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GAS SOLUBILITY IN FORMATION WATERS OF THE NORTH GERMAN BASIN – IMPLICATIONS FOR GEOTHERMAL ENERGY RECOVERY

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ABSTRACT

Geothermal heating power plants in the North German Basin produce 50 to 100°C fluids from Upper Triassic and Jurassic sandstones at depths of 1000 to 2500 m. The Na-Cl geothermal fluids are characterized by salinities as high as 250,000 ppm, pH's of 5-7, and noncondensable gas contents as high as 10% of the total mass flow.

Operation of the investigated heating plants requires that the geothermal fluid remains pressurized so that carbon dioxide gas can not exsolve and that oxygen can not enter the system and react with iron. Geochemical modeling with SOLMINEQ.88 confirms the operating experience that cooling and a drop in the pressure of the geothermal fluid will not result in oversaturation of the water as long as oxygen entry and a pressure drop below a plant specific water degassing level are avoided.

Oxygen measurements show that diffusion of oxygen into the system is minimal during routine operations. In contrast to normal production periods, oxygen can enter the system during plant shutdowns or when slop water (leakage water accumulated during maintenance work) is pumped back into the system.

1. INTRODUCTION

Low enthalpy, high salinity, anoxic Na-Cl formation waters stored within Mesozoic aquifers are the main geothermal energy resources of northern Germany (Figure 1). The primary reservoir rocks in the North German Basin are sandstones range in depth from 1000 to 3000 m (Figure 2) and have temperatures between 40 °C and 130 °C.

Geothermal heating plants have been in operation for many years in northern Germany. Energy recovery in these geothermal heat plants occurs through production of hot formation water, heat exchange and re-injection of cooled water back into the reservoir horizon. High capital costs require that these heating plants be designed to operate for at least 25 years. Long-term profitable operation of the plants requires avoidance of scaling in surface equipment and plugging of the re-injection horizon. Reinjection of low-enthalpy geothermal fluids into sandstone reservoirs has been problematic at several sites, for reasons that are not completely understood (Stefansson, 1997). It is therefore necessary to determine if modifications of temperature, pressure, oxidation-reduction potential, and pH can cause scaling and blocking within the thermal water cycle.

The study objective was to determine the potential risk of scaling and reservoir plugging during long-term production of Na-Cl type formation waters supplying the Neubrandenburg and Neustadt-Glewe geothermal heating plants. Fluid for these plants is produced from geological conditions typical of northern Germany. Information gained from this study should be applicable to other northern Germany reservoirs. Chemical analyses of the waters, a detailed geochemical study of the gas phase, a mineralogical/chemical analysis of filter cakes, scaling precipitation, and complex reservoir characterizations were the base of the study. Oxygen measurements are a component of the geothermal plants monitoring program. Geochemical modeling was performed with the program SOLMINEQ.88 (Kharaka et al., 1988). It focused on calculating the water's saturation state between the production and the re-injection wells.

2. METHODS

2.1 Reservoir Characterization

Reservoir characterization was done by core investigations and log interpretation (Hoth et al., 1997). Geological and geochemical investigations of the reservoir rocks and the surrounding shales and siltstones were focused on sedimentary structures, morphology, texture, grain size, and the mineralogical/geochemical composition. The latter was obtained by XRD, XRF, and ICP-MS analysis. Analyzed petrophysical parameters include porosity, permeability, formation factor, pore size distribution, and constrictivity.

2.2 Water Chemistry

Our investigations were based on work by Kühn (1997). The standard detection methods ICP-OES and ionchromatography were used to analyze the cations and anions respectively. Details of the analytical and dilution procedures are given in Naumann (2000) and Kühn (1997). Measurement of pH, Eh, and temperature was done during water sampling in the geothermal plants.

2.3 Gas Analysis

On-line gas monitoring was done in the thermal water loop of both geothermal heating stations (Naumann, 1999). Small volumes of thermal water were extracted directly downstream of the producing well and passed through an automatic degassing system. This system was combined with a quadruple-mass- spectrometer (analysis of N_2, CO_2, CH_4, Ar, He, H_2, O_2), a gas-chromatograph (CH_4, C_2H_6, C_3H_8, C_4H_{10}), and a radon-α-spectrometer.

