Geochemical characteristics of the formation fluid identified during stimulation tests on the Rotliegend geothermal reservoir in the NE German Basin (NEGB)

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Abstract

World-wide experience in high-enthalpy geothermics showed that, while geothermal fluids are exploited, scaling as well as corrosion cause the main problems. Their character is affected by the chemical composition of reservoir fluids and their interaction with reservoir rocks or with injection fluids. During the stimulation and hydraulic tests in the well Groß Schönebeck E Gr Sk 3/90, geochemical investigations on more than 80 drilling fluids, produced fluids, down-hole samples, and wellhead gas samples were conducted since December 2000. In parallel, the diagenetic evolution was reconstructed. The characterisation of pore space filling minerals is based on petrographic determinations of thin sections from approx. 200 drill cores of Permo-Carboniferous rocks from the NEGB. Secondarily formed minerals - mainly quartz, carbonates, anhydrite, hematite, and illite - correspond with the pore fluid. This reservoir fluid, represented by the deep well, is characterised by high temperature (150°C), high salinity (260 g/l), and high contents of heavy metals such as iron. The latter may be caused by the missed geochemical barrier of sulfide. There is a distinct tendency to precipitate iron minerals, especially when contaminated with O_2. The influx of O_2 is connected with the supply of injection fluids during stimulation tests. Geochemical models show the risk of precipitation of baryte, anhydrite and amorphous silica, conditionally of calcite or aragonite, respectively.
Beside chemical interactions among the involved fluids and rock composition, changes of temperature, pH and Eh are responsible for the scale precipitations.

Keywords: stimulation tests, geothermal fluids, North-German Basin, fluid-rock interaction

1 Introduction

The north German deep waters which are found down to a depth of 2,500 m and with max. temperatures of 100°C are well known from the operation of several Geothermal Heating Plants (GHP) [1,2]. Due to the high salt contents and the acid media, they support the corrosion. In addition, the content of solute iron(II) is high resulting in sensitive reaction to changes of the pH value and the entry of oxygen. They contain gases with changing composition which may lead to degassing when relieved from pressure [3]. The smooth circulation of the thermal water within in loop is endangered accordingly by

- changes of the mineral solution balances due to the alternating conditions during production and cooling-down of the reservoir fluid
- fluid-rock reactions in the reservoir
- fluid-fluid reactions (reservoir fluid and drilling fluid).

When the temperature is > 100°C, deep waters may become interesting for electric power generation. With a mean geothermal gradient of 3-3.5 K/100 m, wells have to be drilled down to 3,000 – 4,000 m for this purpose. In this depth, Rotliegend sandstones are found in the North German Basin.
In 2000, the former gas exploratory well was re-opened and deepened down to 4,294 m to serve as a down-hole laboratory for investigation of the usability of the formation fluids for electric power generation from geothermal heat. The most important influx of geothermal fluids was expected from the Rotliegend aeolian sandstones as these rocks form the gas reservoirs preferred by the oil/gas industry. Furthermore, laboratory measurements on cores attested fairly good permeability. The initial hydraulic parameters were determined in a primary test in 2001 [4]. This test showed that the permeabilities of the 4,000 m deep Rotliegend rocks are too low for any efficient production of the 150°C hot formation water. To enhance the existing pathways and form new migration paths, hydraulic fracturing was tested.
In order to avoid unfavourable reactions with external waters during injection (hydraulic injection tests) and to secure smooth production and reinjection of the formation fluid in later operation, the fluid chemistry must be known exactly.

2 Experimental

2.1 Geological overview

The tested well cuts through 2,370 m of Cenozoic and Mesozoic sediments followed by 1,492 m of Zechstein evaporites, 368 m of Rotliegend sediments and bottoms in Mg-rich andesites in a depth of 4,240 m. The open-hole section extends from 3,910 m down to 4,240 m. The Rotliegend section underlies the Zechstein (depth: 3,881 m) and can be subdivided into three main sections, from top to bottom: siltstones (203 m), sandstones (180 m) and basal conglomerates (29 m)-(Fig.1). The sandstones are lithoclast-bearing quartz-sandstones cemented by major amounts of quartz and carbonate as well as smaller amounts of albite, anhydrite, chlorite and hematite. Relatively high porosities of up to 15% and permeabilities of up to 10^{-14} m^2 (10 mD) indicate that these sandstones could locally be the main supplier of geothermal fluids. Permo-Carboniferous, vesicular, Mg-rich andesite was drilled through between 4,230 m and 4,294 m. This rock sequence is expected to be about 200 m thick (Beneck et al., 1996). These igneous rocks are strongly fractured, altered, and contain a large number of vesicles. Individual vesicles are up to 5 mm large and linear disposed. Secondary minerals occur in parageneses similar to those of the sandstones. Carboniferous siltstones and mudstones underlie the volcanic rocks.

