Numerical simulation of pore space clogging in geothermal reservoirs by precipitation of anhydrite

R. Wagner\textsuperscript{a,}\textsuperscript{*}, M. Kühn\textsuperscript{b}, V. Meyn\textsuperscript{c}, H. Pape\textsuperscript{a}, U. Vath\textsuperscript{d}, C. Clauser\textsuperscript{a}

\textsuperscript{a}Applied Geophysics, RWTH Aachen University, Lochnerstr. 4-20, D-52056 Aachen, Germany
\textsuperscript{b}CSIRO Exploration and Mining, 26 Dick Perry Avenue, Kensington, Perth, WA 6151, Australia
\textsuperscript{c}Institut für Erdöl- und Erdgastechnik (ITE), Agricolastr. 10, D-38678 Clausthal-Zellerfeld, Germany
\textsuperscript{d}Allerberg 15, D-37130 Gleichen, Germany

Accepted 3 May 2005
Available online 1 July 2005

Abstract

Anhydrite cementation in hydrothermal reservoirs can decrease porosity and permeability significantly. In these cases, the amount of hot water produced by hydrothermal heat mining installations is far too low for an economical use of the resource. We study two such cases in the North German sedimentary basin where a secondary anhydrite cementation drastically reduced the original high permeability of a Rhaetian sandstone reservoir. Core-flooding experiments under reservoir conditions indicate that in contrast to the instant dissolution of anhydrite in saline reservoirs, the nucleation probability of anhydrite and the speed of epitaxy on anhydrite crystals (10 s\textsuperscript{-1} m\textsuperscript{-3} and 5 \times 10\textsuperscript{-12} m\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}, respectively) are very low. We performed numerical simulations of reactive flow on the local and regional scale in order to understand the apparent conflict between constricted nucleation, observed in laboratory experiments, and a complete filling of the pore space by anhydrite cementation found in core samples from boreholes at Neuruppin and Allermöhe. A highly resolved cylindrical reservoir model was used to simulate a chemical stimulation of the Allermöhe reservoir, i.e. the forced increase in porosity and permeability around the borehole in response to the injection of cold brines. Studying the dissolution process for different brine temperatures and salinities, we found that an injection of 5600 m\textsuperscript{3} cold, highly saline brines will break through a cemented barrier of a radius of 5 m around the borehole after 10 days of stimulation. An additional study of the combined effect of hydraulic fracturing and chemical stimulation showed that both types of borehole stimulation increase the permeability by approximately the same amount if dissolution can act directly on the fracture walls. On the reservoir scale, numerical simulations indicate that strata-bound convective flow in the Rhaetian reservoir, driven by temperature differences due to the topography of the aquifer, is insufficient to explain the observed high degree of cementation. However, it can be shown that Ca\textsuperscript{2+} and SO\textsubscript{4}\textsuperscript{2-} dissolved in the reservoir brine are forced to precipitate around the fracture zone, if additional hot fluids flow up along faults, heat up the aquifer, and mix with the colder reservoir brine.

Keywords: Anhydrite cementation; Borehole stimulation; Numerical simulation; Reactive flow; Cementation patterns; Reservoir engineering; Geothermal energy

1. Introduction

Hydrothermal heat mining installations are major capital investments. They usually involve two or more production and injection wells. Permeability and porosity of the reservoir are key parameters for an economical heat mining. Unfortunately, the pore space of reservoir sandstones can be clogged by precipitation of minerals such as anhydrite. We study two such cases in the North German sedimentary basin in detail. (1) The Rhaetian aquifer was drilled at Neuruppin (60 km northwest of Berlin, Germany, in 1987 and 1988) in order to assess the potential of the reservoir for geothermal heat mining. Although the distance between the two...
boreholes (Np Gt/Nn 1/88; Np Gt/Nn 2/87) is only 1.5 km, core samples from the Rhaetian formation in one borehole (Np Gt/Nn 1/88) are strongly cemented by anhydrite, while cementation is minor in core samples from the other one (Np Gt/Nn 2/87) [1,2]; (2) an abandoned oil well near Hamburg, Germany, (Allermöhe 1) was deepened to a depth of 3300 m in 1997 in view of hot water production for geothermal energy use. It taps the Rhaetian sandstone aquifer (Keuper) with a total thickness of 70 m and a temperature of 123 °C at this location. Although thickness and temperature of the aquifer are favorable for geothermal energy use, the pore space, with an original porosity of 20% is filled to a very large extent by anhydrite. The extractable amount of water produced by pumping tests (3–8 m³ h⁻¹), is far too small for an economical use of the resource [3]. These two examples illustrate that the processes causing pore space clogging in originally high-permeability sandstone formations need to be understood in more detail in order to reduce the exploration risk with respect to heat mining. These processes can be studied by numerical simulation of reactive flow with coupling of mineral reaction, flow, and heat transport.