2.4 Oxygen Measurement

Oxygen measurements were performed to identify operating conditions during which oxygen can enter the thermal water loop. The measurements were carried out with an ORBISPHERE Laboratories oxygen sensor, model 2713. Measured values are corrected with respect to salinity and temperature. Of the two geothermal heating plants only one is

designed with a special protection system to avoid oxygen entry. Measurements were done during normal operation, maintenance periods, and during startups. The oxygen measurements were obtained in the thermal water loop directly after the filter units, which are located in front of the injection well (Fig. 3).

2.5 Mineralogical/Chemical Analysis of Filter Cakes

Filtered substances of the filter bags from the filter units located between the production and reinjection wells were analyzed periodically. This was mainly done by XRD, XRF, and electron microscopy coupled with energy dispersive X-ray analysis.

2.6 Geochemical Modeling

The program SOLMINEQ.88 (Kharaka et al., 1988) was used to calculate the scaling potential at different temperatures, pressures, and partial pressures of carbon dioxide. Compared to other modeling tools it allows computations at elevated pressures, like those in the studied aquifers. Most of the calculations of activity coefficients of ionic species were based on the DEBYE-HÜCKEL equation. Although the PITZER equation is suitable for higher salinity waters, it could not be used due to the lack of available PITZER coefficients. Calculated values for the activity coefficients of the DEBYE-HÜCKEL method are in most cases lower than those calculated by the PITZER method.

3. RESULTS

3.1 Reservoir Properties and Chemistry of Formation Waters

Both geothermal heating stations produce thermal waters from "pore storage"- type sandstones of Upper Triassic and Lower Jurassic age. Generalized lithologic profiles of the reservoir horizons for the production and the reinjection wells of both fields are shown in Fig. 2. The usable "effective reservoir thickness" is greater than 20 m in all four wells. A minimum usable reservoir thickness of around 20 m is one of the limiting conditions for efficient geothermal energy recovery according to experience gained with sandstone reservoirs in Northern Germany (Rockel et al. 1997).
Sandstones from the investigated wells have quartz contents between 85 and 98 % and a low matrix percentage. They are also characterized by 1 – 5 % sheet silicates. Additional phases are feldspars and carbonates. The preservation of a high proportion of their primary pore space is due to a relatively low intensity of sandstone diagenesis. These reservoirs are therefore characterized by low formation factors, low constrictivities (pore body / pore throat - ratio), and pore spaces with more than 50 % of pore sizes larger than 5 µm - so called pores of the mega and macro type. This causes very high porosity and permeability ranging from 20 to 34% and between 0.3 $*10^{-12}$ and 1.5 $*10^{-12}$ m² respectively. The higher burial depth and temperature for the productive sandstones in Neustadt-Glewe has resulted in more intense compaction and quartz cementation. Therefore, these sandstones are in general less permeable and porous than the ones from Neubrandenburg (Hoth et al. 1997).

The formation waters are anoxic Na-Cl solutions with pH values between 5.5 and 6.5. The primary species are chloride ions with almost 50 mmol (eq)-% and sodium ions with 43 to 47 mmol (eq)-%. Table 1 presents water analyses of the produced thermal waters at both geothermal heating plants. The high iron contents of 60 and 11 mg/l are of special significance. The waters contain 3 to 10 vol.-% gas which is dominated by CO_2, N_2, and CH_4 (Table 1). Argon, H_2, He, and higher hydrocarbons are trace components (total < 1 %). An "on-line" gas monitoring system revealed very low variations in the composition of the gas phase over a period of two years (Naumann et al., 1999).

3.2 Oxygen Measurement

When reinjecting anoxic waters, potential oxygen contamination at the surface should be avoided. Oxygen contamination can result in iron hydroxide precipitation, which can quickly load of the filters. There is also the even more severe risk of reservoir damage when oxygen-containing waters are re-injected in the reservoir horizon, because iron hydroxides can block the downhole filter installations and the open borehole wall or plug pore throats within the reservoir.

Generally, oxygen is present in the thermal water at an average concentration of only 1.7 ppb during normal operation. This low background is independent of the existence of a nitrogen loading system. During startup after filter replacements, an oxygen content of 100 ppb was measured. After 2.5 hours, the dissolved oxygen content declined to normal operation levels.

Special attention is required when the units are started after major outages. Oxygen concentrations during the startup of a geothermal heating plant drop below 50 ppb within about 30 minutes, which corresponds to the production of 65 m³ of water (Figure 4). The oxygen reduction correlates with an increase in the temperature signaling the arrival of fresh formation water at the surface.

