Validation of Hydrochemical Analyses and Gas Concentrations of Deep Geothermal Aquifers

T. Baumann

Technische Universität München, Institute of Hydrochemistry, Marchioninistrasse 17, D-81377 München

tbaumann@tum.de

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ABSTRACT

Data collected in previous projects indicates that the hydrochemical parameters recorded at surface level are not necessarily a good approximation of the water under reservoir conditions. With increasing temperature and gas loading the pH value is significantly affected by degassing. Thus geochemical calculations based on the measured values at surface level and without taking the individual degassing procedures into account are likely to give false predictions. This restriction partly also applies to depth samples. Here, degassing and changes of the hydrochemical parameters have to be taken into account as soon as the sample is opened in the laboratory to insert e.g. the pH probe. The techniques presented in this study present a reliable and reproducible way to calculate the hydrochemical composition and the gas loading under reservoir conditions. Within the scope of this study, it was also evident, that no geothermal water in the Malm Aquifer in the Bavarian Molasse Basin contained excess CO_2. Although all gas analyses contained CO_2, this CO_2 was stripped from the aqueous solution. The amount stripped from the water depends on the concentration of other gases with lower solubility.

1. BACKGROUND

Most of the geothermal waters in the Molasse Basin in Bavaria contain methane, ethane and other hydrocarbons as well as excess nitrogen [1]. The stripping effect which occurs when producing the thermal water from the reservoir (p > 200 bar) to the ground surface (p $\approx$ 10-20 bar), causes a significant disruption of the carbonate equilibrium which hampers the technical operation and efficiency. Furthermore, as most of the thermal waters contain sulfur in its reduced state, degassing can lead to high concentrations of H_2S in the gas phase. Concentrations in the percent range are common and a significant safety concern. Therefore, the analysis of the gas load and composition is a key requirement for safe and efficient operation of geothermal facilities. Current sampling protocols for thermal water were adopted from groundwater sampling protocols, often using the same equipment and the same on-site measurements. However, as sampling of boiling thermal water at temperatures of close to or above 100 °C is not feasible, sample coolers are put in place to cool the sample down to temperatures in the 40-60 °C range. On-site measurements of pH-value, alkalinity, and acidity are significantly affected by the temperature and degassing against atmospheric pressure. These measurements are therefore not always reliable and do not reflect the conditions in the aquifer or reservoir. Collection of pressurized samples in stainless steel cylinders is an alternative applied frequently. This sampling method is quite reliable, but