2.2 Drilling and testing

The following operations were executed and are planned for advancing studies:

1990 Drilling of the Groß Schönebeck well down to 4,240 m for gas exploration.
1990 Filling and capping of the well.
2000 Re-opening and deepening of the well down to 4,294 m [5].
2001 Primary test for determination of initial parameters (Hurter et al., 2002).
2002 Stimulation of Rotliegend sandstones in packer-isolated test intervals with high-viscous fluids (polymers) and proppants (specifications see below).
2002 Pump tests producing 700 m^3 of the formation fluid.
2003 Open-hole stimulation (water-frac) in Rotliegend rock

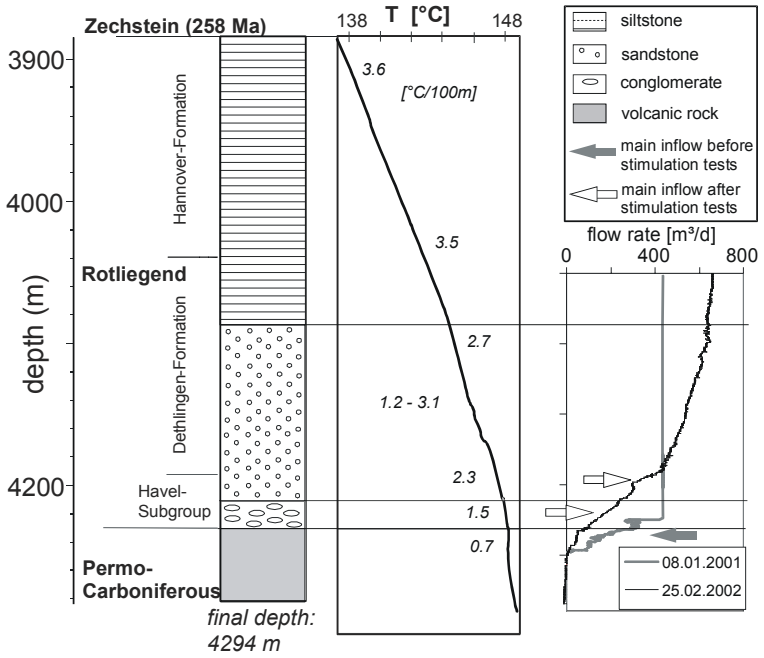


Fig. 1: Stratigraphy, lithology, flow log, and vertical temperture distribution of well E Gr Sk 3/90.

The well E Gr Sk 3/90 was re-opened and deepened by flush drilling using a basic bentonite-water mixture (pH ≈ 12). During the primary test in 2001, totally 334 m³ of fluid were produced. Prior to the beginning of production, the well was filled with drilling mud (V ≈ 125 m³).

Fluid samples were analysed regularly in situ in order to monitor the progress of unhindered production. The ex-mixing of the mud fluid by the formation fluid could be well observed. At the end of the production period, the share of the formation fluid was more than 95 %. When the influx profiling was completed, downhole samples (cf. Table 1) were taken which represented the quasi-pure formation fluid [6].

In January 2002, tests started with circulation of NaCl brine (density: 1.12 g/cm^3). The open-hole stimulation of Rotliegend sediments was targeted at two intervals in the sandstones: 4,130-4,190 m and 4,081-4,118 m. The stimulation concept was based on the experience from oil and gas exploration. Packers isolated the test interval, and thickened fluid and proppants (Carbolite) were applied for fracturing. The applied frac-fluid consisted of a cationic polymer with a net-like structure (1-1.3 %) and water. By building-in water molecules into the intermediate layers of the polymer, a viscosity of approx. 2,000 cP was achieved. Citric acid was added to the frac-fluid in order to keep dissolved in the formation fluid in particular the high contents of iron(II) ions. When in contact with oxygen and pH increases, the iron(II) ions will oxidise to iron(III). Subsequent precipitation of complex oxihydroxide may lead to blocking of the reservoir section. The nitrogen lift tests following the stimulation of the Rotliegend sandstones were aimed at re-production of the decomposed frac-fluid from the formation and record of the influx.

