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Agenda

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15:00	Experimental investigation of silica solubility	Morten Tjelta
15:15	Silica polymerization from natural water resources	Öykü Çağ Hasköylü , Alper Baba, Mustafa M. Demir
15:30	Density and heat capacity of geothermal brines: from experimental data to modelling results	Ulrike Hoffert, Harald Milsch , Sylvain Guignot, Arnault Lassin, Laurent André
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16:05	Summary of REFLECT: What did we achieve?	Simona Regensburg and the REFLECT Team



Sampling and laboratory analysis for the characterisation of natural high-saline geothermal fluids

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Within work package 2.1 saline fluid samples (type C fluids) from several geothermal sites across Europe were collected in order to determine their properties, and thus contribute to the Fluid Atlas (WP3). In June 2020 and from April through March 2022, type C fluid samples have been taken from seven geothermal or hydrothermal sites in the Netherlands, Belgium, Germany and Austria. Figure 1 shows the locations of the conducted sampling campaigns.

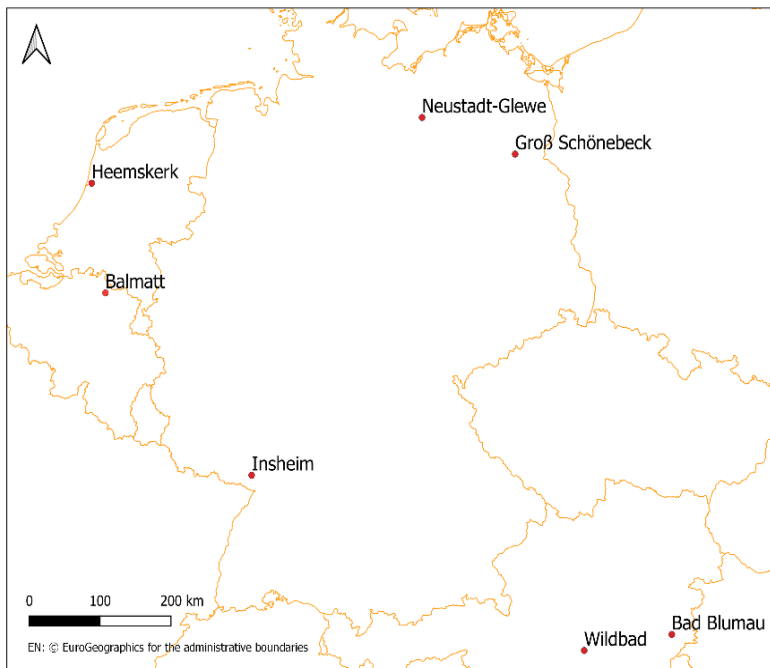


Figure 1: Overview of location of conducted sampling campaigns

The samples were analysed for major and minor ions, dissolved gases and isotopes. Higher hydrocarbons (C2-C5) were measured at Hydroisotop via gas chromatography (GC-FID) according to procedure QMA 504-2/15. Carbon-13 ($\delta^{13}\text{C}$) on these phases were measured in ‰_{VPDB} with isotope ratio mass spectrometry (IRMS) according to procedure QMA504-2/16 and with $1\sigma = \pm 0,5 \text{ ‰}$. The main cations and ions were analyzed with IC according to DIN EN ISO 14911 (E34) for cations and DIN EN ISO 10304-1 for anions. Trace elements and heavy metals were also measured with IC (Li, Ba, Sr, Br, F, I) or ICP-MS (U, As, Pb, Cu, Ni, Zn, Sb, Co, Al). Total iron and manganese were determined photometrically (Multilab P5 with Merck spectroquants at 530 nm for Fe and 445 nm for Mn) as well as silicon (Multilab P 5 with Merck spectroquant at 660 nm for Si). The $^{18}\text{O}\text{-SO}_4$ [‰_{VSMOW}] and $^{34}\text{S}\text{-SO}_4$ [$\text{‰}_{\text{V-CDT}}$] isotopes of sulfate were analyzed by isotope ratio mass spectrometry (EA-IRMS) according to procedure QMA504-2/29 and 2/28 with $1\sigma = \pm 0,5 \text{ ‰}$.