Due to the limited availability of solubility data of common reservoir minerals at high temperatures (> 100 °C) and salinities (> 100 g NaCl L⁻¹), fluid-rock-interaction under reservoir conditions has only been simulated in only a few case studies [4–10]. Only Lee and Bethke [11], to the best of our knowledge, performed simulations with respect to the origin of anhydrite cementation in deep saline aquifers, in particular the nature of diagenetic alteration in the Permian Lyons Sandstone (Denver Basin). In their model, saline groundwater first flow eastward through the Pennsylvanian Fountain Formation and then vertically up, where then discharge into the Lyons sandstone. The brines mix with more dilute groundwater in the Lyons Formation resulting in a reaction that dissolves calcite and precipitates dolomite and anhydrite.

2. Numerical model

For calculating spatial anhydrite cementation patterns we used the simulation code SHEMAT (Simulator for HEat and MAss Transport), a general-purpose reactive transport simulation code for thermal and hydrogeological problems in two and three dimensions [12]. In particular, SHEMAT is well suited to solve coupled problems involving fluid flow, heat transfer, species transport, and chemical water-rock interaction in fluid-saturated porous media [13, 6–8]. SHEMAT is specifically appropriate for reactive flow problems in saline aquifers, because of the coupling implemented between reaction, flow, and transport via a calibrated fractal relationship between porosity and permeability [14], and the extended range of validity of the chemical reactions implemented in SHEMAT with respect to temperature and ionic strength of the solution. In this study we take advantage of the solubility’s temperature dependence of species such as calcium (Ca²⁺) and sulfate (SO₄²⁻) for temperature and ionic strength of up to 150 °C and 100 g L⁻¹, respectively. The Pitzer equations [15] implemented in SHEMAT are currently accepted to be the most appropriate approach for calculating ion activities in high-salinity brines [8]. This allows to simulate chemical reactions which are caused by the mixing of fluids with different temperatures and salinities.

3. Core flooding experiments

In a core-flooding experiment, a saturated CaSO₄ solution with a salinity of 220 g L⁻¹ was injected into a Bentheim sandstone core (porosity φ = 0.22, permeability k = 2 – 4 × 10⁻¹² m²) at a rate of q = 0.072 L d⁻¹ at a pressure of 0.3 MPa. Diameter and length of the core were 29 and 320 mm, respectively. The core was mounted in a pressure cell, which could be placed into an external high-energy X-ray tomograph. Due to the decrease of anhydrite solubility with temperature, the pressure cell was heated up to force a controlled precipitation of anhydrite. Heating pads around the cell maintained a constant temperature gradient along the core from 70 °C at the flow inlet of the core, to a maximum of 123 °C roughly 100 mm before the flow outlet, where the core was cooled down to 70 °C again (Fig. 1). At the inlet the saturation concentration (at 220 g NaCl L⁻¹) of anhydrite is roughly c_in = 41 mmol L⁻¹, and 26 mmol L⁻¹ at the location of the temperature maximum. Due to this difference anhydrite should precipitate from the brine flowing from the inlet to the location of the temperature maximum. Fig. 2 shows that even after 141 days of flooding, the concentration of Ca²⁺ at the outlet of the core had not yet reached the equilibrium value of c_eq(123 °C) = 26.27 mmol L⁻¹. To translate this laboratory experiment to a larger-scale aquifer model, the core was treated like a single model element at a temperature of 123 °C. It is assumed that the variation of Ca²⁺ and SO₄²⁻ concentrations at the outlet can be described by a first-order kinetic reaction law:

\[ c(t) = c_{eq} + (c_{in} - c_{eq})e^{-t/\tau}; \]

where \( c_{eq} \) is the equilibrium concentration of anhydrite at 123 °C, and \( c_{in} \) the concentration of anhydrite at the inlet of the core at 70 °C, both at 220 g NaCl per liter. This function was fitted to the measured Ca²⁺ concentration at the outlet of the core (Fig. 2). The time constant of \( \tau = 138.4 \) days derived this way can be used to calculate the reaction rate constant \( r_0 \) in mol m⁻² s⁻¹
for numerical simulation with SHEMAT, where the amount of anhydrite \( \Delta c_{\text{Anh}} \) precipitating in each time step \( \Delta t \) is calculated from

\[
\frac{\Delta c_{\text{Anh}}}{\Delta t} = A r_0 \frac{c(t) - c_{\text{eq}}}{c_{\text{eq}}},
\]

where \( A \) is the specific surface of anhydrite in \( m^2 m^{-3} \), and \( c_{\text{Anh}} = c_{\text{in}} - c(t) \) (Eq. (1)).

\[
\frac{dc_{\text{Anh}}}{dt} = \frac{c_{\text{in}} - c_{\text{eq}}}{\tau} e^{-t/\tau}. 
\]

In the limit of \( \Delta t \to 0 \), a comparison of Eqs. (2) and (3) yields

\[
r_0 = \frac{c_{\text{eq}}}{\tau A}.
\]