the partial pressure of the gases in the thermal water must not exceed the pressure in the sampling system to avoid degassing in the cylinder. With typical configurations of the sampling devices, this requirement is only valid at concentrations of methane and nitrogen up to 50-100 NmL/L. At higher concentrations a mix of gas and water is sampled. With an usually unsteady flow of gas bubbles in the thermal water, the sampling becomes increasingly random. Frequently, the actual pressure and the temperature of the water in the steel container are not recorded on-site during sampling and the change of the pressure inside the sampling container due to the volume reduction of the thermal water whilst cooling to ambient temperatures ($\approx$ 4 %) is often not reported or not even taken into account. Finally, not all of the gas components are actually measured or analyzed. Often, the concentration of H_2S is calculated from the concentration of reduced sulfur in the water, which is determined by precipitation with zinc acetate. While this is necessary, because of the interaction of reduced sulfur with the steel of the sampling containers, this method results in maximum concentrations of H_2S in the gas phase, which exceed the actual concentrations. Another potential error arises from a shift of the carbonate equilibrium during degassing at low pressures. This has led some analysis laboratories to report the TIC as CO_2, thereby ignoring that a degassing of CO_2 will finally cause precipitation of carbonates. Therefore, this approach is overestimating the total amount of CO_2. The effects of the different sampling and degassing procedures for the operation of a geothermal power plant can be derived from Fig. 1. It shows the calculated degassing of the thermal water at a geothermal power plant running at over 100 L/s and with a temperature of above 140 °C. The calculations were run with PhreeqC [2] and using the reported gas composition and gas loading from three different laboratories. Each laboratory applied its own method for gas sampling and analysis. All samples were taken during a long-term production and injection test within 7 days at comparable conditions. The bubble point, i.e. the pressure at which the first gas bubbles are formed, is in the range from 7.5 to 15 bar, which is clearly not acceptable from a process and safety engineering point of view. In summary of the current procedures it has to be stated that while the data collected at ground level is valid for an assessment of i. e. thermal water discharge into sewers or surface waters, it is not reliable for an assessment or prediction of processes in the thermal water cycle. This data is also not reliable for an assessment of rock water equilibria, which often can be seen by the calculated supersaturation state for the thermal water, which does not make sense given the age of the thermal water of at least 8000-12000 a [1,3].
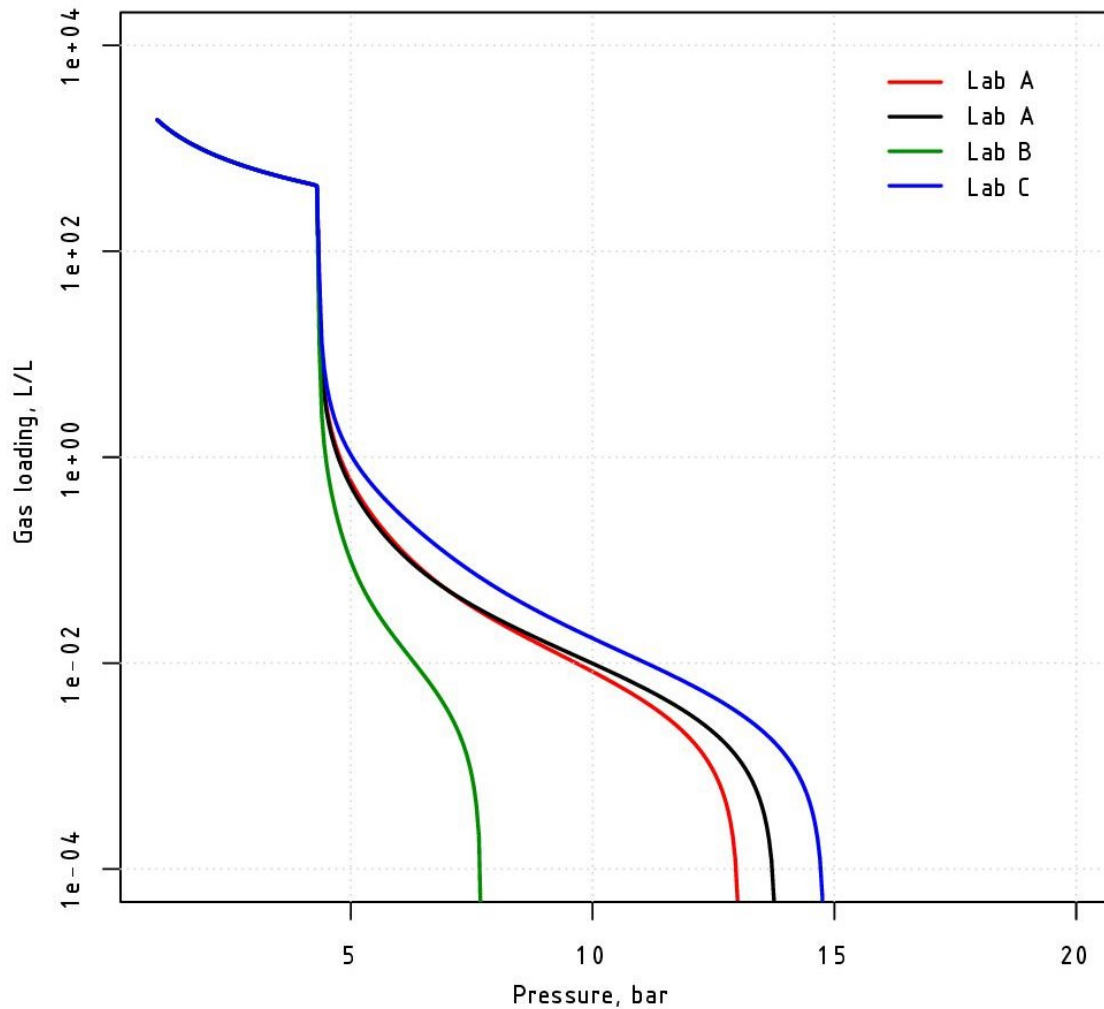
Figure 1: Calculated volume of the gas phase in the thermal water