The sample reservoirs had a diverse background ranging from wells connected to palaeozoic reservoirs in Austria, the Upper Rhine Graben system in Insheim and the Northern German Basin in Groß Schönebeck. Most of the sampled wells have a depth of several kilometers (2.5 to over 4 km). An additional sampling campaign was conducted in a system of shallower wells and springs in Bad Wildbad, Austria which are connected to underlying deeper formations through faults. The content of total dissolved solids of fluid samples from deep wells ranges from around 20 g/L to 250 g/L. The sampled fluids were mostly of type Na-Cl, Ca-Na-Cl or Na-Ca-Cl. The water type varied with location (i.e. reservoir geology) and depth.



Assessing microbial diversity in deep geothermal fluids around Europe

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Deep geothermal fluids used for electricity production present several conditions considered as extreme for life such as high temperature, pressure, and salinity. In addition, sampling of such systems is also challenging. Because of this, the microbial diversity present in the fluids is still largely unknown despite the potential impact of microorganisms on the performance of the power stations. Indeed, microorganisms may be able to withstand the extreme conditions in the reservoir thanks to the formation of dormant resistant structures (e.g., spores), and grow in parts of the power plants in which conditions are favourable for their development (e.g., heat exchanger or injection wells). They may then form biofilms or cause corrosion inside the pipes, reducing the efficient use of geothermal power stations. Therefore, a better understanding of the microbial diversity present in deep geothermal fluids is needed to improve sustainable management.



Within the frame of REFLECT the presence of bacteria, archaea, and fungi in fluids samples from six geothermal power plants around Europe was analysed. Two different DNA extraction methods were used to extract DNA both from easily breakable cells and from dormant cells. The use of these two extraction methods allowed to enrich different communities, demonstrating the broad diversity of microorganisms present in geothermal reservoirs. Moreover, the comparison of power plants in different regions and with different conditions (e.g., temperature), underlined the specificities and common characteristics of microbial diversity in deep geothermal fluids. For instance, in most cases, the lower temperature fluids harbour a highly divergent microbial diversity compared to the one found in fluids at higher temperatures.

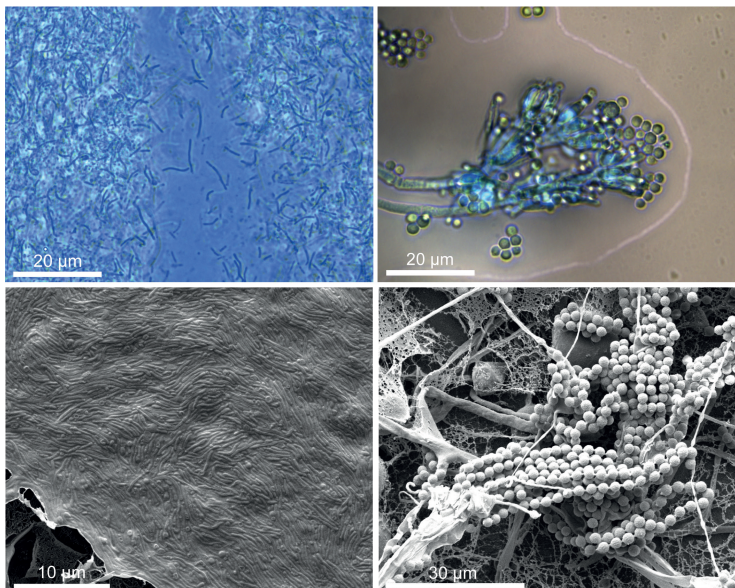


Figure 2: Microscopical images of two microbial strains isolated from geothermal power plants. The two images on the left: Bacteria (Up: Optical microscopy, Bottom: Electronic Microscopy (Made by PME, UniL)). The two images on the right: Fungus (Up: Optical microscopy, Bottom: Electronic Microscopy (Made by PME, UniL)).

Differentiation of the origin of dissolved organic compounds in geothermal fluids of the Bad Blumau site

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The operation of geothermal plants can be influenced by mineral precipitations (scalings) caused by chemical reactions due to changes of temperature and pressure in the fluids. At the Bad Blumau geothermal site, carbonate scalings are avoided by the injection of a scaling inhibitor which also contributes to the pool of dissolved organic carbon (DOC) in the fluids. There are still few data characterizing and describing organic compounds in geothermal fluids. However, they form an integral part of sedimentary basin fluids and organic compounds serve as nutrients for microorganisms or affect the chemical properties of the fluid by complexation.

