

# Stimulation tests in a deep Rotliegend sandstone formation – Geochemical aspects

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## Abstract

A multidisciplinary approach to make feasible the generation of geothermal electricity in the North-German Basin (NGB) was initiated in 2000. To attain this goal, formation fluids from the 4,000 m deep Rotliegend rocks (a well-known gas reservoir) in the NGB needed to be extracted and their geochemistry determined. An in-situ laboratory was established by opening and deepening the former gas well Groß Schönebeck. Subsequent hydraulic and stimulation tests focused on the aeolian sandstones. The in-situ downhole samples of the 150°C hot fluids contain high amounts of dissolved solids (with salinities of up to 265 g/l). To increase permeabilities, rocks were stimulated hydraulically. Temperature and chemistry of injected fluids and the condition of the applied equipment have an important influence, as these control the solution and precipitation of different minerals such as iron hydroxides, sulphates, and carbonates.

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

## 1 Introduction

In Germany, low-enthalpy Mesozoic deep waters of the North German Basin are successfully used for heat production. These waters are of the sodium-chloride type with a maximum salinity of 220 g/l. At a temperature level >100°C, deep waters may become interesting for electric power generation. With a mean geothermal gradient of 3-3.5 K/100 m, drilling depths ranging from 3,000 to 4,000 m are required for that. Rotliegend sandstones are found this deep in the North German Basin. Generally, these Rotliegend formation fluids are highly concentrated saline solutions (up to 300 g/l), which are characterised by a shift of the Na/Ca ratio towards calcium. For efficient geothermal usage, highly permeable rocks are necessary. The normally low permeabilities of Rotliegend rocks require stimulation processes to increase the productivity of geothermal fluids. The commercial fluids to be injected for this purpose must be conditioned adequately in order to avoid formation damages.

The aim of this paper is to present and discuss the geochemistry and origin of formation fluids as well as the variations and changes in fluid composition through heavy fluid injection tests. In this context, fluid-fluid- and fluid-rock- or fluid-casing interactions are especially important.

### 1.1 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). 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  $10^{-14} \text{ m}^2$  (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.

## 1.2 Groß Schönebeck well – drilling and testing

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

- 1990 Drilling of the Groß Schönebeck (Gr Sk 3/90) 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 (Lenz & Hoffmann, 2002).
- 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  $700 \text{ m}^3$  of the formation fluid.
- 2003 Open-hole stimulation (water-frac) in Rotliegend rock

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 of permeability on cores attested fairly good permeability. The initial hydraulic parameters were determined in a primary test in 2001 (Hurter et al., 2002). 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 January 2002, tests started with circulation of NaCl brine (density: 1.12 g/cm<sup>3</sup>). 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 (Seibt, 2000).

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 and 2).

Totally, 532 m<sup>3</sup> 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 tests, the total volume amounting to 938 m<sup>3</sup>. Altogether, 406 m<sup>3</sup> more fluid were produced than injected. This total corresponds to approx. three borehole volumes.

**Table 1: Well Gr Sk 3/90 - produced and injected fluids.**

\*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 <sup>3</sup> ]*	Injected fluid composition
09.01.01	Down-hole sample (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 washout	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 sample (after stimulation)		

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

	Down-hole samples	
	09.01.01 (4235 m)	02.03.02 (4135 m)
Ions	[mg/l]	[mg/l]
Li <sup>+</sup>	204	192
K <sup>+</sup>	2,900	2,800
Na <sup>+</sup>	38,400	38,150
Ca <sup>++</sup>	54,000	52,500
Mg <sup>++</sup>	430	420
Sr <sup>++</sup>	1,900	1,400
Ba <sup>++</sup>	68	170
Fe <sup>*</sup>	114	191
Mn <sup>*</sup>	270	245
Zn <sup>++</sup>	74	72
Pb <sup>++</sup>	100	35
NH <sub>4</sub> <sup>+</sup>	75	80
Cl <sup>-</sup>	164,000	160,000
SO <sub>4</sub> <sup>--</sup>	140	120
HCO <sub>3</sub> <sup>-</sup>	18.9	160
TDS	266 g/l	256 g/l
pH	5.7	5.9