2. MATERIAL AND METHODS

2.1 Hydrogeochemical Modelling

All hydrogeochemical models were implemented in PhreeqC [2], version 3.3.2, using the provided phreeqc.dat database. The setup and calibration of the model are outlined in Fig. 2. The primary step for all simulations was to calculate the unknown composition of the water under reservoir conditions. Here we introduced the measured cations and anions as SOLUTION 99 and added the gases nitrogen, methane, and ethane as EQUILIBRIUM_PHASES. The non-reactive representations of these gases (Mtg(g) instead of CH4(g), Ntg(g) instead of N2(g)) were used to prevent reactions with the gases during degassing. The rationale behind this simplification is that the reaction rates are slow compared to the degassing process. Thermodynamic parameters for ethane were taken from the Lawrence-Livermoore-National-Labs database (llnl.dat) and the Peng-Robinson parameters were taken from PREOS.xls [4]. From this solution the gases methane, ethane, nitrogen, water vapor, CO_2, and H_2S are allowed to equilibrate with a GAS_PHASE at a pressure and temperature which is a complete match of the actual experimental setup. The volume and composition of the resulting GAS_PHASE, the pH value and the alkalinity, and the saturation indices for calcite, aragonite, and dolomite were compared to the measured values for the thermal water after degassing. A fit between measured and calculated values is obtained by changing the pH-value of the water under reservoir conditions and the concentration of the gases in the EQUILIBRIUM_PHASES block. A small program using the integrated Basic interpreter aids the manual fitting procedure. After each change the simulation is run again, until an acceptable match with the measured values is reached and the saturation indices are within $-0.2 < SI < 0.2$, thus indicating quasi equilibrium conditions [5]. This solution is then saved as SOLUTION 1.
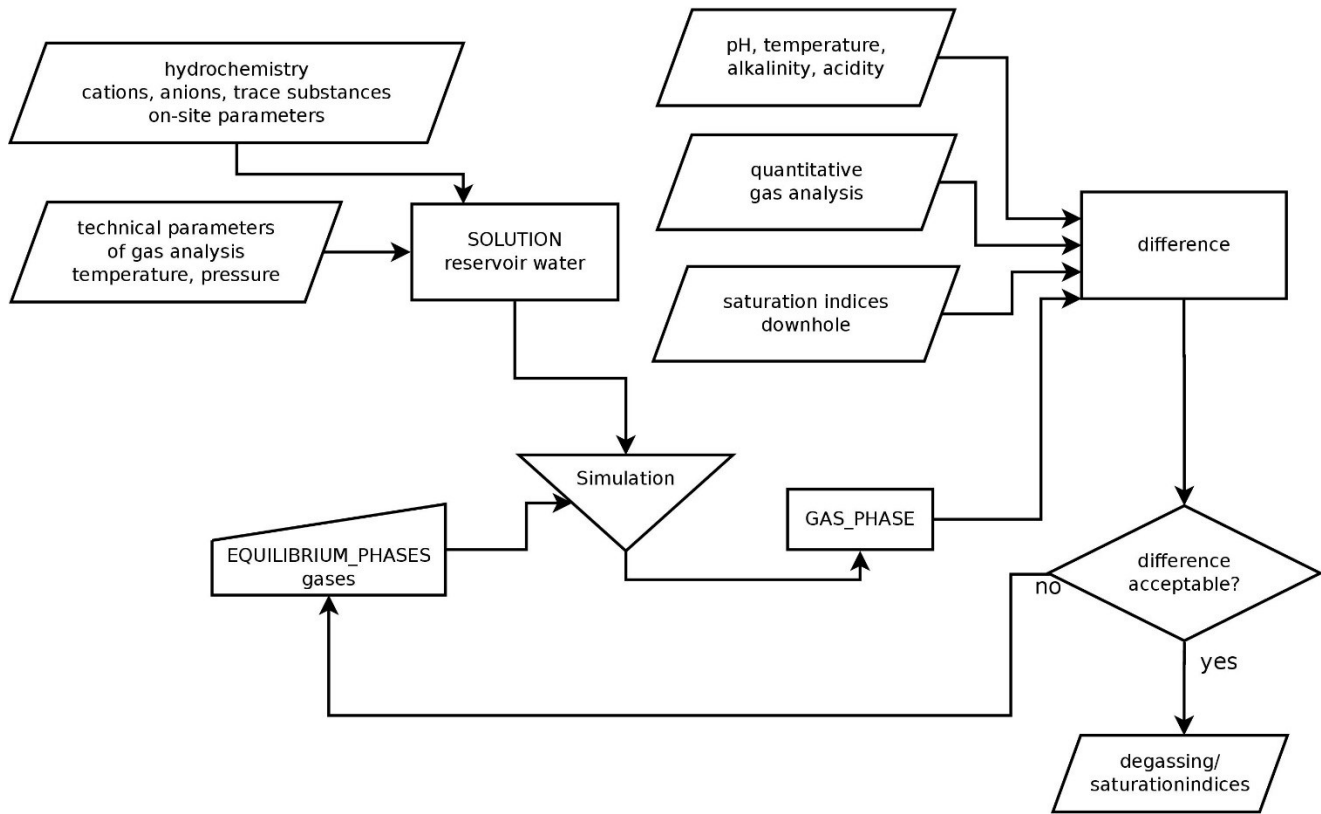
Figure 2: Flowchart for the calculation of the composition of the thermal water under reservoir conditions

