The use of numerical modelling for characterizing deep geothermal reservoirs: a case study of the Upper Rhine Graben

Berenice Vallier[1]

[1]Independent researcher, Lower Hutt, New Zealand

vallier@unistra.fr

Keywords: *Geothermal reservoir, Thermal conductivity, Permeability, Numerical modelling, Cap-rock, Thermal gradient, Gravimetry, Brine rheology*

ABSTRACT

Over the last few decades, numerous numerical models of deep geothermal reservoirs in the Upper Rhine Graben (URG) have been developed to study natural hydrothermal circulation and the effects of industrial exploitation. However, there is a lack of numerical methods that incorporate multi-physical and multi-scale measurements. This research examines a natural, large-scale hydrothermal circulation and its associated multi-physical and multi-scale data through a homogenized thermo-hydro-mechanical (THM) model. The aim of this research is to develop a THM model that provides useful engineering tools for the exploration of future geothermal sites. To validate this approach, inversion of key rock physical properties has been conducted using observed temperature and stress depth profiles. The model provides new insights into the relationship between geophysical data and hydrothermal circulation. It also highlights the crucial impact of brine viscosity on circulation. Furthermore, the model provides a practical tool for linking measurable surface thermal gradients with reservoir temperature in relation to cap-rock depth. This method could be very useful for exploring future geothermal reservoirs in New Zealand.

1. INTRODUCTION

One primary objective of the numerical modelling applied to geothermal reservoirs is the development of predictive and practical engineering tools for assisting the exploration and exploitation phases. The numerical models have been used to integrate several types of data, characterize the natural hydrothermal circulation, and manage short- and long-term management of the geothermal reservoir (Sanyal et al., 2000; Jain et al., 2015; Tomac and Sauter, 2017).

The Upper Rhine Graben (URG) is an ideal study case for developing numerical modelling processes that can be extended to other geothermal contexts. Indeed, the region is one of the most studied for geothermal industries, with more than thirty years of research (Genter et al., 2010; Huenges and Ledru, 2011; Lu, 2017). As demonstrated in Figure 1, the URG exhibits a distinctive heterogeneous thermal distribution, characterised by localised areas of high temperature compared to the mean value observed in Central Europe. The Soultz-sous-Forêts (Soultz) geothermal site has successfully exploited one thermal anomaly, using Enhanced Geothermal System (EGS) technology. Soultz has provided a substantial collection of geophysical, geochemical and geological measurements (Sausse et al., 2010; Schaming et al., 2016), enabling the calibration of numerical models and subsequent understanding of future reservoirs.

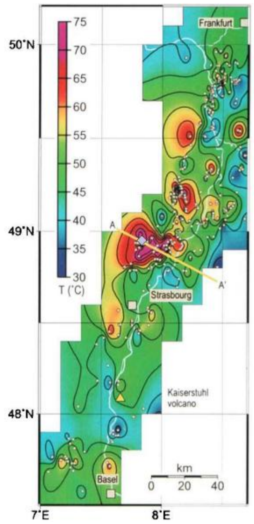

Figure 1: Temperature map extrapolated to the URG at 800 meters deep (Pribnow and Schellschmidt, 2000). Temperatures above 75°C are indicated by the same color (i.e. purple). The triangle, squares, dots and diamond correspond respectively to the Kaiserstuhl volcano, towns, well data locations and the Soultz-sous-Forêts (Soultz) location.

The modelling process developed for Soultz, or any reservoir in the URG, can be extended to encompass current and future geothermal projects in New Zealand. The primary applications are other potential EGS projects, such as in Mangakino or at the margins of current geothermal sites (Fagan et al., 2006; Rustandi et al., 2016). The development of a numerical modelling approach within the URG framework has the potential to offer novel insights into 'Super Hot' geothermal projects. This is predicated on the adaptation of the numerical modelling to the specific thermal conditions of the 'Super Hot' geothermal projects.

The paper aims to present a number of practical tools from numerical modelling that have been developed for the URG and applicable to different geothermal contexts. The model integrates thermo-hydro-mechanical (THM) couplings using a finite element approach, and the specificity of our approach is twofold. Firstly, the reservoir is homogenized at a scale of 100m. Secondly, particular attention is paid to the detailed description of the brine rheology. In this paper, we describe the approach toward the homogenized numerical model by presenting the geological, thermo-hydro-mechanical settings and assumptions provided for the model. Then, the forward solving of the THM system and the inversion process used to validate our approach are described. And finally, the main practical tools and insights for characterizing any geothermal reservoir are detailed.

2. METHODS

2.1 Towards a reservoir-scale homogenized model

2.1.1 Geological setting from one geothermal site

Fig. 2a shows a sketch of the main geological units of an EGS reservoir in the URG: Soultz. The uppermost part of the geological structure starts with a sedimentary cover. From top to bottom, it includes a Pliocene-Quaternary sequence, Eocene formations, Jurassic formations, and a Triassic sequence. Below the sediments, a granitic basement extends to the base of the cored domain. Evidence of paleo-weathering from the Permian age can be seen at the very top of this granite, making the transition to the sediments difficult to identify. The upper part of the granitic basement consists of a porphyritic monzonite with clear signs of significant hydrothermal circulation through the fracture system. Below, there is a first transition to a granite enriched in biotite and amphibole, and a second transition to a rather different leucogranite containing muscovite and biotite.