Different analytical methods to characterize organic compounds were performed to elucidate the impact of inhibitors, added to the geothermal fluid, on the natural DOC of the fluid. We applied ion chromatography (IC), liquid chromatography – organic carbon detection (LC-OCD) and Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) in positive atmospheric pressure photoionization (APPI) and negative electrospray ionization (ESI) mode to the fluid samples taken from the production and injection side as well as the heat central of the Bad Blumau site. DOC concentrations generally decreased from the production to the injection side within the range of 10 – 7 mg C/L which could be indicative of microbial degradation. The DOC is predominantly composed of low molecular weight organic acids (LMWA), especially the organic acid anion acetate. The injection of the scaling inhibitor to the fluids results in approximately 1 mg C/L of macromolecular DOC to the fluids.

Up to 41.6 % (ESI) and 62.7% (APPI) of the detected molecular formulas in the fluid samples originate from the inhibitor (Figure 3). FT-ICR-MS analyses provide a molecular resolution of the DOM in the fluids and lead to differentiation between natural DOM of the fluid and DOM deriving from the inhibitor. Signals not being recognized as inhibitor-based might derive from other contaminants and cannot automatically be assigned as natural DOM. Therefore, further in depth analyses of the FT-ICR-MS data with comparison of natural DOM from other sources is needed. A comprehensive study including all results of the here performed analyses is currently in preparation.

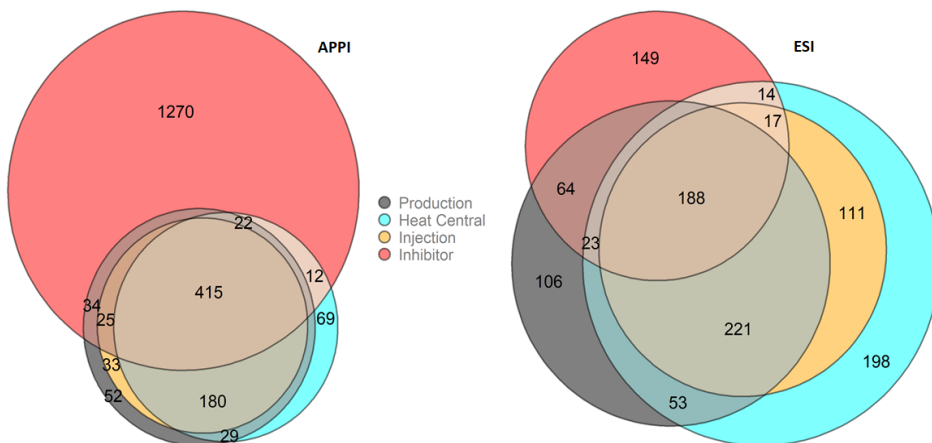


Figure 3: Venn diagrams showing common and unique formulas for APPI (left) and ESI (right) mode.

Acknowledgements: We would like to thank our partners Hydroisotop GmbH and Spa Therme Blumau Betriebs GmbH who organized and helped with the sampling campaigns.

The European geothermal Fluid Atlas

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In the REFLECT project, the formerly existing and newly measured data of geothermal fluids are visualised through the European Fluid Atlas. Fluid data have been collected from 21 European countries. In the Atlas, the layers provide point feature information presented on a base map, including geography, geology and depth range, as well as physical, chemical and microbial properties of fluids. Data of wells, rocks and reservoirs are also available. The focus is on fluids used for electricity generation (> 100 °C), but data from heat projects are also included.

For the Atlas, a free and open-source cross-platform is used, in which the geographic information system provides the environment to view, edit and analyse geospatial data. The interface includes query and filtering tools to explore the database with a map based visualization.

The presentation will show the beta-version of the Fluid Atlas. Query possibilities will be presented via the web version of the Fluid Atlas.