Only after the fitting procedure has been successfully completed and the degassing process happening at ground surface or in the laboratory has been implemented in the model, the composition of the water under reservoir conditions (SOLUTION 1) is known and further simulations can be performed. The calculation of the degassing pressure (or bubble point) at different temperatures is implemented through another GAS_PHASE block combined with REACTION_PRESSURE to define the range of pressures. The gas volume and the gas composition are recorded in a SELECTED_OUTPUT file and later plotted against the pressure. The geothermal cycle was implemented in the model by changing the temperatures through REACTION_TEMPERATURE and the pressure through REACTION_PRESSURE and a corresponding GAS_PHASE. Large scale reactions of the cooled water with the sediments in the surrounding of the injection well are implemented by putting SOLUTION 1 in equilibrium with EQUILIBRIUM_PHASES matching the lithostratigraphy. This approach is not valid for the simulation of the reactions in the vicinity of the wells, because the flow velocities are high compared to the reaction rates. Here, the reaction rates were defined in the RATES block and the time dependent reaction was implemented using a KINETICS block. Likewise the amount of precipitates during degassing was implemented. The PhreeqC simulations were checked for the gases with the lowest solubilities against published values [6] and a published regression equation [7]. The deviations (see Tab. 1) were within 10 % of the published values. The effects of increasing salinity are negligible at ionic strengths < 0.01 [8].

Table 1: Validation of gas solubilities in PhreeqC

		Temperature °C	Pressure bar	Ref. mol/L	Simulation mol/L
D'Ans-Lax	N_2	75	25	0.011	0.012
D'Ans-Lax	N_2	100	200	0.081	0.092
Seibt	N_2	98	10	0.0044	0.0046

2.2 Degassing of thermal water

Three different setups were used to measure the gas loading of the thermal waters. System A, the on-site degassing unit, was made of a plastic tank (volume 12 L) with two connectors in the lower third of the tank serving as inlet and outlet of the thermal water. A third connector at the top of the tank was used to transfer the accumulated gas into a gas cylinder (glass or sulfinert coated steel) or a Teddlar bag. At the beginning the sampling tank was filled completely with thermal water with the outlets for water and gas open. After a constant flow of water was established and measured, the gas outlet was closed. The gas which then accumulated inside the container was measured as a function of time using an imprinted scale. System B, the stripping unit, was built by SWM Services GmbH, Munich. It consists of a stainless steel cylinder with a diameter of 0.4 m a height of 1.2 m. The thermal water enters the cylinder through a shower head at the top to increase the degassing. Both, water and gas flux, are measured using a water meter and a gas meter, respectively. The water level, the temperature and the pressure inside of the cylinder are recorded. System C, the lab degassing unit, consists of a small gas vessel which is first evacuated and then connected to a sulfinert coated stainless steel cylinder which was previously filled with the thermal water at a defined pressure. After the connection between the sulfinert cylinder and the gas vessel has been established the pressure in the evacuated vessel rises depending on the gas loading. To withdraw samples from the gas vessel the system is filled with helium which is the carrier gas for GC/MS, to a pressure of 1.050 bar. The relevant details of the three systems are given in Table 2. The gas loading is calculated from the ratio of the water and gas fluxes (systems A and B), or from the final pressure in the gas vessel (system C) using the gas laws. The gas loadings are normalized to standard conditions (1.013 bar, 273.15 K). The gas composition was measured using GC/MS (Shimadzu GCMS-QP2010 Ultra, Kyoto, Japan) using a ShinCarbon ST100/120 NOC column (O_2, N_2, CO_2, CH_4, C_2H_6, …) and a Rxi-lms column (H_2S).

