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Experimental interaction of hydrothermal Na-Cl solution with fracture surfaces of geothermal reservoir sandstone of the Upper Rhine Graben

Roman B. Schmidt [a, *], Kurt Bucher [b], Kirsten Drüppel [a], Ingrid Stober [a]

[a] *Karlsruhe Institute of Technology, Institute of Applied Geosciences, Adenauerring 20b, 76131 Karlsruhe, Germany*
[b] *University of Freiburg, Institute of Geosciences, Albertstraße 23b, 79098 Freiburg, Germany*

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ABSTRACT

The Upper Rhine Graben (URG) is a Tertiary rift structure in central Europe offering favorable conditions for geothermal energy utilization. Relatively high heat flow combines with sufficiently high permeability of the hydrothermal reservoirs. One of the target stratigraphic levels is the lower Triassic sandstone formation (Buntsandstein), where hot water resources at temperatures up to 250 °C can be utilized. Extensional neotectonics and hydraulic stimulation form new fracture surfaces in the reservoir rocks (enhanced geothermal system, EGS). The exposed fresh rock fracture surface reacts with the highly saline reservoir brines (Na-Cl up to 200 g l^{-1}) with consequences for the permeability of the reservoir.

In order to better understand the dynamic evolution of fault systems caused by fluid-rock interaction, we conducted batch-type experiments in a stirred autoclave system and reacted arkosic sandstone with synthetic 2 molal Na-Cl solution at temperatures of 200 °C and 260 °C. After 45–55 days reaction time altered rock samples were compared with the starting material and the geochemical-mineralogical processes were deduced with the help of XRD, SEM methods and EMP measurements. Fluid compositions were examined by ICP-MS, ICP-OES and IC.

The arkosic sandstones show a surprisingly high reactivity during the experiments. Quartz grain surfaces show deep dissolution features and all reaction fluids were saturated with respects to quartz. Illite and kaolinite from the primary sandstone cementation completely dissolved from the sample surface. Perfectly euhedral crystals of metastable analcime formed during the experiment as separate crystals on quartz, as groups or clusters and as surface covering mats. The overall net transfer process dissolves quartz + illite + kaolinite ± K-feldspar and precipitates analcime + chlorite ± albite. The process is accompanied by a total volume increase of the solids of 20–30 vol%. K-feldspar dissolution is hampered by albitization rims shielding K-feldspar and efficiently preventing an equilibration of the Na–K exchange with the fluid. The experiments show changes on the rock surface, leading to an increase of the aperture of a single fracture during the early phases of reaction and later to a decrease as the fluid-rock reaction progresses. Alteration of the fracture surface also generates loose fragments and altered minerals. This fine material may efficiently reduce the fracture aperture at narrow points along the fracture.

1. Introduction

The economic success of utilizing deep geothermal energy at a specific site depends on a maintainable high temperature of the heat transfer fluid and on a high permeability of the particular reservoir rock at target depth. Low enthalpy geothermal reservoirs reside typically at several km depth, e.g. Soultz-Sous-Forêts at 5 km depth and 200 °C (Gérard et al., 2006; Genter et al., 2010). The permeability of continental crust at several km depth is related to fractures and faults providing pathways for fluid migration (Stober and Bucher, 2005; Bucher and Stober, 2010), which are generally filled with saline fluid (Gascoyne et al., 1987; Hanor, 1994; Pauwels et al., 1993; Stober and Bucher, 2014).

Permeability of crustal rocks at reservoir depth is a dynamic property of the system (see several contributions in Gleeson and Ingebritsen, 2016). Permeability changes as a result of continuous mechanical deformation and ongoing chemical interaction

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* Corresponding author.
E-mail address: roman.schmidt@kit.edu (R.B. Schmidt).
URL: http://www.agw.kit.edu

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between the fractured rocks and the fluid residing in the fracture porosity. This paper reports on the experimental geochemical alteration of fracture surfaces in sandstones resulting from fluid-rock interaction at reservoir temperatures (200 °C and 260 °C).

The Upper Rhine Graben (URG) in Central Europe, is an Oligocene rift structure (Illies, 1972; Illies and Greiner, 1978; Behrmann et al., 2003; Schwarz and Henk, 2005) offering favorable conditions for utilization of geothermal energy. Fluid temperatures are up to 250 °C at 4 km depth in the Permian and Triassic metasediments of the graben center (Dezayes et al., 2008; Sanjuan et al., 2016). Geothermal installation in these strata are e.g. Bruchsal, where in a depth of 1800–2500 m a fluid temperature of 128 °C is produced (Pauwels et al., 1993). Also at Rittershoffen two wells have been drilled to 2600 m and 3200 m in these sandstone reservoirs, where the saline fluid has a temperature of 170 °C (Baujard et al., 2017).

The URG fluids are Na-Cl dominated brines with a total of dissolved solids (TDS) up to 200 g l^{-1} (Pauwels et al., 1993; Komninou and Yardley, 1997; Aquilina et al., 1997; Stober and Bucher, 2014; Sanjuan et al., 2016). Fracture surfaces created by neo-tectonics in the stressed graben or as a consequence of hydraulic stimulation of geothermal reservoirs (enhanced geothermal systems, EGS) result in an exposition of fresh sandstone mineral assemblages to the 200± 50 °C hot brine. Due to the disturbance of the equilibrated system in the reservoir formation, a reaction of the sandstone with the brine is highly presumable.