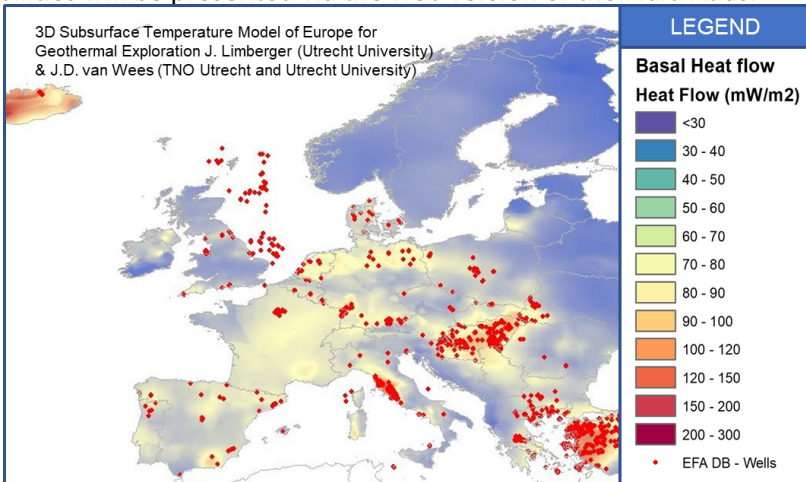


Figure 4: Location of the 2400 wells where formerly existing well, fluid, rock and reservoir data have been collected.

A Downhole Sampler for High-Temperature Geothermal Wells

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In the EU funded project REFLECT a downhole sampler and fluid transfer system for high-temperature geothermal wells ($>200^{\circ}\text{C}$) is developed. The sampler is designed to tolerate harsh environments at high pressures and elevated temperatures, capable to sample from individual feed-zones at specific depths giving information that is otherwise lost once the fluid flashes and/or mixes with shallower feed-zones while flowing up the well. The fluid sampler will be able to sample high-temperature geothermal wells of $200\text{-}300^{\circ}\text{C}$, but the more ambitious aim is to make it adaptable for sampling at even higher temperature (up to 400°C) and supercritical pressures. The chemical data obtained from fluids at different depths will contribute to conceptual models of reservoirs. Hence, better understanding of hydrothermal reservoirs through their production lifetime. A prototype of the sampler will be built in the year 2022 with subsequent testing and in-situ sampling for validation.

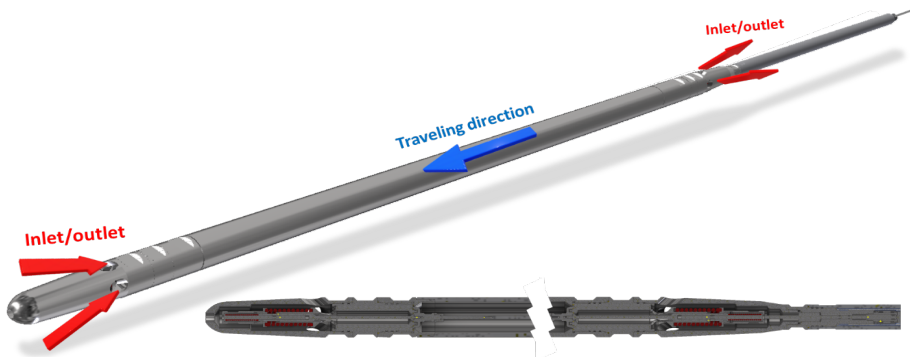


Figure 5: REFLECT downhole sampler that has been developed to be able to sample various phases (liquid, two-phase, steam) at low to high temperature/high pressure superheated/supercritical conditions in geothermal wells.

CO₂ degassing kinetics of geothermal fluids

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Decreasing pressures towards the production well can lead to the exsolution of gas from geothermal waters in the near-well region. This can cause problems like corrosion of the facilities or reduced water production. This study aims to improve the understanding of the conditions under which free gas forms with a specific focus on CO₂.

Both degassing in bulk and in porous media is examined here. The former through a series of visualization experiments of the CO₂ degassing process at reservoir conditions in a pressure cell using a high-speed camera.