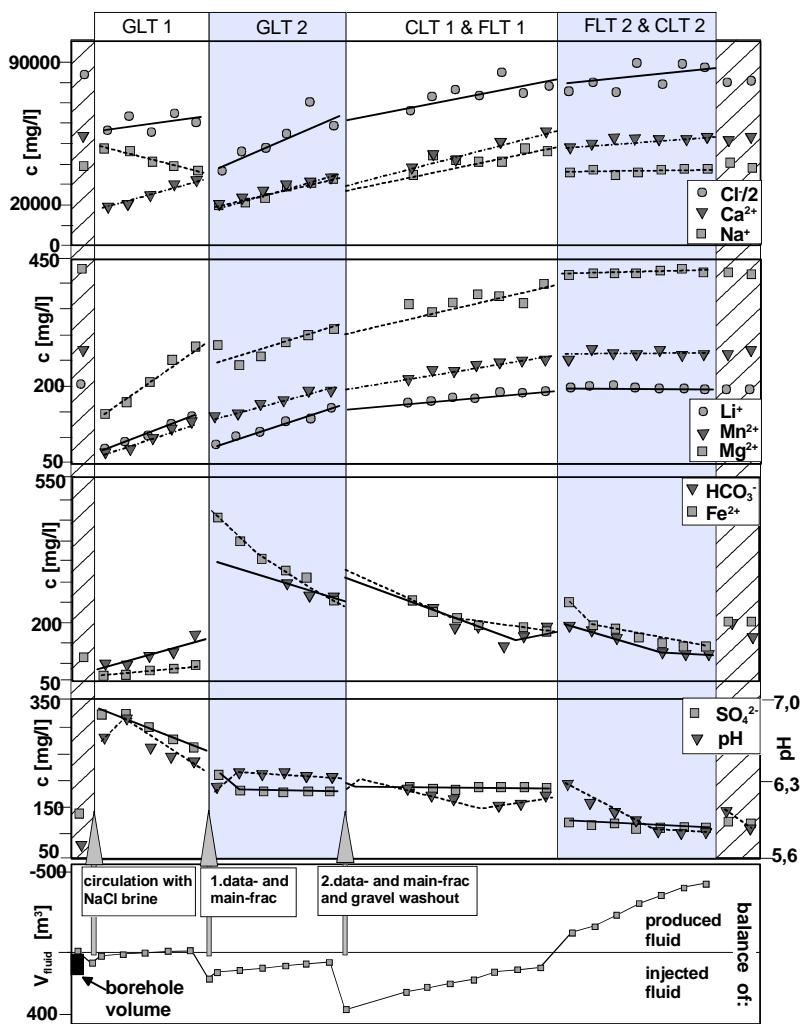
## 2 Geochemical data

### 2.1 Composition of reservoir fluids

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, 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 6 was measured. The calcium and sodium contents are around 20 meq-% with a dominating share of calcium. Chloride is the main anion. The formation fluid can be assigned to the Ca-Na-Cl type and classified as typical Rotliegend fluid (Wolfgramm et al., 2002). 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 up to 140 mg/l.  $\text{HS}^-$  and  $\text{S}_2^-$  were not detected.

The reservoir fluid contains 0.9 Nm<sup>3</sup> of dissolved gases per Nm<sup>3</sup> of fluid. Gaseous phases include more than 80% by vol. of nitrogen and approx. 14% by vol. of methane. Carbon dioxide plays a minor role. 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 (Naumann, 2000). The composition of noble gases was determined from a headspace sample. The  ${}^3\text{He}/{}^4\text{He}$ -ratio of  $\sim 3 \times 10^{-8}$  is typical for the continental crust and differs significantly from the atmospheric ratio of  $1.4 \times 10^{-6}$ . The  ${}^{21}\text{Ne}/{}^{22}\text{Ne}$ -isotopic ratio is increased with respect to the atmospheric air composition, whereas



**Figure 1: Changes of fluid composition through stimulation related to the volume of injected and produced (-) fluids.**

the  ${}^{20}\text{Ne}/{}^{22}\text{Ne}$ -ratio does not differ significantly from that of air. These isotopic data exclude a mantle source. Relation of  ${}^{87}\text{Sr}$  to  ${}^{86}\text{Sr}$  is relatively high with 0.716 and results in a high-grade diagenetic overprint of fluids (Clauer and Chaudhuri 1993).

## 2.2 Change of the fluid composition through stimulation

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. In Figure 1,

the results of lift samples and down-hole samples before and after stimulation are plotted in relation to time and the lift, respectively.

The different ion concentrations and parameters show similar values before and after the tests. It seems that the major part of the injected fluids was removed from the deep aquifer as a result of the lift tests. Generally, ions can be distinguished according to two main groups with two sub-groups, respectively:

(Ia)	$\text{Na}^+$	(Ib)	$\text{Cl}^-$ , $\text{Ca}^{2+}$ , $\text{Li}^+$ , $\text{Mg}^{2+}$ , $\text{Sr}^{2+}$ , $\text{K}^+$ , $\text{Mn}^{2+}$
(IIa)	$\text{HCO}_3^-$ , $\text{Fe}^{2+}$ ,	(IIb)	$\text{SO}_4^{2-}$ , $\text{H}_3\text{O}^+$ (pH)

Ions of group I who behave like tracers show smooth re-mixing without retention. This effect, which is comparable to chromatography, is not observed in the case of group II ions. Their concentration can be influenced through reactions of interaction with the matrix rock of the reservoir and the injected fluids. Partly, the ion concentration behaviour of the sub-groups a and b is opposite.