The specific surface \( A \) can be derived from the number and size of anhydrite crystal nuclei, which were observed in X-ray tomography after a total time \( \Delta t \) of 141 days. All crystals nucleated in a pore volume \( V = 8.8 \times 10^{-6} \text{ m}^3 \) of the core, 100–160 mm before the flow outlet. No nuclei were found within the first half of the core. Here the temperature is obviously too low to cause instant nucleation. In order to estimate the nucleation probability of anhydrite crystals, X-ray tomography was performed at seven different times during the experiment. Analyzing the growth and number of crystals at defined locations yields a speed of epitaxy on anhydrite crystals of \( 5 \times 10^{-12} \text{ m}^4 \text{mol}^{-1} \text{s}^{-1} \) and a nucleation probability \( w = 10 \text{ m}^{-3} \text{s}^{-1} \). The number \( n \) of nuclei in the volume \( V \) follows from the density of

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**Fig. 1.** Top panel: Cross section of the core flooding experiment set-up; Bottom panel: Temperature along the core axis in a core-flooding experiment. The hatched area shows the core volume where anhydrite crystal nuclei were identified in X-ray tomography.

**Fig. 2.** Variation of calcium sulfate concentration at the flow outlet of the core (squares: data; line: exponential fit).
nuclei, \( w \Delta t \):
\[
n = w \Delta t V \phi
\]
\[
= 10 \text{ m}^{-3} \text{s}^{-1} \times 141 \times 86400 \text{s}
\times 4 \times 10^{-5} \text{ m}^3 \times 0.22 = 1072.
\]
(5)

Results from X-ray tomography show that no additional nuclei were formed after 141 days. We try to estimate an average specific surface assuming spherical nuclei with a constant number-density \( n/V \). The amount of anhydrite \( V_{Anh} \), which has precipitated in the partial core volume \( V \) in \( t = 141 \) days can be integrated, if we assume that \( n/V \) does not change:
\[
V_{Anh} = \int \frac{v_{Anh}}{V} \frac{\partial c_{Anh}}{\partial t} dt
\]
\[
= v_{Anh} \int (c_i - c_{eq}) \left[ t - \tau(1 - e^{-t/\tau}) \right] dt
\]
\[
= 2.6 \times 10^{-6} \text{ m}^3,
\]
(6)
where \( v_{Anh} = 4.6 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \) is the molar volume of anhydrite. Each nucleus has a volume \( V_i \) of \( V_i = V_{Anh}/1072 = 4/3 \pi r_i^3 \), where \( r_i \) is the radius of the spherical anhydrite nucleus. The real crystal growth is skeletal-like. The quartz grains of the sandstone core are embedded into the anhydrite crystals, when they grow larger than the quartz grains. Therefore, the anhydrite crystal volume and its surface refers to the total core volume.

Then, the specific surface \( A \) of all nuclei is
\[
A = \frac{4 \pi r_i^2}{3 \pi r_i^3} = 3611 \text{ m}^2 \text{ m}^{-3},
\]
(7)
which yields a reaction rate constant \( r_0 \) of
\[
r_0 = \frac{26.37 \text{ mol m}^{-3}}{138.4 \times 86400 \text{s} \times 3611 \text{ m}^{-1}} \approx 9.6 \times 10^{-10} \text{ mol m}^{-2} \text{s}^{-1}.
\]
(8)

Using these results for \( A \) and \( r_0 \) a simulation of reactive flow in a reservoir with similar temperature and salinity conditions, yields a precipitation rate identical to the one observed in this core-flooding experiment. Since the surfaces of crystals grow with time the reaction rate constant \( r_0 \) also increases with time. Currently, this second order effect is not implemented in SHEMAT, but will be studied in the future.

4. Chemical borehole stimulation

Because the solubility of anhydrite decreases with temperature, a stimulation of a cemented pore space, such as the Rhaetian aquifer at Allermöhe, can be chemically stimulated by injecting cold brines into the reservoir. During an injection test of the Allermöhe well in 1998, 39 m³ of acidic water were pumped into the lowermost part of the Rhaetian aquifer at a depth of 3200–3280 m [16]. During this stimulation test no pressure drop occurred and a temperature log showed that most of the water had infiltrated a small zone at a depth of approximately 3260 m. A stimulation with saline brine instead of acidic water might have been more successful in dissolving anhydrite, because the solubility of anhydrite strongly increases with salinity.

The initial distribution of small-scale vertical variation in porosity, permeability and anhydrite content around the borehole are key parameters for an accurate numerical simulation of such a chemical stimulation. One way to predict permeability is based on a fractal relationship between porosity and permeability [14]. It is based on the Kozeny–Carman equation [17] which describes permeability \( k \) as a function of porosity \( \phi \), tortuosity \( T \) and the effective hydraulic pore radius \( r_{eff} \).