Table 2: Technical parameters of the gas stripping systems

	A	B	C
Temperature, °C	< 100	40-80	20
Pressure. bar	p_{air} + 0.010	p_{air} + 0.005	< 10
Water volume (typ), L	20-100	500	0.5
Measurement time, min	10	10-600	1

3. RESULTS

3.1 Thermal water composition under reservoir conditions

At site A two different laboratories were commissioned to measure the composition and gas loading of the thermal water. The samples for the determination of the gas loading were taken during a long-term pumping test within 3 days. Sample A-1 was taken before the heat exchanger using an on-site stripping device coupled to a cooling trap to remove water vapor and an on-site gas meter. Sample A-2 was taken after the heat exchanger, transferred into a gas sample container and analyzed in the laboratory. The results of the gas analyses given in Tab. 3. Values for sample A-1 were originally reported in % together with the gas loading, values for sample A-2 were reported in NmL/L (mL of gas per L of water at standard conditions). In the simulation, only Nitrogen, Methane, and Ethane were added as EQUILIBRIUM_PHASES. CO_2 and H_2S in the simulated GAS_PHASE were stripped from the solution. The same result was obtained for other geothermal wells in the Molasse Basin. In any case excess CO_2 was necessary to simulate the gas composition.

Table 3: Comparison of the reported gas analyses

Sample	Reported values					After simulation			
	A-1 NmL/L	%	A-2 NmL/L	%	Δ %	A-1 NmL/L	%	A-2 NmL/L	%
CO_2	58.6	43.1	89.2	60.3	52.2	58.0	45.7	90.6	60.0
CH_4	43.1	31.7	37.1	25.1	-13.9	49.3	33.2	38.1	24.6
$\Sigma\ C_nH_{2n+2}$	1.29	0.9	0.9	0.6	-30.2	1.3	0.9	0.5	0.6
N_2	26.2	19.3	19.4	13.1	-26.0	26.9	19.6	20.2	13.2
H_2			0.36	0.2	36.0				
Ar			0.56	0.4	56.0				
H_2S	6.9	5.1				0.8	0.6	2.3	1.5
	136	100.0	148	100.0	8.8	136.3	100.0	151.0	100.0
bubble point, bar	4.1		3.2		-21.4	5.2		3.9	

The reported gas loading is almost identical with 136 mL and 148 mL of gas per L of thermal water at standard conditions. However, the reported composition of the gas phase differs significantly. H_2S could not be determined in gas sample A-2 because of interactions with the material of the sample container. The differences for N_2 and CH_4 are significant and lead to a bubble point 4.1 bar instead of 3.6 bar at 145 °C if used directly. At this site the degassing pressure seems to be controlled by the vapor pressure of the water which is 4.1 bar at 145 °C. Taking the sampling and degassing procedures into account, causes small but significant changes which result in an increase of the bubble point to 5.2 and 4.2 bar respectively. The results of the hydrochemical analyses are given in Tab. 4. The production stratum of site is dominated by Calcite and there is an inflow of reservoir water from higher strata. A hydrochemical analyses performed a few days earlier during the same circulation test (sample A-0) showed comparable concentrations of sodium, potassium, fluoride and sulfate, but significantly higher concentrations of calcium, magnesium, bicarbonate, and chloride indicating decreasing effects of a chemical stimulation. This explains why the calculated SI for Calcite and Dolomite are still way below equilibrium for samples B-0 and B-1. The use of the saturation index as target variable in the fitting procedure has to be assessed very carefully under such circumstances. The calculated pH-values under reservoir conditions increase slightly for sample B-1 and decrease significantly for sample B-2. The approximation of the saturation indices is good for sample B-2, but even further from equilibrium for sample B-1. However, sample B-2 does not fit into the hypothesis of decreasing stimulation effects.