(I) The concentration of all ions decreased significantly after circulation of NaCl brine, except sodium and sulphate compared to the down-hole sample taken in 2001 (formation fluid). This effect can be explained by the injection of the sodium-rich fluid. The following lift test (GLT 1, Figure 1) resulted in a decrease of the content of sodium down to the initial value. Compared to that, the values of group Ib ions increased moderately. However, the initial concentration is not achieved.

The 1st data- and main-frac induced another heavy decrease of the concentration. In the following lift test (GLT 2), the values of ions increased moderately. The 2nd data- and main-frac as well as the washout of gravel did not show any considerable variation of the ion concentration. Through the later lift tests CLT 1 and 2, the ion concentrations increased slowly up to the initial values. A small concentration gap between the two lift tests was stated.

(II) Iron and carbonate concentrations of water decreased after circulation of NaCl brine (Table 1, Figure 1). In the lift test GLT 1,  $\text{HCO}_3^-$ - and  $\text{Fe}^{2+}$ -values increased at a small rate. The 1st data- and main-frac resulted in a very heavy increase of the concentrations. With a small concentration gap between both CLT, the concentrations decreased down to the initial values.

Sulphate content and pH value increased due to the circulation of NaCl brine (Figure 1). Subsequently, the values decreased moderately.

Generally, major changes of the concentration after circulation of NaCl brine and the 1st data- and main-frac can be observed. Between the lift tests CLT 1 and CLT 2, a small concentration gap was recorded. After the production lift test, the chemical and physical properties of the extracted fluid corresponded to the values of the down-hole sample of 2001.

### 3 Discussion

The fluid lifted in the first test (GLT 1) is a mixture composed of NaCl brine and formation fluid. The sodium content can be attributed to the influx of an injected fluid with higher sodium content. The increase of the sulphate content could be reduced by decreasing the fluid temperature, and the related increase of sulphate solubility by injection. In this case, the concentration of  $\text{HCO}_3^-$  should have increased as well, because the saturation index of both sodium and sulphate in 4,200 m depth, at 150°C

and 430 bar is nearly zero. But the  $\text{HCO}_3^-$  concentration does not show any similar trend although the solubility behaviour is similar. The commercially available NaCl (salt) is contaminated by materials from the evaporitic deposits it is produced from. Therefore, the preferred assumption is that the injected NaCl brine was contaminated by anhydrite or gypsum.

After the 1st data- and main-frac, a decrease of the concentration of most ions except iron and  $\text{HCO}_3^-$  can be observed. The use of citric acid in the injection fluid (pH=2) is responsible for the solution of carbonate cements and cogenetic secondary minerals such as hematite. Furthermore, proppants were injected at the end of every main-frac, which rubbed off the rust from the pipes. Iron mobilised in this way forms complex compounds with the citric acid. The high concentrations of solute iron(II) ions proven in the formation fluid require adequate conditioning of the injected fluid to keep it dissolved. Compared to the increase of iron ions, the formation of complex iron oxyhydroxides represents a far bigger problem with a view to a reservoir damage.

The influence of the second data- and main-frac on the chemical composition of the lifted fluids was less important than the first one (Figure 1). The small gaps between the two casing lift tests (CLT 1&2) is to be interpreted as the delayed dissolution of viscous gel and consequently as a delayed release of the injected low-salt water.

After finalisation of the test phase, the chemical and physical properties of the produced fluids complied with those of the deep sample prior to the test.

## 4 Conclusions

Within the framework of tests on the Groß Schönebeck well from December 2000 to March 2002, extensive geochemical investigations were carried out. Along with the high salt contents, the geochemical condition of the Rotliegend sandstone deep thermal waters is characterised by high heavy metal contents, in particular of iron. Especially when contaminated with oxygen and pH is increased, there is a major tendency towards precipitation of voluminous iron compounds, which must be observed mainly in experiments with the commercial frac-fluids. Exclusively by proper conditioning of the fluids to be injected, follow-up reactions damaging the formation will be prevented.

For safe and reliable generation of geothermal electric power in the future, more intensive research in the field of fluid geochemistry is a must with a view to both the process-inherent dangers and the thermic output.

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