The various injection and production tests and the volumes of the respective fluids are given in Table 1. The down-hole samples were taken for comparison of the fluid composition before and after stimulation (Tables 1).

Totally, 532 m^3 of frac-fluid and NaCl-brine as well as 20 t of proppants were injected. A large share of the injected fluids together with Rotliegend formation water was produced during several lift and pump tests, the total volume amounting to 938 m^3. Altogether, 406 m^3 more fluid were produced than injected. This total corresponds to approx. three borehole volumes.

Table 1: Produced and injected fluids - well E Gr Sk 3/90 *shadowed – produced fluid, normal – injected fluids, GLT – production test, CLT – casing lift production test, FLT – flowmeter test, Z – citric acid, HTU – viscous gel

Date	Process	Fluid volume [m^3]*	Injected fluid composition
09.01.01	down-hole sampling (before stimulation)		
21.-23.12.01	Circulation	**57**	NaCl brine
17.01.02	1.GLT	**-65**	
18.01.02	1. data-frac	**90**	1.0%HTU+0.5%Z
20.01.02	1. main-frac	**80**	1.3%HTU+0.5%Z
22.01.02	2. GLT	**-100**	
26.01.02	2. data-frac	**75**	1.3%HTU+0.5%Z
28.01.02	2. main-frac	**90**	1.3%HTU+0.5%Z
31.01.02	gravel packing	**140**	1.0%HTU+0.5%Z
02.-03.02.02	1. CLT	**-264**	
3.02.02	1. FLT	**-69**	
25.02.02	2. FLT	**-133**	
27.-28.02.02	2. CLT	**-307**	
02.03.02	down-hole sampling (after stimulation)		
06.-09.02	pump tests	**-700**	
15.10.02	down-hole sampling (after pump test)		

After about 4 months, a pump test was carried out in order to identify the hydraulic properties in the near-well zone and to return more produced frac-fluid [7]. Totally, 700 m³ of deep fluid were produced over a period of 2 months. Then, another downhole sample was taken.

3 Hydrochemical results

3.1 Share of formation fluid in the produced fluid

Continuously, the fluids produced during the different lift tests were analysed in-situ (temperature, pH, Eh, density) for monitoring the progress of the freeing from the injected fluids. 25 samples were subjected to detailed chemical analysis. Figure 2 shows the change of the ratio of the Ca ions over the Na ions in the course of the respective test. The fluid lifted in the first test (GLT 1) is a mixture composed of NaCl brine and formation fluid. As expected, the sodium content decreases with the Ca content increasing.

Through the first stimulation, the formation fluid became quasi-diluted resulting in the continuous increase of both the Ca and Na contents of the produced fluids. This becomes evident also in Figure 3 presenting the lithium concentration c (Li) as a function of the TDS (Total Dissolved Solids). The lithium concentration of the samples correlates with the TDS. Ions behaving like tracers (e.g., Li) show smooth ex-mixing without retention [6]. At the end of the production test after the first frac (GLT 2), the share of the formation fluid in the mixed fluid was 80 %.

Upon completion of the 2nd test phase, c (Li) and TDS complied with those of the downhole samples taken in 2001.