Oxygen can also enter the system when leakage water (slop water), which is accumulated during maintenance work and stored in special tanks, is fed into the thermal water flow and re-injected. Figure 5 shows the water oxygen concentration versus time during slop water discharge into the thermal stream at the Neubrandenburg plant. A maximum oxygen concentration of 500 ppb was recorded there during the discharge of 1 part slop water to 55 parts of normal thermal fluid within a time period of more than 200 minutes.

3.3 Determination of the Flashing Pressure in the CO_2-N_2-CH_4-Brine System

Produced geothermal fluids contain differing amounts of dissolved gases which can exsolve when the pressure drops. Compared to the Neubrandenburg plant, the Neustadt-Glewe site has higher temperature, salinity, and gas content which is dominated by CO_2 (Table 1). Another specific feature of the system in Neustadt-Glewe is the low injection pressure during low flow rate operation . When CO_2 escapes the system, there is the risk that calcium compounds will scale the piping. Therefore, pressure must be maintained to keep the CO_2 dissolved.

For determination of the overall gas exsolving pressure, the solubility behavior of CO_2, CH_4, and N_2 in water is considered first. In water, CO_2 is much more soluble than methane and nitrogen, with nitrogen being least soluble. The solubility of

these gases decreases as the temperature increases, passes a minimum and increases again. Solute salts reduce the solubility. The solubility of each gas component in brine can be determined when its solubility in water is known, from equation (1)

$$R_{gas,\ b} = R_{gas,\ w} \cdot \left(\frac{\rho_b - TDS}{1000} \right) \cdot L_{rel.} \quad (1)$$

$R_{gas,\ b}$ gas content of brine [m³/m³]
$R_{gas,\ w}$ gas content of water [m³/ m³]
TDS total dissolved solids [kg/m³]
ρ_b density of brine [kg/m³]
$L_{rel.}$ relative solubility depending on the salt content of the solution

For the gases N_2 and CH_4, L_{rel} can easily be determined from equation (2) (Harting et al., 1981)

$$L_{rel.} = e^{\left(-0315 \cdot c + 0.01452 \cdot c^2 \right)} \quad (2)$$

c molality [mol/kg]

The higher influence of divalent ions on the gas solubility has to be taken into account. This is done by multiplying the molality of $CaCl_2$ by a factor of 1.8 (Harting et al., 1981), which gives an equivalent NaCl concentration causing the same gas solubility reduction. For the molality c = 4.2 (Seibt et al., 1999), as determined for the formation water used in the Neustadt-Glewe plant, $L_{rel.}$ is 0.35 referred to pure water ($L_{rel.}$=1).

Carbon dioxide behaves differently than nitrogen and methane in that dissolved carbon dioxide forms a weak acid. According to the comparison with the solubility data given in the relevant literature, the solubility of CO_2 in this thermal water is only 47 % of that in pure water (Seibt et al., 1999). The solubility figures for carbon dioxide, nitrogen, and methane in pure water taken from the literature (Harting et al., 1981) were calculated according to (1) for the Neustadt-Glewe thermal water. According to the mol fraction solubility of the individual gases (carbon dioxide x_{CO2}, methane x_{CH4}, nitrogen x_{N2}) in the mixture

$$x_{CO2} = \frac{n_{CO2}}{n_{CO2} + n_{CH4} + n_{N2}} \quad (3)$$

n_i amount of the substances [mol]

solubility is related to pressure. Under the Neustadt-Glewe conditions, a gas hold-up pressure of 0.2 MPa is determined at the production well head according to equation (4)

$$P = x_{CO2} \cdot P_{CO2} + x_{CH4} \cdot P_{CH4} + x_{N2} \cdot P_{N2} \quad (4)$$

P total pressure [MPa]
P_i partial pressure of the gases [MPa]

In Figure 6, the pressure dependent solubility of the gas mixture is shown for different temperatures. With due observation of the pressures in the plant, it should be possible to avoid pressure drops below 0.2 MPa so that degassing should not occur.