Table 4: Hydrochemical composition of thermal water

	B-0	B-1	B-2
Na^+	139.8	112	115
K^+	23.1	16.8	17.5
Mg^{2+}	8.76	4.98	4.5
Ca^{2+}	58.6	13.2	27.9
F^-	3.61	4.19	
Cl^-	202.56	122	110
SO_4^{2-}	9.57	6	11
S^{2-}	3.7	10.7	30.5
HCO_3^-	268.49	177	222
pH	6.09	6.12	6.94
SI (Calcite)	-0.15	-0.41	0.60
SI (Dolomite)	-1.23	-1.94	-0.29
downhole values (calc.)			
pH		6.15	6.4
SI (Calcite)		-0.55	0.09
SI (Dolomite)		-2.23	-1.32

These findings are in line with data collected in previous projects [1,9] which indicate that the hydrochemical parameters recorded at surface level are not necessarily a good approximation of the water under reservoir conditions. With increasing temperature and gas loading the pH value is significantly affected by degassing. Thus geochemical calculations based on the measured values are likely to give false predictions, because the saturation state with regard to carbonates and other minerals is strongly dependent of the pH value. This restriction also applies to depth samples. Here, degassing and changes of the hydrochemical parameters have to be taken into account as soon as the sample is opened in the laboratory to insert e.g. the pH probe. This stripping of CO_2 has fatal consequences for the development of carbonaceous scalings, because at the high flow rates used in the geothermal facilities even small detoriations of the carbonate equilibrium lead to massive scalings affecting pipes, pumps, and heat exchangers negatively.

3.2 Gasloading and Bubble Point as a Function of the Analyses Method

Tab. 5 shows the effects of the type of analyses on the degassing pressure. All gas compositions result in the same molality of the thermal water under reservoir conditions. However, if used without explicit implementation of the degassing procedures in the model, the resulting bubble pressures would differ significantly.

Table 5: Effects of gas sampling and degassing setup on the gas composition

System		on-site A	Lab B	Lab B	Stripper C
T_w	°C	43	25	25	90
p_{gas}	bar	1.023	0.02	1.06	1.06
Methane	%	70.5	48.3	75.1	60.6
Ethane	%	1.9	1.2	1.8	1.5
H_2S	%	0.3	1.7	0.2	0.4
Nitrogen	%	11.0	6.9	11.6	8.8
CO_2	%	15.6	41.9	11.2	28.7
Gasloading	NmL	261	422	235	329
Gasloading incl. H_2O	NmL	282		243	1037