In this model, the fractal pore space, \( T \) and \( r_{eff} \) are functions of \( \phi \) and the fractal dimension \( D \), which is a fundamental structural parameter. This relationship was used to calculate permeability from industry porosity logs run in the Allermöhe borehole. A classification of the pore space with respect to free fluid, capillary bound water and clay bound water was based on the interpretation of a Schlumberger NMR log [18]. For the Rhaetian sandstones at Allermöhe the relationship between porosity and permeability can be described by the following equation, which is used for all simulations in this paper:
\[
k = 0.309(100\phi)^{4.85}[10^{-18} \text{ m}^2].
\]
(9)

Eq. (9) was used to calculate the vertical variation of permeability in the lowermost part of the aquifer.

![Fig. 3. Variation of porosity, permeability, and anhydrite content in the Allermöhe borehole (solid line: current situation; dashed line: situation before later anhydrite cementation; symbols: strata with highest degree of cementation above a layer without any anhydrite). Porosity was derived from an industry NMR log. Permeability was calculated from Eq. (9).](image-url)
between 3280 and 3260 m depth (Fig. 3). The current anhydrite content was calculated from a gamma density log. From the current anhydrite content, the variation of porosity and permeability with depth prior to anhydrite cementation can be calculated (dashed lines in Fig. 3). Obviously, most of the anhydrite occurs in coarse sandstones with an originally high porosity (>15%).

The fine-grained facies was not cemented by anhydrite possibly because anhydrite crystal nuclei are unstable in insufficiently large pores [1].

The data in Fig. 3 was used to define a highly resolved cylindrical finite-difference grid. With this model we simulated the increase in porosity and permeability around the borehole due to anhydrite dissolution (Table 1). We assumed that the cementation by anhydrite is confined within a radius of 5 m around the borehole, and that beyond 5 m from the well the pore space is completely free from anhydrite. The properties of this region are shown by the dashed line in Fig. 3. With this model we studied the effect of different fluid temperatures and salinities on the hydraulic breakthrough time.

Fig. 4 shows the increase of the injection rate due to the increase in permeability for different stimulation brines of varying salinity and temperature. The injection head was kept constant at 3500 m during the entire simulation, while the reservoir head was set to an initial value of 3250 m. The permeability of the borehole itself was fixed at 10$^{-12}$ m$^2$, corresponding to an initial injection rate of approx. 5 m$^3$ h$^{-1}$. This equals roughly the amount of hot water which had been produced during earlier pump tests. The simulations show that the rate of dissolution around the borehole increases strongly with salinity. A hydraulic breakthrough occurs after 13 days of continuous stimulation for fluids with a salinity of 1700 mmol L$^{-1}$ (100 g NaCl L$^{-1}$). On the contrary, no breakthrough occurs even after 3 weeks of continuous stimulation for a fluid with a salinity of 170 mmol L$^{-1}$. Fluids with lower temperature (60–70 °C, dashed lines in Fig. 4) and 100 g NaCl L$^{-1}$ salinity correspond to lower injection rates compared to the same brines at 80 °C. This effect is due to the higher viscosity of water at lower temperatures which is considered in numerical simulation of reactive flow. Thus, a decreasing temperature decreases the hydraulic conductivity significantly.

Fig. 5 shows the porosity in the model after 1 day and 11 days of stimulation, following an injection of a brine with a salinity of 1700 mmol L$^{-1}$ at 80 °C. After 11 days a breakthrough occurs just below the layer between $z = 14–16$ m, which is strongly cemented by anhydrite (see Fig. 3). In the beginning, most of the brine is injected into the formation between $z = 2–4$ m and $z = 6–14$ m, where rock permeability is higher than in the cemented layers. Soon, anhydrite is dissolved at the bottom of the highly cemented layer above $z = 14$ m.

### Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0$</td>
<td>1.5 $\times$ 10$^{-12}$ m$^2$</td>
</tr>
<tr>
<td>$\phi_0$</td>
<td>0.15</td>
</tr>
<tr>
<td>$z_{1/2}$</td>
<td>2.0 mJ m$^{-2}$ K$^{-1}$</td>
</tr>
<tr>
<td>$\phi_{0,c}$</td>
<td>3.0 m m$^{-1}$</td>
</tr>
<tr>
<td>$k_{0,c}$</td>
<td>0.15–0.45 m</td>
</tr>
<tr>
<td>$z_{3/4}$</td>
<td>3500–7250 mm</td>
</tr>
<tr>
<td>$k_{3/4}$</td>
<td>2.0 mJ m$^{-2}$ K$^{-1}$</td>
</tr>
<tr>
<td>$\phi_{3/4}$</td>
<td>0.25 m</td>
</tr>
<tr>
<td>$z_{5/8}$</td>
<td>3000–7000 mm</td>
</tr>
<tr>
<td>$k_{5/8}$</td>
<td>3.0 m m$^{-1}$</td>
</tr>
<tr>
<td>$\phi_{5/8}$</td>
<td>0.15–0.45 m</td>
</tr>
<tr>
<td>$z_{1/1}$</td>
<td>1700–7000 mm</td>
</tr>
<tr>
<td>$k_{1/1}$</td>
<td>2.0 mJ m$^{-2}$ K$^{-1}$</td>
</tr>
<tr>
<td>$\phi_{1/1}$</td>
<td>0.25 m</td>
</tr>
<tr>
<td>$z_{1/2}$</td>
<td>3000–7000 mm</td>
</tr>
<tr>
<td>$k_{1/2}$</td>
<td>2.0 mJ m$^{-2}$ K$^{-1}$</td>
</tr>
<tr>
<td>$\phi_{1/2}$</td>
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</tr>
<tr>
<td>$z_{1/3}$</td>
<td>1700–7000 mm</td>
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<tr>
<td>$k_{1/3}$</td>
<td>2.0 mJ m$^{-2}$ K$^{-1}$</td>
</tr>
<tr>
<td>$\phi_{1/3}$</td>
<td>0.25 m</td>
</tr>
<tr>
<td>$z_{1/4}$</td>
<td>3500–7250 mm</td>
</tr>
<tr>
<td>$k_{1/4}$</td>
<td>2.0 mJ m$^{-2}$ K$^{-1}$</td>
</tr>
<tr>
<td>$\phi_{1/4}$</td>
<td>0.15–0.45 m</td>
</tr>
</tbody>
</table>

The concentration of dissolved anhydrite in the reservoir brine and the upwelling fluid are slightly smaller than the corresponding equilibrium values.
creating a small but highly permeable volume. As injection continues, more and more brine is injected into this highly permeable volume. However, such an experiment cannot be considered seriously in real practice due to the long time (13 days) and the large quantities (558 t) of NaCl which is required for a breakthrough (Fig. 4). As a more practical alternative, we consider a combination of mechanical and chemical stimulation in the next section.

5. Combined mechanical and chemical stimulation

Hydraulic fracturing is a standard technique for increasing reservoir permeability. This technique is commonly used in the hydrocarbon industry. A combination of mechanical and chemical stimulation techniques may provide additional significant improvement of reservoir properties. We studied this effect using a horizontal, two-dimensional Cartesian FD grid representing the most cemented layer of the Allermöhe reservoir from $z = 14–14.15$ m (Fig. 3). Because of the large computing time for a full three-dimensional model, we concentrated on the analysis of anhydrite dissolution in one horizontal layer only. Due to the different model geometry (Cartesian instead of cylindrical grid), the cemented volume around the injection well has a rectangular instead of a circular symmetry. Apart from this, all other model parameters are like in the corresponding model volume in the cylindrical model, shown at $z = 14–14.15$ m in Fig. 3. For the analysis of the effect of a combined chemical and mechanical stimulation, we consider a combination of mechanical and chemical stimulation in the next section.

Fig. 4. Increase of injection rate with time and salinity of the injected brine due to the dissolution of anhydrite around the borehole. Pressure was kept constant during the entire stimulation (reservoir temperature: 125°C, injection temperature 80°C, 70°C, 60°C: full line, small dash, long dash). The numbers at the arrows indicate the total amount of salt and the stimulation time.

Fig. 5. Simulation of a chemical borehole stimulation by brine injection based on a vertical cylindrical model. Anhydrite cementation is confined within 5 m around the injection well. The borehole (thick black line) is shown to the left; left panel: porosity after 1 day, right panel: porosity after 11 days.
stimulation, a fracture with an aperture \( d = 10 \text{ mm} \) was embedded in the model space. It penetrates the cemented volume completely. For the fracture an equivalent porous medium permeability was calculated from the so-called “cubic law” (e.g. [19]):

\[
k = \phi_i \delta \frac{d^2}{12}.
\]

(10)

A factor \( \delta = 0.25 \) was introduced to achieve a more realistic permeability value which accounts for the rough fracture wall surface [20]. Since SHEMAT is restricted to flow in porous media, an arbitrary porosity \( \phi_i = 0.1 \) needed to be specified for cells which represent the fracture. However, the porosity of the fracture cells does not influence the results, because all fracture cells were defined to be chemically inactive. Besides, after 1 h of stimulation, the pressure field in the fracture is almost in a steady state. Therefore, the specific storage coefficient and thus the porosity do not affect the flow field any more. Fig. 6 shows the injection rate increase due to the dissolution of anhydrite around the well. The dashed line shows the increase in injection rate in this small layer, when a fracture connects the well with the highly permeable reservoir beyond the cemented volume at a distance of 5 m from the well. The solid line in Fig. 6 corresponds to the unfractured case. Here, the increase of injection rate is caused by chemical dissolution only, while the much stronger increase of the combined mechanical and chemical stimulation is caused by chemical dissolution at the fracture wall. The difference between the two injection rates at time zero shows the additional permeability provided by the fracture itself. The sharp increase in injection rate shown by the dashed line is caused by the dissolution of anhydrite at the fracture wall. After approximately 5 days, the injection rate is dominated by the effect of chemical dissolution around the borehole. This is indicated by the gradient of the dashed line, which equals that of the solid line. This shows clearly that a combined mechanical and chemical stimulation can achieve a much more effective stimulation of cemented reservoirs than a purely mechanical or chemical stimulation alone.