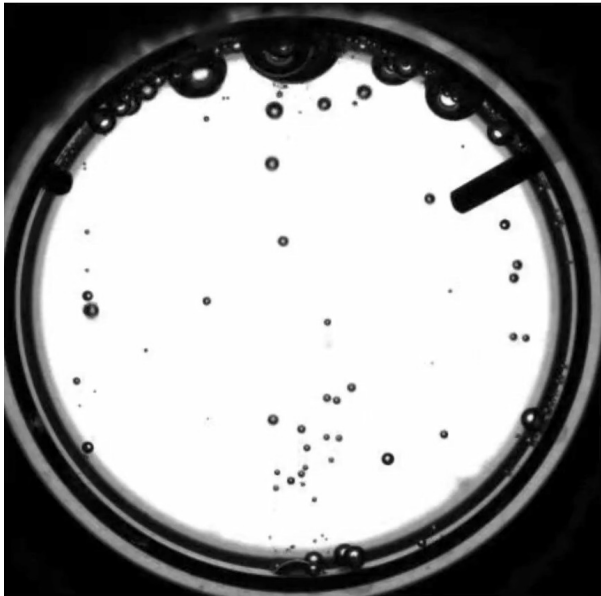


Figure 6: Visual monitoring of bubble formation in a pressure cell.

The latter by performing coreflood experiments and using pressure monitoring and CT visualization to assess the influence of the free gas bubbles on the flow. A model for CO₂ solubility in brine was created to assess whether the start of degassing (i.e. the bubble point) can be predicted accurately by comparing its results to that of the experiments. The coreflood experiments showed that the formation of free gas can reduce the water relative permeability by up to 50% in a high permeability Bentheimer sandstone and up to 90% in a low permeability Berea sandstone. The bubble point does not vary between the two different rocks. The CT assisted corefloods show the increasing gas saturation inside the core as the pressure is reduced. Gravity override due to a difference in density between the gas and liquid phase was also observed in these experiments.



Experimental investigation of silica solubility

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In geothermal energy production, precipitation/scaling and potential plugging of wells is one of the major threats to flow assurance. Mitigation strategies should be considered at the design stage, but in order to do so knowledge about solubility across a relevant space of temperature, pressure and fluid composition is needed.

In hot fluids, silica scaling is often found to be the major concern. Predictive models available in literature give good agreement with experimental values in the region where data are available, but there is limited data available at high temperatures and low pressures, in particular in the presence of salt.

This work describes an experimental setup designed to carry out solubility experiments up to 500 °C and 400 bar. A main feature of the setup is the ability to dilute the sample fluid in the hot zone in order to avoid precipitation during sampling. Kinetic information is obtained from packed column solubility experiments with variable flow rates. Dissolution kinetics is interpreted using absolute rate theory to obtain information about precipitation kinetics.

Silica polymerization from natural water resources

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Scaling is a major operational problem for geothermal power plants. The main ingredient of the scales is metal silicates particularly for the plants located in west-coast of Turkey. The formation of metal silica deposits is driven by the nucleation of silica polymer in the existence of various metal cations in geothermal brine. For the understanding of silica formation, it is necessary to understand kinetics of polymerization under various circumstances of geothermal systems. In this study, silica polymerization is performed under various low temperatures (< 90 °C). The kinetics of polymerization is monitored by colorimetric spectroscopic methods using ammonium molybdate. Rate law is determined along with activation energy of the polymerization process. The process is also performed in the presence of metal cations such as Fe^{2+} , Ca^{2+} , and Mg^{2+} to understand the effect of metal ions on the polymerization kinetics in terms of order of silica polymerization reaction, activation energy, and rate constants.



Density and heat capacity of geothermal brines: from experimental data to modelling results

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Thermophysical data of geothermal fluids like density or heat capacity are required for reliable geothermal site assessment and development (e.g. for exploration, well and pump design, and power plant layout). While reliable collections of such data can be found in the literature for binary aqueous electrolyte solutions, information for more complex (e.g. ternary solutions) and highly saline fluids is scarce.

First, we performed laboratory scale measurements of fluid density and heat capacity on synthetic NaCl and CaCl₂ aqueous mixtures. Different cation ratios were explored for total molalities up to 6 mol·kg⁻¹. Pressure and temperature ranged between 0.1 and 40 MPa, and 20 and 80°C, respectively. An Anton Paar DMA4500M was used for density measurements at ambient pressure, whereas the DMA HP external density measuring cell measured density up to 70 MPa and 200 °C. About 700 new experimental points have been generated.

Then, the model of Lassin and André, 2023 for the NaCl-CaCl₂-H₂O system based on the Pitzer equations and including the partial dissociation of the CaCl₂ electrolyte was used to calculate density and heat capacities of the solutions experimentally investigated. The model is able to describe salt solubility in the NaCl-CaCl₂-H₂O system over the whole range of mixture ratios, at least up to 403 K. We also observed a very good match for density and heat capacity calculations in NaCl solutions with errors lower than 2% (except when chloride concentration exceeds 9 mol·kg⁻¹). For calcium chloride system, a good match is observed up to 3 mol·kg⁻¹.