3.3 Calculation of the bubble point

Due to the active development of PhreeqC many of the batch calculations nowadays can be run from within PhreeqC itself. For instance, the calculation of the volume and composition of a gas phase at different pressures can be performed by iterating REACTION_PRESSURE. The pressure in GAS_PHASE is passed from the REACTION_PRESSURE. In previous versions of PhreeqC (< 3.1.2) an automatic iteration required the use of an external program, e.g. perl, to generate the input files, run PhreeqC, and parse the output. This is still required to run Monte-Carlo simulations to assess the robustness of the simulation. While a generic approach is offered by the PEST program (http://pesthomepage.org), a perl program was used to prepare the input files, run PhreeqC, and parse the output files. Fig. 3 shows the gas volume as a function of the pressure for site C. This forward simulation took the 95 %-confidence levels of the variations of the gas loading and composition from a three-week sampling campaign [10] as input for a Monte-Carlo simulation with PhreeqC. The predicted degassing pressure is in a range from 8.5 bar to 16.5 bar. Keeping in mind, that degassing of thermal water is the main cause for carbonate scalings, the operators would like to make sure that the pressure in thermal water system does not fall below the upper value for the degassing pressure. This example also indicates, that a single analyses of the gas composition is not sufficient to define the operational parameters of the geothermal facility.
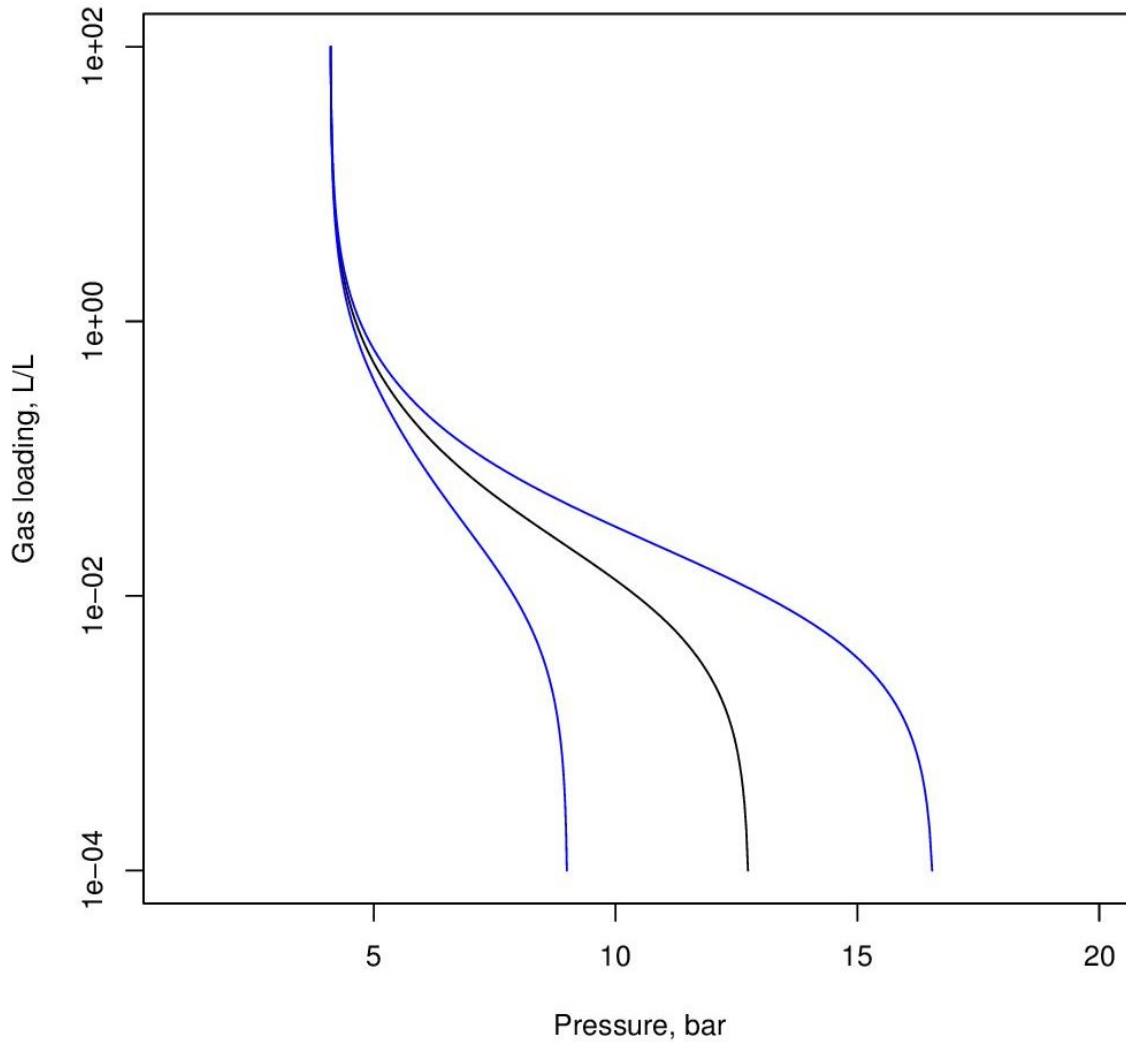
Figure 3: 95 % range for the degassing pressure at site C running at 100 L/s and a temperature of 145 °C

4. CONCLUSION

Given the sensitivity of the hydrochemical models, most attention has to be paid to the accurate measurement of the pH-value and a detailed recording the on-site sampling parameters complemented by a detailed description of the conditions for the handling and analysis steps in the laboratory. Based on this information a reliable model of the sampling procedures can be built from which the hydrochemistry of the thermal water under aquifer conditions can be derived. Using such models, the occurrence of scalings, the formation of gas bubbles, and possible reactions in the reservoir can be predicted. The model can be run as Monte-Carlo simulation to assess the uncertainty of the prediction. Care has to be taken before using analysis data, published or unpublished, as input data for models or prediction, if the sampling and analysis conditions are not explicitly given and a back-calculation using a hydrogeochemical model was not applied or described.

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