3.4 Geochemical Modeling

Mineral precipitation may be caused by pressure and temperature changes in the thermal water loop which shift solubility balances. The dissolved carbon dioxide is of special importance under depositing conditions. The carbonic acid system is dominated by water-mineral reactions which themselves depend on the pH and the dissolved solids. The comparison of the determined ion activities product (IAP) with the solubility product (L_P) shows, whether a solid phase in a system is over- or undersaturated. The so called saturation index (SI) of the mineral under consideration, is calculated according to

$$SI = \log \frac{IAP}{L_P} \quad (5)$$

A positive SI value indicates that the mineral will precipitate. The solution is undersaturated when the saturation index is negative. The thermodynamic balance is indicated when SI = 0, i.e., the amount of the dissolved mineral is equal to that which simultaneously precipitates.

Figure 7 gives the boundary parameters on which the geochemical modeling is based, and the calculated saturation indices of selected minerals for specific locations in the thermal water loop. Although the solubility of the minerals increases with increasing pressure, the pressure drop (step 2) when producing thermal water does not significantly influence the saturation indices. Even with a pressure difference of more than 200 bars, the calculations indicate a thermodynamic balance of the solid phases with the water or a clear undersaturation. Cooling of the thermal water to 70 or 30 °C leads to clear mineral-specific reductions of the SI values for carbonate and iron compounds (increasing undersaturation). Saturation indices significantly exceeding 0.2 which indicate the mineral is to be expected to precipitate from the solution are characteristic only for the 5th step of the process. From Figure 6, it follows clearly that the oversaturation with regard to the precipitation of dolomite, calcite, magnetite and amorphous iron hydroxide remains restricted to those sections of the plant, where the pH value of the thermal water increases due to CO_2 degassing.

3.5 Investigation of the Filter Cakes

The significance of the modeling results regarding the oversaturation of individual compounds can be tested by direct monitoring of precipitation products in the thermal water loop. Adequate opportunities are given by the analysis of the filter cakes as well as by inspection of the surface and subsurface piping during maintenance (e.g., inspection of the wells with a downhole camera, testing of the well sump). Since the summer of 1996, the Neustadt-Glewe plant filter cakes have been investigated several times.

The ratio of the mass of precipitated solids in the filters to the passed thermal water volume is, in normal operation, very low. Under the condition of regular filter replacement (about every three months), the content of the solids which are not soluble in distilled water was generally well below 200 g.

Quartz, feldspar and sheet silicates mobilized from the reservoir have been detected in the filter cakes collected from the 3 µm filter bags installed downstream of the production well. Iron and lead sulfides and magnetite have been found as actual precipitation products. Sulfides are the dominating residues; magnetite occurs only in trace amounts. It is assumed that the separation of sulfide is due to the influence of sulfate-reducing bacteria (Köhler et al., 1997). As a peculiarity, various lead carbonates and lead hydroxides (such as $NaPb_2(CO_3)OH$ and PbClOH) have been found in the filters. Processes causing the precipitation of these components are not completely understood. The role of organic and Cl-complexes (see Metcalfe 1996) is still under investigation.

The investigation of the filter cakes showed in general a low scaling potential for the investigated sites provided that the system is operated properly. However, possible special conditions of these brines at other locations, like a higher sulfate content of the waters or enhanced bacteriological activity, can change the situation and also need to be studied.

4. CONCLUSIONS

Cooling of the thermal water and the dropping the pressure will not lead to mineral oversaturation as long as oxygen entry is avoided and the pressure reduction will not allow water degassing. A gas dissolving point of around 0.2 MPa was estimated for the specific conditions of the Neustadt-Glewe geothermal heating plant. A drop below this pressure will cause a CO_2-degassing and an increase in the pH of the water. This change leads to the precipitation of carbonate and iron minerals within the loop system.

The detection of these minerals within the filter bags and at special parts of the tube system proves the modeled scenario of the precipitation risk. The study shows that the knowledge of the gas content and its chemical behavior is of great importance for planning and operating geothermal heat plants.