### 6. Strata-bound convective flow

Density-driven free convection is a possible mechanism for transport of dissolved anhydrite in the Rhaetian sandstone over distances of several kilometers. Our reactive transport model is based on the assumption that anhydrite is available from the margin of salt structures only. We studied strata-bound convective flow around the Allermöhe borehole location. The model extends 11 × 11 km in the horizontal and 5 km in the vertical. The three-dimensional structure of the model space was obtained by digitizing two-dimensional maps of the most important stratigraphic units in the “Tectonic Atlas of Northwest Germany” [21]. The three-dimensional (3-D) stratigraphic units were converted in to a block-centered, 3-D FD grid with uniform block size of 250 m × 250 m × 50 m. The structure of the stratigraphic units is dominated by the two salt diapirs Meckelfeld and Reitbrook. Fig. 7 shows the map view of the model area including both diapers, the topography of the Keuper bottom, and the location of the Allermöhe well. The extent of the model area corresponds with the geological map sheet TK 2526 of Hamburg [22]. The different stratigraphic units correspond to model regions with uniform physical properties. Table 2 summarizes thermal capacity \( \rho c \), thermal conductivity \( \lambda \), porosity \( \phi \), and permeability \( k \) of rock types which were used to define the stratigraphic units. The Keuper was divided into a high-permeability unit of 250 m thickness (Rhaetian sandstone) and a layer with properties which correspond to clay beneath (Table 2). The composition of the Keuper formation water was derived from laboratory measurements of the formation water at Allermöhe [9] which has a total amount of dissolved species of 218 g L\(^{-1}\) (1250 mg K\(^{+}\), 75 g Na\(^{+}\), 6690 mg Ca\(^{2+}\), 1300 mg Mg\(^{2+}\), 132, 3 g Cl\(^{-}\), 465 mg SO\(_4^{2-}\) and 240 mg HCO\(_3^{-}\)) and a pH of 5.4. The Rhaetian sandstone is assumed to be initially free of anhydrite.

With this simulation we aim to determine precipitation patterns of anhydrite within the entire area of the Allermöhe map sheet. Additionally, we wish to test whether the cementation observed in the Allermöhe
borehole can be attributed to anhydrite, which was dissolved at the margins of the salt diapirs. In order to economize computing time the model was limited to the depth interval 1750–4750 m which comprises the entire Keuper formation. The transient simulation extended over 50,000 years and it was assumed that the brine is always in chemical equilibrium with the rock and that precipitation of anhydrite occurs as fast as dissolution. A temperature log recorded in 1998 [16] prior to the pumping tests is used to check the heat flow boundary condition at the model bottom and the assumed thermal conductivities of the different strata. We found no significant difference between calculated and measured temperature (Fig. 8).

Table 2
Rock types and properties used for numerical simulation of reactive flow around the Allermöhe borehole ($\rho c$: thermal capacity; $\lambda$: thermal conductivity; $\phi$: porosity; $k$: permeability; compiled by [9])

<table>
<thead>
<tr>
<th>Rock type</th>
<th>$\rho c$ (MJ m$^{-3}$ K$^{-1}$)</th>
<th>$\lambda$ (W m$^{-1}$ K$^{-1}$)</th>
<th>$\phi$ (–)</th>
<th>$k$ (m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand, sandstone (dry)</td>
<td>1.6</td>
<td>1.3</td>
<td>0.1–0.3</td>
<td>$10^{-14}$–$10^{-12}$</td>
</tr>
<tr>
<td>Clay</td>
<td>2.04</td>
<td>1.28</td>
<td>0.005</td>
<td>$1 \times 10^{-16}$</td>
</tr>
<tr>
<td>Limestone</td>
<td>2.5</td>
<td>2.2</td>
<td>0.16</td>
<td>$1 \times 10^{-13}$</td>
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<tr>
<td>Halite</td>
<td>1.95</td>
<td>6.1</td>
<td>0.0001</td>
<td>0.0</td>
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<tr>
<td>Rhaetian sandstone</td>
<td>1.6</td>
<td>1.3</td>
<td>0.07</td>
<td>$0.4 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