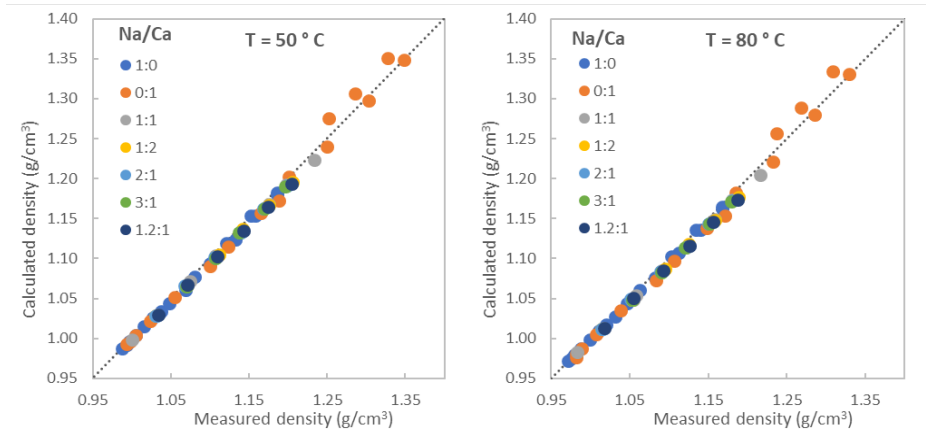


Figure 7: Density and heat capacity in the $\text{NaCl-H}_2\text{O}$ and $\text{CaCl}_2\text{-H}_2\text{O}$ systems. For heat capacity, symbols are experimental data and solid lines are numerical results .

Reference: Lassin, A. and André. L.; A revised description of the binary $\text{CaCl}_2\text{-H}_2\text{O}$ chemical system up to solution-mineral equilibria and temperatures of 250 °C using Pitzer equations. Extension to the multicomponent $\text{HCl-LiCl-NaCl-KCl-MgCl}_2\text{-CaCl}_2\text{-H}_2\text{O}$ system. *Journal of Chemical Thermodynamics*, 176, 106927, 2023, DOI: <https://doi.org/10.1016/j.jct.2022.106927>



porousMedia4Foam: An open-source multiphase reactive transport platform based on OpenFOAM® and PHREEQC for geothermal applications

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In a geothermal system, brine is transported from aquifers – subsurface water reservoirs – to the surface, with the aim of extracting the thermal energy of the brine. However, the pumping of these fluids toward the surface disturbs the chemical equilibria causing potential scaling in facilities.

A numerical code (*porousMedia4Foam*) was developed in order to predict these scaling risks. It is an open-source, multi-scale and multiphase package, where OpenFOAM® is coupled with PHREEQC to investigate hydro-geochemical interactions. The flow, transport of species, evolution of porous media properties and temperature are handled by solving equations implemented in OpenFOAM® whereas, the chemistry is exclusively handled by PHREEQC code.

This numerical approach allows a fine description of the fluid behaviour inside the well, especially at the junction between two different well cross-sections. An extremely fine simulation reveals existence of vortices at corners of expanding cross-sections of well involving re-circulation of fluids and potential mineral precipitation.