The geochemical-mineralogical dynamics in geological reservoirs have a major influence on the permeability and the lifetime of a geothermal system (Bertrand et al., 1994; Milodowski et al., 1989; Morrow et al., 2001). Dissolution of primary minerals increases fracture apertures, whereas precipitation of secondary minerals from the brine seals fractures and joints reducing fluid flow permeability.

Fluid-rock interaction experiments at hydrothermal conditions mostly used powder or granulated samples as starting material (Savage et al., 1992; Shao et al., 2011; Xie and Walther, 1993) and typically with a reaction fluid of low salinity (Vaughan et al., 1986; Moore et al., 1983; Bertrand et al., 1994; Kuncoro et al., 2010). Recently several experimental fluid-rock interaction studies using high saline solutions were conducted in the context of the geological storage of CO_2 (Kaszuba et al., 2005; Shiraki and Dunn, 2000; Shao et al., 2011; Fischer et al., 2010, 2011; Hu et al., 2011; Lafay et al., 2014). Experimental studies of fluid-rock interaction have been conducted on basement rocks and minerals (Hövelmann et al., 2010), sedimentary rocks (Bertrand et al., 1994; James et al., 2003) and specifically of rocks from the URG (Pauwels et al., 1992). In these studies, typically various clay minerals including illite and chlorite from hydrothermal alteration of basement rocks were produced.

In this paper we present an experimental study on the consequences of reaction of URG reservoir sandstone surfaces (rock surfaces) with a synthetic geothermal fluid with a salinity typical of URG reservoir fluids. We investigated rock samples from the Buntsandstein before and after these experiments. The analytical data permit an evaluation of reaction paths controlling the alteration of primary mineral assemblages at temperatures that are relevant for geothermal applications (200–260 °C).

The study focuses on the geochemical, mineralogical and textural changes of water-conducting joints and fractures (represented by fresh sample surfaces) from a fresh to an intensely altered sandstone surface, due to the reaction with highly saline solution. Additionally, consequences concerning the evolution of the reservoir permeability are deduced.

2. Material and methods

2.1. Rock material

Two different sandstones have been used as representative reservoir rocks in the hydrothermal experiments: Pfinztal Sandstone (PfSst) and Tennenbach Sandstone (TenSst) as proxies for the lower Triassic Buntsandstein formation in the Upper Rhine Graben (URG). Both samples have been collected in local quarries, close to the URG, as blocks of about 30 × 30 × 40 cm^3. In the laboratory cores of ~22 mm were drilled from the sandstone blocks. They were broken perpendicular to the core axis to get a fresh rock surface. Then, the core pieces were shortened to a height of 5–20 mm. Afterward, the samples were washed properly with deionized water and dried before use in the experiments.

2.2. Composition of the solution

A 2 molal Na-Cl solution (116.9 g kg^{-1}) was prepared with deionized water and NaCl salt and used as reactive solution for the experiments, which approximate to the URG brines (TDS of 94–200 g l^{-1}, Stober and Bucher, 2014). The pure Na-Cl solution used in the experiments closely reflects the Na-Cl constitutes of 88–94 mol.% of the reservoir brines (Pauwels et al., 1993). This initial solution contained also a small amount of inorganic carbon given by the carbon exchange of the deionized water with the atmosphere (alkalinity of <0.1 mmol l^{-1}). Also, small quantities of O_2 should be solved through contact with atmosphere. The initial pH of the solution was 5.5, measured at 25 °C.

2.3. Experimental setup and procedure

Batch-type experiments in a stirred autoclave system (Limbo li, buechi) were performed (Fig. 1). In the autoclave we reacted sandstone surfaces with the 2 molal Na-Cl solution at elevated temperatures. One additional experiment has been conducted with 1.5 molal Na-Cl solution (PfSst, 260 °C). The vessel and every component in contact with the solution is composed of stainless steel (X6NiCrTiMoVB25-15-2, EU standard 10269). The total volume of the vessel is 450 ml. Solution volume during the experiments was 350 ml with an atmospheric headspace. The stirrer speed was about 100 rpm. Three cylindrical solid samples were used in each experiment. From the anisotropic PfSst samples broken surfaces, parallel as well as perpendicular to the bedding, were used.

The duration of the experiments was 46 d for PfSst and 54 d and 55 d for the TenSst. Temperatures during the experiments were 200 °C and 260 °C for both lithologies, respectively. These temperatures are reported (measured and maximum geothermometer temperatures) from reservoirs in the URG (Aquilina et al., 1997; Sanjuan et al., 2016). Experiments were carried out under pressures of ~16 bar and ~44 bar at 200 °C and 260 °C, respectively, given by the boiling conditions of the 2 molal Na-Cl solution.

2.4. Analysis of the fluids

The fluid in the autoclave was cooled down rapidly after each experiment. Electric conductivity (Mettler Toledo Inlab 371) and pH (ProMinent PHER-112) were measured immediately. Carbonate alkalinity was determined by titration with 0.01 M HCl. The experiment solution was filtered with a 0.2 μm cellulose acetate membrane for further fluid analyses. To prevent precipitation reactions, the fluid samples were diluted with ultra-pure water by a factor of 10 and, for cation measurements, acidified with distilled HNO_3. Samples were stored in 30 ml polyethylene bottles and