Fig. 9 shows in plan view the extent of the projection of the Lias bottom onto the Allermöhe map sheet, the location of the Allermöhe borehole, and the diapirs of Meckelfeld and Reitbrook. The arrows show the simulated Darcy flow field within the Rhaetian sandstone at the Allermöhe borehole after a simulation time of 50,000 years. It can be seen that the flow circulates clock-wise, in general. Starting from the western border of the Reitbrook salt dome east to the Allermöhe well, the main flow is directed south, down-dip in the Rhaetian formation. Approximately 2000 m to the south of the Reitbrook diapir, flow turns west towards the Meckelfeld diapir. Approximately 1500 m to the north of the Meckelfeld diapir the main flow is
directed north down into the deepest point of the formation. Emerging from this trough, the brine flows up-dip towards the east to the Allermöhe borehole and back to the Reitbrook diapir. The gray areas in Fig. 9 indicate reservoir regions where anhydrite content exceeds 10 mol m\(^{-3}\) due to the transport of solutes from the salt structures and the subsequent precipitation of anhydrite at deeper and therefore warmer locations in the reservoir. It appears that significant amounts of anhydrite occur only in the southern parts of the model area, but not around the Allermöhe borehole. This is owed to the fact that the large convection cell turns clockwise and the solutes, leached from the salt structures, first flow down into deeper and hotter parts of the 3-D structure, where anhydrite is precipitated. Flow towards the location of the Allermöhe well is directed up-dip the Rhaetiansandstone, towards lower reservoir temperatures with a correspondingly lower probability of precipitation. It is most unlikely that reservoir brines enriched in calcium sulfate leached from the salt domes would reach the location of the Allermöhe well by advective transport. However, this result demonstrates that density driven flow bound to strata with complex topography may carry dissolved species over distances of several kilometers and over long times. After 50,000 years of simulation roughly 10molm\(^{-3}\) of anhydrite precipitate in the Rhaetian aquifer (Fig. 9). For our purpose, the average flow velocity of the strata-bound convection flow, \(v_D \approx 1\text{ m yr}^{-1}\), is the most important result of this simulation. The transport time of dissolved species in one cell of 250 m length is therefore roughly 500 years. This corroborates the assumption of equilibrium chemical conditions.
7. Episodic high-temperature events

With a molar volume of \(4.6 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}\), the total amount of anhydrite which precipitated in the Rhaetian aquifer model corresponds to a decrease in porosity of nearly \(4.6 \times 10^{-4}\). Roughly 2000–4000 mol m\(^{-3}\) of anhydrite are required to fill in the entire pore space. Therefore, the almost complete pore space clogging observed at Neuruppin and Allermöhe [1], can be explained only by assuming a temporary high-temperature event, which reduces the solubility of anhydrite locally. Hot fluids from deeper reservoirs may quickly flow upward along seismically activated faults. Then Ca\(^{2+}\) and SO\(_2\)\(^{-}\) dissolved in the reservoir brine will precipitate where the hot fracture flow heats up the reservoir locally. Gaupp [23] suggests that such a high-temperature event is the reason for the anhydrite cementation observed in the Rhaetian aquifer near Hannover (Germany). Fluid inclusion data suggest that the original reservoir fluid was mixed with a mineralized hot fluid, probably upwelling from a deeper reservoir, resulting in a precipitation of anhydrite in the more shallow and therefore colder reservoir. A second evidence for a temporary in-flow of hot fluids is the increased coal rank \(R_0\) of samples from the Rhaetian aquifer at Neuruppin (Np Gt/Nn 2/87, anhydrite cementation, \(R_0 = 0.57\)) in contrast to samples from Siedenlangenbeck (Dp Sgk 1/84, no anhydrite cementation, \(R_0 = 0.33\)). Both locations experienced a similar sedimentation history, implying a residence time of at least 10 Ma in roughly 2000 m depth, corresponding to a reservoir temperature of approximately 60–70°C. The anomalously high coal rank \(R_0 = 0.57\%\) of samples from Np Gt/Nn 2/87 indicates a high-temperature event at this location, as it can be attributed to a local increase in temperature. In order to test this assumption, several coal rank scenarios were calculated considering various temperature differences (Table 3). Obviously, the measured coal rank of \(R_0 = 0.57\%\) of specimen of Np Gt/Nn 2/87 can only be explained by the temperature-time scenarios in the first four rows of Table 3, while the coal rank of specimen Dp Sgk 1/84, \(R_0 = 0.33\%\) results from the assumed sedimentation history alone.