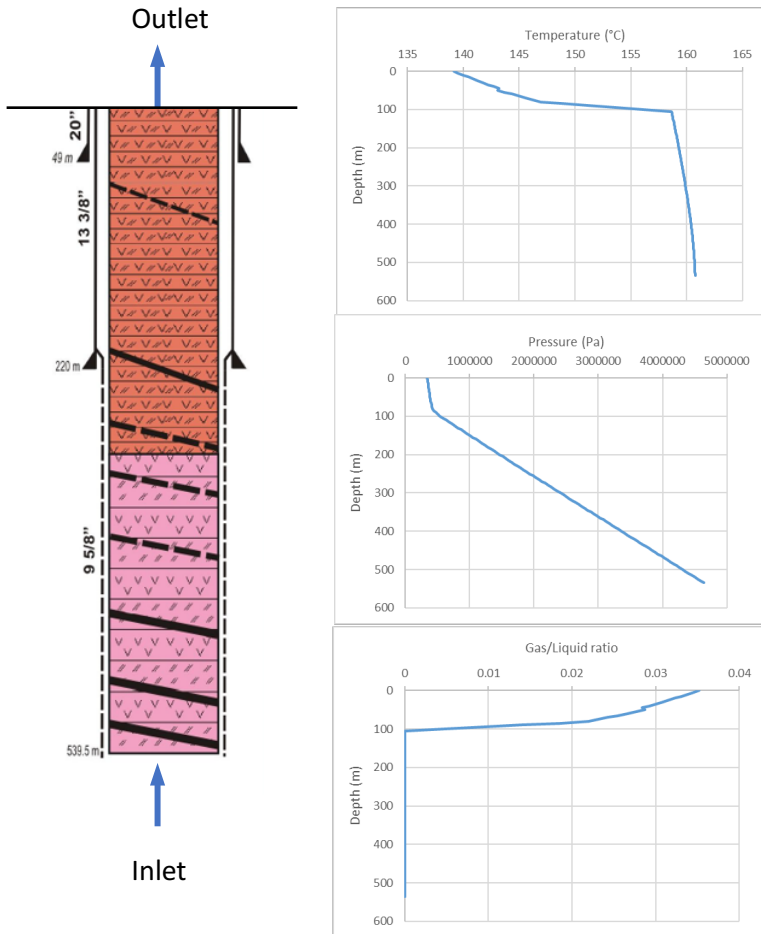


Figure 8: Temperature, pressure and gas/liquid ratio profiles in a geothermal production well

3D Modelling and Characterization of Stibnite Scale Formation in Germencik Geothermal Site, Büyük Menderes Graben, Western Turkey

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Scale problems in geothermal power plants are among the most critical problems affecting power plant efficiency and cause loss of production. Today, scale problems occur in many geothermal power plants in the world. Germencik geothermal power plant is a binary cycle power plant located in an active tectonic zone in western Turkey. Sb scaling in the preheater system is the most crucial problem in the power plant where the geothermal waters are of Na-Cl-HCO₃ water type. Sb clogs the tubes of the preheater system and causes efficiency loss in the power plant. In this study, the scale problem in the study area is discussed under two headings:

(1) Possible types of scale in geothermal wells, (2) Sb scaling in the preheater system. The scale types emerging in the geothermal wells and the preheater system were examined in detail, and it was understood that different Sb types could occur in the preheater system with geochemical models. In addition, the required reinjection temperature was calculated as 95°C to control Sb scaling using the saturation indices diagrams.



Figure 9: Stibnite scaling in the preheater system of the Germencik Power Plant

3D Modelling and Characterization of Scale Types in Hyper Saline Geothermal System in Tuzla Geothermal Power Plant, NW Turkey

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Tuzla geothermal field (TGF) is located in an active tectonic zone on the Biga Peninsula in Northwestern Turkey. Geothermal waters offer hypersaline water characteristics, and the reservoir temperature of geothermal waters can reach 173°C. Scale problems in the TGF are the most important problems affecting the efficiency of the power plant. In this study, the scale types in the TGF are examined in full detail under two headings: (1) the scale types in the surface equipment system, (2) the scale types in the geothermal wells. The morphology, structure, and elemental composition of scale types were revealed by XRD, XRF, and SEM observations. The findings revealed that the scale types are mainly composed of PbS (galena) and aragonite and calcite forms.



Figure 10: Silica based scaling in the Tuzla Power Plant

Impact of geochemical uncertainties on geothermal fluid production and scaling precipitation in geothermal plants and facilities

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Scaling is one of the most common operational challenges occurring in geothermal plants. In order to evaluate its associated risks, a proper understanding of the interaction between the geothermal brine composition, operating conditions and pipe materials is key. However, uncertainties in geothermal brine composition, due to sub-optimum sampling, added inhibitors or measurement uncertainties, can significantly impact the accuracy and precision of the prediction of geothermal fluid production, and scaling and corrosion potentials. In this work we have evaluated the risk of scaling in geothermal plants under composition uncertainties. For a better understanding of the impact of compositional uncertainties on fluid properties, two non-intrusive uncertainty propagation methods were employed (Monte-Carlo and Sobol sampling). A fluid composition database was used to characterize the composition uncertainty bounds for different minerals. The work was demonstrated for the barite precipitation in a simplified modelled heat exchanger. At higher temperatures in the heat exchanger the width of distribution was found to be relatively small due to many samples resulting in no scaling at all, while the difference between the distribution mean and nominal value was relatively high at 46%. At lower temperatures scaling was predicted to occur for all samples considered, and while the range of possible scaling amount values increased, the distribution mean was significantly closer to the nominal value (13%).