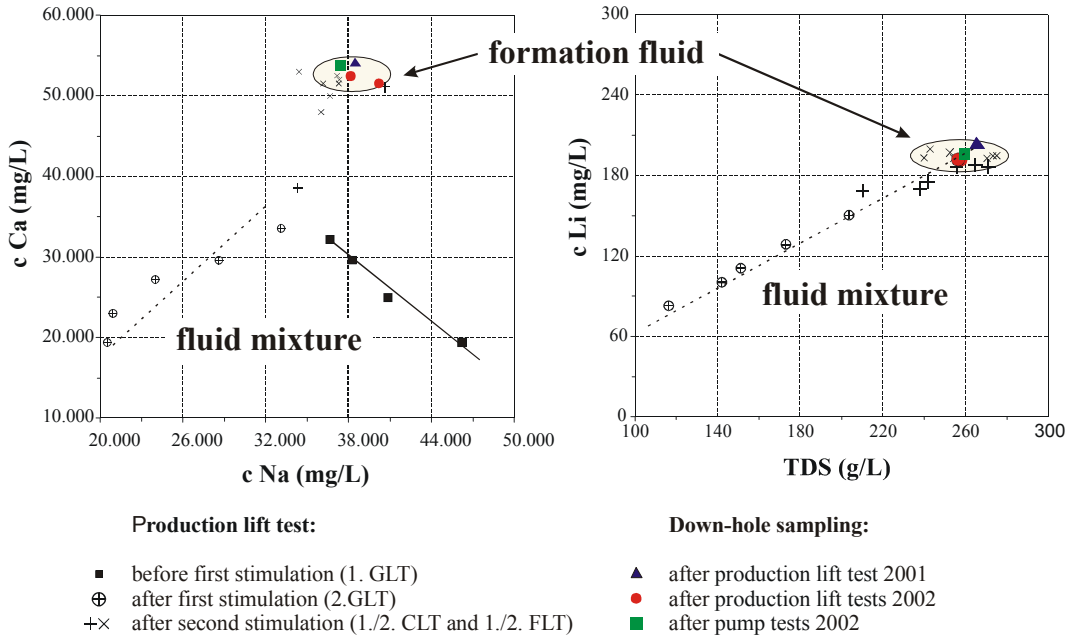


Fig. 2: Calcium vs sodium content

Fig. 3: Lithium content vs salinity

3.2 Hydrogeochemical characteristics of the formation fluid

Table 2 gives a comparison of the hydrogeochemical parameters according to the results of the downhole sampling in 2001 and 2002. In 2001, the samples were taken from the zone of the main influx (Fig. 1), and in 2002 from the stimulated sections. The comparison of the chemical data showed good correspondence. The formation fluids exhibit a TDS (Total Dissolved Solids) of approx. 260 g/l. A pH-value of around 5.7 was measured. The calcium contents are around 30 meq-% and the sodium content 20 meq-%, only. Chloride is the main anion. The deep fluid can be assigned to the Ca-Na-Cl type and classified as typical Rotliegend fluid [8]. The contents of potassium and strontium are lower by one order of magnitude. Relatively high values of iron, manganese, lead, zinc and copper indicate a metal-rich source rock. The fluids contain sulphate with up to 140 mg/l. HS^- and S_2^- were not detected. The higher iron(II) contents in the downhole samples after the stimulation measure are due to the feeding of citric acid into the frac fluid, as this causes – among others – the ex-solving and mobilisation (pH =2) of iron from the hematite-bearing formation.

During pumping with a mean flowrate of 1 m³/h, lead precipitated due to electrochemical reactions among the solute metal ions in the fluid (above all lead - cadmium, nickel, copper play a minor role) and the more base iron of the steel tubing which were proven both in the well sump and on the pump. This is reflected when comparing the downhole and the headspace samples (Table 2).

The reservoir fluid contains 1 Nm³ of dissolved gases per Nm³ fluid. Gaseous phases include more than 80 % by vol. of nitrogen and approx. 14 % by vol. of methane. Carbon dioxide plays a minor role in 2001 (1.7 % by vol.). After the stimulation measures, the gas content increased by around 100 Nm³ of dissolved gases per Nm³ of fluid, compared to 2001. Simultaneously, the share of CO_2 (4.7 % by vol.). The use of citric acid in the injection fluid is responsible for the solution of carbonate cements. Helium and hydrogen show values of 0.4 % by vol., similar to the amounts found in other deep geothermal fluids of the NE German Basin [9]. The composition of noble gases was determined from a headspace sample. The $^3He/^4He$-ratio of $\sim 3 \times 10^{-8}$ is typical for the continental crust and differs significantly from the atmospheric ratio of 1.4×10^{-6}. The $^{21}Ne/^{22}Ne$-isotopic ratio is increased with respect to the atmos-

pheric air composition, whereas the $^{20}Ne/^{22}Ne$-ratio does not differ significantly from that of air. These isotopic data exclude a mantle source. Relation of ^{87}Sr to ^{86}Sr is relatively high with 0.716 and results in a high-grade diagenetic overprint of fluids [10].