The effect of a local increase in temperature on the degree of cementation was also studied by numerical simulations, based on a horizontal 2-D FD grid containing a fault, along which hot fluids discharge into the reservoir. The model has a horizontal extent of 1000 m × 1000 m and a thickness of 20 m, which adequately represents the dimension of the high-permeability zones of the Rhaetian aquifer at Neuruppin [1]. The amount of dissolved Ca\(^{2+}\) and SO\(_2\)\(^{-}\) in the reservoir brine which has a temperature of 70°C and a constant horizontal Darcy velocity of \(v_D = 2 \text{ m yr}^{-1}\), are assumed to be in chemical equilibrium. The size of the square FD blocks increases continuously by a factor of 1.2 from 1 m up to their maximum values at the margin of the model space. The specific discharge \(q\) of the upwelling fluids is a model parameter for which there is not even a rough indication. Similarly we lack information about the dimension and shape of the fracture zone from which the hot fluids discharge. Therefore, we approximated the fracture zone by a single model block with a constant discharge rate \(q = 0.1 \text{ L s}^{-1}\). Nevertheless, a fracture was found in specimen from the Gt/Nn 2/87 well, which is possibly part of the deep north–south running Neuruppin fault-system, which is part of the North-East German basin [24]. For highly resolved grids with correspondingly small grid blocks, kinetic control is required for the chemical reactions, because chemical equilibrium will not occur in the small blocks at these flow rates. The cementation scenario described above was simulated assuming kinetically controlled precipitation with a reaction rate of \(A \times R_0 = 2.2 \times 10^{-6} \text{ mol m}^{-3} \text{ s}^{-1}\). Table 1 summarizes the model parameter of this simulation. The pore space was initialized with a specific volume \(A = 3614 \text{ m}^2 \text{ m}^{-3}\) of anhydrite corresponding to the precipitation rate measured in the core-flooding experiment. Although the model space is assumed to be initially totally free of anhydrite, a specific surface \(A\) needs to be defined for each cell so that dissolution or precipitation may occur.

Fig. 10 summarizes the results of the numerical simulation of the Neuruppin-scenario. Panels a and b show the distribution of anhydrite content and porosity, respectively, after 1000 years of simulation, panels c and d after 10,000 years. The reservoir brine flows from left to right, until it reaches the inflow zone in the center of the model. Due to the solubility difference of calcite and sulfate between the reservoir brine at 70°C and the upwelling fluid at 125°C, anhydrite precipitates upstream from the heated inflow. After 1000 years, porosity is decreased by precipitation from originally 15% to approximately 13%, corresponding to a reduction of permeability of 4.85% × 2% = 9.70% (\(\Delta k/k = 4.85\Delta \phi/\phi\), see Eq. (9)). However, after 10,000 years the pore space around the inflow region is almost

<table>
<thead>
<tr>
<th>Time (Ma)</th>
<th>Temperature (°C)</th>
<th>(R_{O_{2c}})</th>
</tr>
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<tbody>
<tr>
<td>0.001</td>
<td>180</td>
<td>0.583</td>
</tr>
<tr>
<td>0.01</td>
<td>160</td>
<td>0.568</td>
</tr>
<tr>
<td>0.1</td>
<td>140</td>
<td>0.573</td>
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<tr>
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</tr>
<tr>
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<td>90</td>
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</tr>
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<td>0.320</td>
</tr>
<tr>
<td>100</td>
<td>60</td>
<td>0.342</td>
</tr>
</tbody>
</table>

Data computed using the %EASY%\(R_O\) software [25].
completely clogged to 2.5% porosity, which corresponds to a decrease of permeability by $4.85\% \times 12.5\% = 60.6\%$. To the right of the injection area, the reservoir brine does not mix with the upwelling fluid, and no anhydrite precipitation occurs as long as the hot fluids discharge from the fracture zone. This phenomenon may possibly explain the fact that the Rhaetian aquifer is almost completely cemented by anhydrite at the borehole Np Gt/Nn 1/88, while almost no anhydrite was found at the neighboring borehole Np Gt/Nn 2/87, only 1.5 km away.

Additional parameter studies were performed where $q$ and $v_D$ were varied independently by orders of magnitude: the ratio $v_q/v_D$ of the horizontal Darcy velocity $v_q$ at the boundary of the cell representing the fracture and the velocity $v_D$ of the reservoir brine, dominates the shape of the cementation pattern and the amount of anhydrite which precipitates around the fracture zone. For $v_q/v_D > 10$, the inflow displaces the reservoir brine. In this case, the heat energy of the inflow and the anhydrite precipitation is spread over a huge reservoir volume. On the contrary, if the inflow is very small ($v_q/v_D < 10$), it will be mostly absorbed by the reservoir brine, and precipitation of anhydrite is therefore limited to a very small volume near the fracture zone.

8. Summary

Our regional simulations suggest that minerals such as anhydrite may clog the pore space near of fault zones which had been activated temporarily by seismic events. Without an additional heat event, anhydrite will only precipitate in small amounts where strata-bound flow is directed down-dip into deep and warmer regions of the reservoir. This suggests that it may be impossible to predict anhydrite cementation patterns from reservoir topography alone. However, coal rank data from reservoir rock samples can provide clues about the occurrence of pore-filling minerals near the borehole.

With respect to unproductive boreholes, drilled for instance for heat mining installations, our reservoir simulations show that a cemented pore space, such as in the Rhaetian aquifer at Allermöhe, can be stimulated by injection of highly saline brine. However, a combination of both mechanical and chemical stimulation results in an additional and significant improvement of the reservoir.
Acknowledgements

The research reported in this paper was supported by the German Federal Ministry for Economy and Technology (BMWi) under Grant 0327095 to RWTH Aachen University. Two anonymous reviews are gratefully acknowledged for constructive and helpful comments.

References