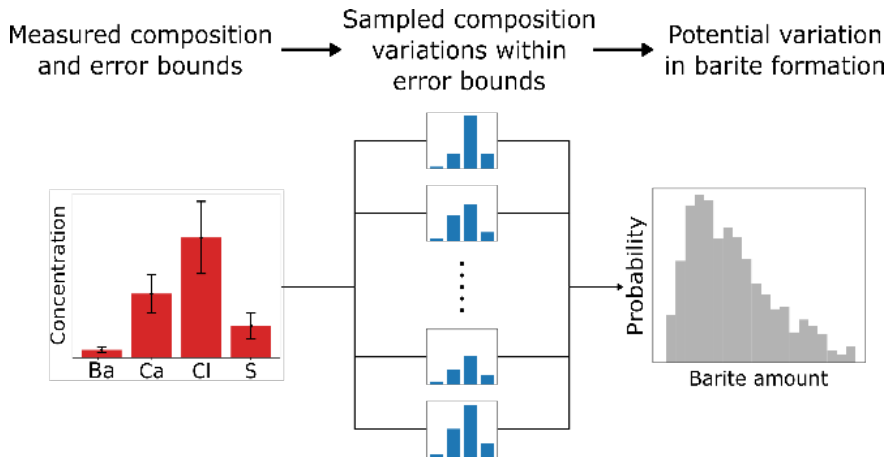


Figure 11: Schematic overview of the general uncertainty quantification workflow

Thermoelectrical properties of salt solutions and monitoring of mineral precipitation by impedance spectroscopy

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Calcite is one of the most abundant scaling minerals in geotechnical installations and the precise knowledge of the hydrochemical solution equilibria is key to predict its precipitation behaviour. In the framework of the EU-funded REFLECT project we perform solubility experiments in the H₂O-NaCl-CO₂ system to broaden the database for temperatures up to 210 °C. Here, we present preliminary results from a series of ongoing solubility measurements as a function of temperature and CO₂ partial pressure (0 – 50 bar) at various salinities ranging between 0 – 20 wt% NaCl. We use electrical conductivity measurements to monitor the progress in dissolution or precipitation from the solutions and to define equilibrium conditions. For this, we have developed a new 4-point electrode system, which was successfully tested at temperatures of up to 213 °C and a maximum system pressure of 70 bar.

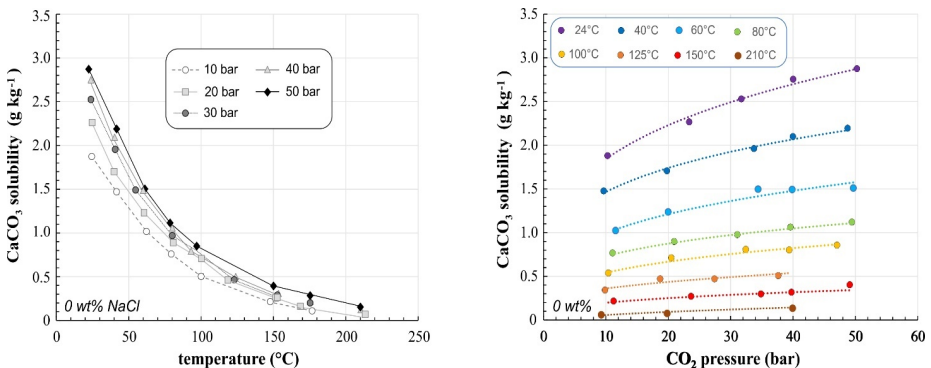


Figure 12: CaCO₃ solubilities in dependence of temperature and CO₂ pressure.

19 October 2022, Berlin, Germany



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PROJECT COORDINATOR

- Helmholtz Centre Potsdam - German Research Centre for Geosciences, GFZ

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