensure a sustainable energy production from the heat storage, an appropriate removal of silicium and barium e.g., by filtration in the surface facility may be critical to prevent clogging of the injection well due to the reprecipitation upon cooling of the brine. As the aqueous concentration of both elements increases sharply above 100 °C, keeping the storage temperature below 100 °C, as observed at other heat storage facilities (Kabus and Wollgrienn, 2009), may help reduce the chemical effects of the heat storage on the reservoir and thereby any injection problems. The results show that care should be taken when injecting a Ca-depleted formation water into a reservoir. This may pose a problem in all reservoirs in which calcite contributes to the geomechanical properties of the reservoir. In our experiment, the core material disintegrated after being flushed with a Ca-depleted brine due to dissolution of the cementing calcite and the precipitated dolomite appeared not to be able to maintain the strength of the plug. Thus, it is important to investigate potential effects of the removal of selected ions from the formation water to avoid e.g. scaling problems on the reservoir properties since this may introduce new problems.

CRediT authorship contribution statement

Hanne D. Holmslykke: Methodology, Software, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. Claus Kjeller: Conceptualization, Methodology, Software, Validation, Supervision, Project administration. Ida L. Fabricius: Conceptualization, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This research was funded by the Danish Council for Strategic Research (now Innovation Fund Denmark) as part of the Heat Storage in Hot Aquifers (HeHo) project (grant 10-093934). We thank three anonymous reviewers for their constructive comments.

Supplementary materials


References

Chen, D., Qing, H., Yang, C., 2004. Multistage hydrothermal dolomites in the Middle Devonian (Givetian) carbonates from the Guilin area, South China. Sedimentology 51, 1029–1051.