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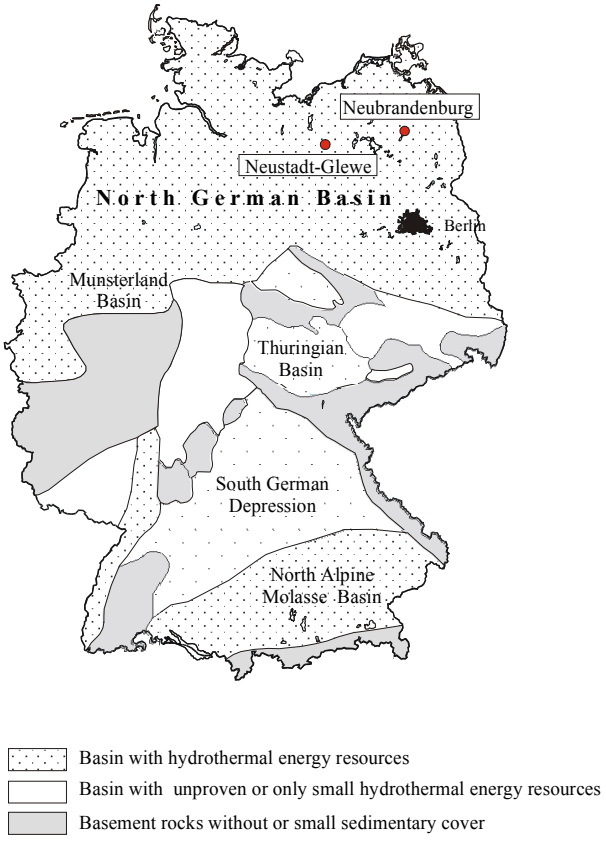


Figure 1. Location map showing main sedimentary basins in Germany and the sites of the investigated geothermal heating plants (Neustadt-Glewe, Neubrandenburg).

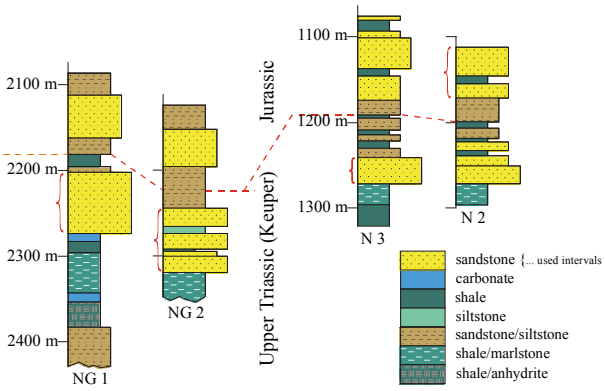


Figure 2. Lithologic profiles of the reservoir horizons in the production and reinjection wells at Neustadt-Glewe (NG 1 and NG 2) and Neubrandenburg (N2 and N3).

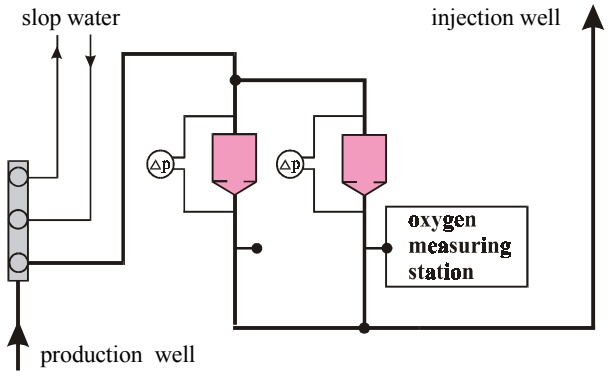


Figure 3. Simplified flow sheet of the filter units upstream of the injection well and the location of the oxygen measuring station.

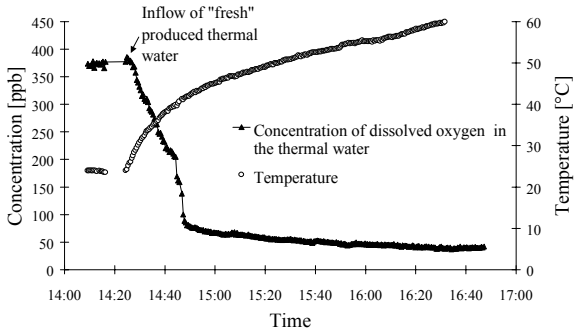


Figure 4. Concentration of dissolved oxygen in the thermal water versus time. Measurements were done during the start of the geothermal plant after one-week maintenance outage. The water cycle was pressurized and protected by nitrogen all the time.