Table 2: Composition of the Rotliegend fluid from well E Gr Sk 3/90 before and after stimulation

	Downhole sampling before and after stimulation		**Sampling after pump tests downhole and headspace samples**	
	09.01.01 (4235 m)	02.03.02 (4135 m)	15.10.02 (4130 m)	11.09.02
Ions	**[mg/L]**	**[mg/L]**	**[mg/L]**	**[mg/L]**
Li^+	204	192	230	230
K^+	2,900	2,800	3,100	3,200
Na^+	38,400	38,150	38,700	38,200
Ca^{++}	54,000	52,500	56,500	56,300
Mg^{++}	430	420	380	380
Sr^{++}	1,900	1,400	1,550	1,530
Ba^{++}	68	170	26	47
Fe*	114	191	68	156
Mn*	270	245	257	243
Zn^{++}	74	72	85	80
Pb^{++}	100	35	200	<2
NH_4^+	75	80	200	100
Cl^-	164,000	160,000	160,400	160,300
SO_4^{--}	140	120	51	62
HCO_3^-	18.9	160	112	170
TDS	266 g/L	256 g/L	262 g/L	261 g/L
pH	5.7	5.9	5.5	5.7

4 Origin of the waters of the well E Gr Sk 3/90

The waters of the well E Gr Sk 3/90 show chemical signatures which are known for the waters from Permo-Carboniferous fluids in the NEGB (Figure 4). The waters – as these are known for the different lithologic units – are presented in Figure 4 in an excess-deficit plot according to [11]. For the Zechstein waters it became clear that mainly the evaporation of fluids and related halite precipitations have to be considered as the processes influencing the fluid composition. The post-Permian fluids, however, show signatures close to the norma sea water plot indicating little influencing only. The Rotliegend waters indicate an exchange of 1 Ca ion for 2 Na ions, as it is typical for the albitization of plagioclases. The following reaction can be assumed for this:

$$CaAl_2Si_2O_8 + 4\ SiO_2 + 2Na^+ \text{--}> \ 2\ NaAlSi_3O_8 + Ca^{2+}$$

This process is known within the framework of the fluid development with regard to the Permo-Carboniferous volcanic and sediment rocks and represents one of the most important diagenetic processes [12]. The influence of saliniferous Zechstein waters on the waters in the well E Gr Sk 3/90 can be excluded (according to Figure 4 and [12]). Also the $^{87}Sr/^{86}Sr$ ratios of 0.715628 – 0.715644 of the waters in well E Gr Sk 3/90 show a strong late-diagenetic influence on the waters and do not indicate any influence of the Zechstein waters according to [13].