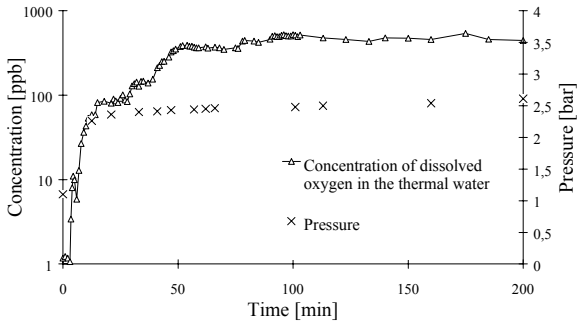


Figure 5. Concentration of dissolved oxygen within the thermal water vs. time and simultaneously measured pressure. Measured above the filter unit as slop water was added to the system. The ratio (slop water to thermal water) was 1:55. The measurements were done in the Neubrandenburg geothermal plant where the water cycle is not pressurized and protected by nitrogen all the time.

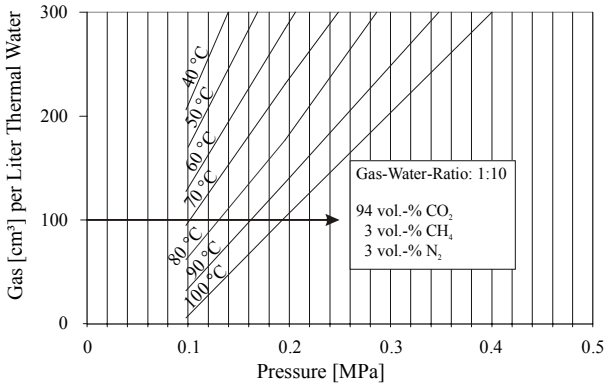


Figure 6. Pressure and temperature dependence of gas mixture solubility in the produced thermal water of the Neustadt-Glewe site.

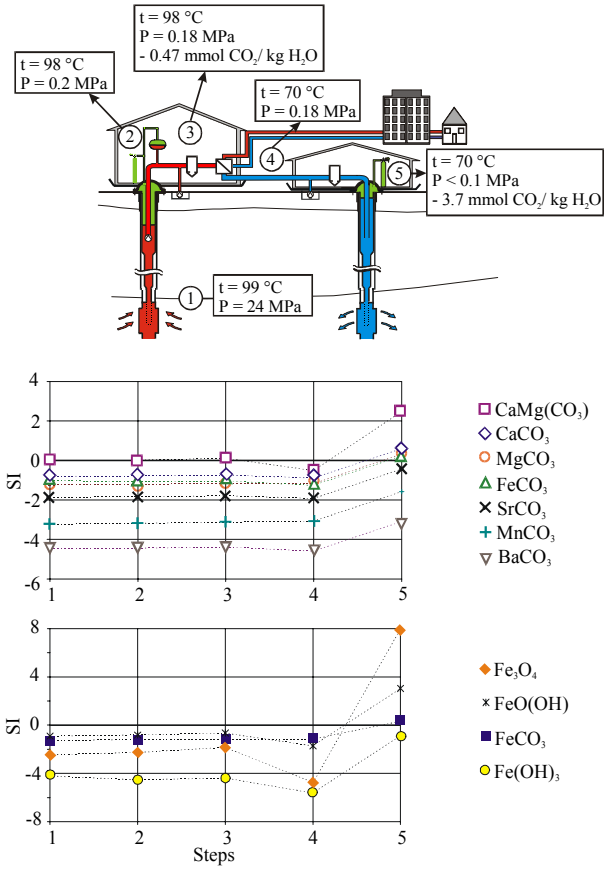


Figure 7. Calculated saturation indices of carbonate and iron minerals at different locations in the thermal water loop of the Neustadt-Glewe plant.

Location	**Neustadt-Glewe**	**Neubranden-burg**
Temperature	99 °C	55 °C
pH	5.3 (50 °C)	6.2 (50 °C)
Eh	- 10 mV	97.5 mV
Density	1.147 g/cm ³	1.089 g/cm³
Element/Ion	Content [mg/L]	Content [mg/L]
Potassium	782	171
Sodium	80,010	53,000
Calcium	8,409	2,100
Magnesium	1,410	642
Strontium	440	106
Iron	60.0	11.0
Lithium	8.3	2.0
Manganese	10.0	0.6
Copper	0.053	0.05
Chloride	137,000	80,000
Bromide	390	98
Sulfate	470	961
Bicarbonate	40.0	204
Gas-Water-Ratio	1:10	1:33
Carbon dioxide	94 vol.-%	57 vol.-%
Nitrogen	3 vol.-%	42 vol.-%
Methane	3 vol.-%	<1 vol.-%

Table 1. Thermal water compositions .