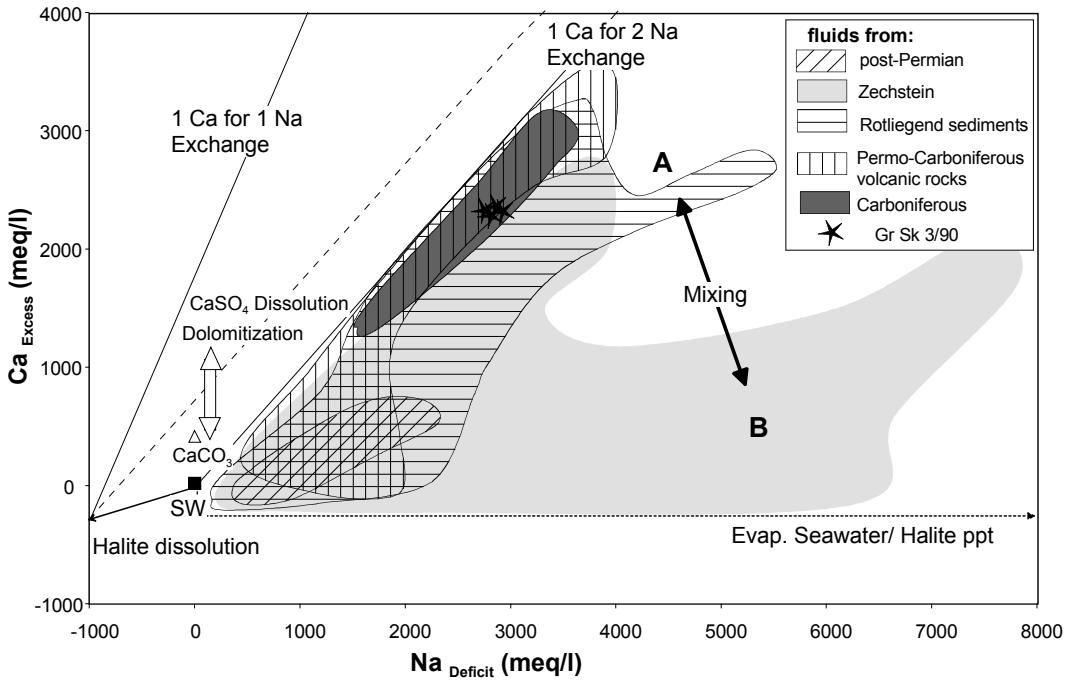


Figure 4: Excess-deficit plot showing model predictions for different processes (according to [11]); the fields for the waters of the different stratigraphic horizons – as these are known for the NEGB – were taken over [12, 14, 15, 16]; in addition, the data obtained from well E Gr Sk 3/90 were included.

The genesis of the waters can be understood as follows (according to [12]): The surface and groundwaters existing during the Rotliegend get deeper and deeper following increasing subsidence. Starting from a depth between 3,000 and 4,000 m, the adjacent rocks are subjected to far-reaching diagenesis. This causes an alteration particularly of the primary feldspars. Consequently, albite, quartz, illite, chlorite, and other minerals are formed secondarily [17]. Among others, this mineral reaction is responsible for the relative increase of the Ca content (cf. Figure 4). Close to the Zechstein, these Rotliegend formation waters mix with the Zechstein waters. This mixing takes place in major depths along far-reaching fault zones, only. Waters ascending from the vulcanites mix rather with waters from the overlying coarse-grained Rotliegend sediments. Exactly these waters were found in the well Groß Schönebeck 3/90.

5 Conclusion

International experience gained in the field of high-enthalpy geothermal energy use show that scaling and corrosion are the main problems when utilizing geothermal waters which is due to their geochemical composition.

The high concentrations of solute iron(II) and manganese(II) ions proven in the formation fluid may present major problems when using it for energetic purposes. When in contact with oxygen and pH increases, the iron(II) ions oxidize to iron(III). The follow-up precipitation of complex oxihydroxides may be dangerous for the surface thermal water loop, but in particular for the near-well reservoir zone during reinjection. In this context, the role of the high contents of solute manganese ions still needs to be reviewed. Even other heavy metals such as lead may cause blockings in the surface thermal water loop. Investigations have to be directed here to suitable materials for well and plant construction. In addition, the risk of scaling caused by silicic acid as well as earthy base carbonates and sulphates ($BaSO_4$ and $[Ba,Sr]SO_4$) must be considered. Along with the thermodynamic regularities, kinetics play an essential role here.

The high salt contents of the solution do not cause corrosion only, but they change sustainably also the physical properties such as specific heat capacity, density and dynamic viscosity.

With due consideration of the their importance for the energetic yields, this forms an important field of more research.
Within the framework of tests on the well Groß Schönebeck E Gr Sk 3/90 from December 2000 to October 2002, extensive geochemical investigations were carried out. The geochemical condition of the deep thermal waters lifted from the Rotliegend in the NEGB is characterised, among others, by high salt contents which may lead to scaling, corrosion and thermic losses. For the reliable generation of electric power in the future, more intensive research regarding the fluid geochemistry with a view to the process-inherent risks as well as to the thermal output is absolutely required.

Acknowledgments
The data presented here were obtained within the framework of a geothermal project coordinated by the GeoForschungsZentrum Potsdam. It is funded by the Federal Ministry of Economics and Technology, the Federal Ministry of Research and Education of Germany, and the Ministry of Science, Research and Culture of the Federal Land of Brandenburg. Thanks are due to Thomas Wiersberg, Martin Zimmer, Jörg Erzinger, Samuel Niedermann, Rolf Romer and Asaf Pekdeger for the analyses of the formation fluids.

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