Well logs, microseismicity and vertical seismic profiles have been combined in order to characterise fracture networks, particularly in Soultz. Two main natural fracture systems have been identified in the granitic basement:

- A strongly connected network of small-scale fractures. Open small-scale fractures have been identified through granite core analysis. According to the core analyses in Soultz, the fractures have a mean aperture of 1.5 mm and a maximum aperture of 250 mm. They are organised into clusters of high fracture density.

- A set of large-scale fractures forming an anisotropic porous medium. Large-scale fractures have been identified using well logs, microseismicity analyses and VSPs. These have been incorporated into a geological model for Soultz (Sausse et al., 2010). Microseismic studies have estimated the area of the fractures to be around 100 m, though a few extend up to 3 km (Evans et al., 2005; Genter et al., 2010). The fractures are oriented parallel to the NNW-SSE orientation of the Rhine Graben.

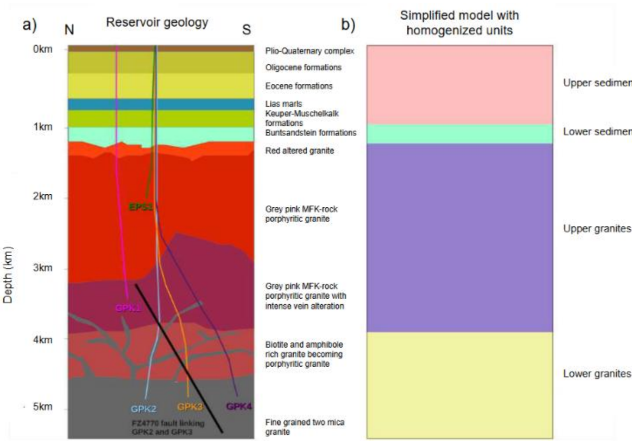

Figure 2: (a) A 2D conceptual model of the geology at Soultz, modified from Dezayes et al. (2005a, Fig. 28) and Aichholzer et al. (2016, Fig. 3). (b) A simplified reservoir model for the present work, comprising four main geological units homogenized at a scale of about 100 meters within the REV.

2.1.2 Hydrothermal aspects

Fig. 3a shows temperature-depth profiles in Soultz wells at equilibrium. Despite their spatial separation at a depth of more than 1km, the first striking observation is that they all exhibit three major common trends with depth. The strong overall similarities between the T-logs suggest that large-scale faults have a weaker influence on the temperature profiles than the strongly connected network of small-scale fractures. Notably low values of the local geothermal gradient at the sediment-granite and upper-lower granite transitions compared to the Central European gradient are interpreted from a large-scale active hydrothermal circulation. The native fluid has been identified as a heavy brine similar to a NaCl solution, containing 100 g/L of total dissolved solids and having a pH of around 5 (Sanjuan et al., 2006; André and Vuataz, 2005). Moreover, the contribution of natural granite is also considered (Vallier et al., 2019).

2.1.3 Geomechanical aspects

Fig. 3b illustrates the linear trends of the principal stress component's magnitudes with depth. They have been deduced from analyses of borehole TeleViewer images, gamma density logs, distribution and magnitude of breakouts through the different boreholes in order to characterise the natural stress state at Soultz (Cornet et al., 2007; Evans et al., 2009). The stress-depth trends are assumed to be similar for Rittershoffen (Vallier et al., 2018). The orientation of the maximum horizontal stress determined by analysis of breakouts and drilling-induced tension fractures, is within the range of N169°E ± 14° and N175°E ± 30° (Cornet et al., 2007; Evans et al., 2009).

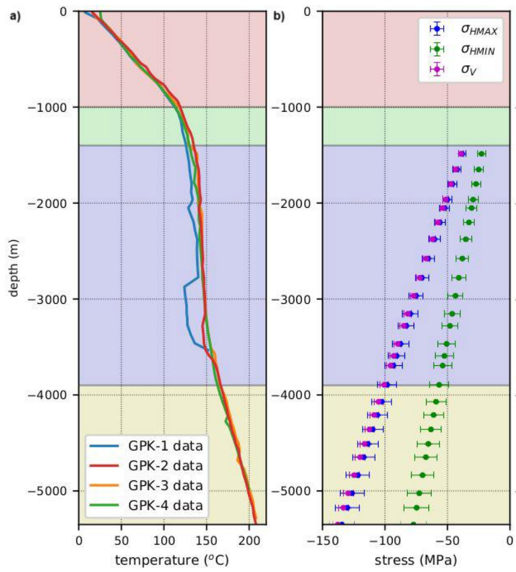

Figure 3: (a) Equilibrium temperature profiles obtained from a log run in the Soultz wells following the drilling operation (Cuenot et al., 2008). (b) Experimental correlations of the principal stress components in Soultz (Evans et al., 2009).

2.1.4 Assumptions for homogenization

The objective of the present–work is to develop practical engineering tools for exploring future geothermal reservoirs. To this end, the simplest numerical model consistent with the main characteristics of a geothermal reservoir is proposed.

Consequently, the model does not aim at describing the whole complexity of the geology: the small-scale but pervasive network is assumed to have a larger influence on the thermal state than the large-scale but sparse fault system. The Soultz geology has been idealized as four homogenized units, as illustrated in Fig. 2b. The effective porous medium is assumed to be fully saturated with a single-phase heavy brine.

2.2 Inversion method with a Finite Element THM model

2.2.1 Governing equations of rock and brine rheology

The THM coupling was described under the assumption that the four units are homogenized as a porous medium, fully saturated with a single-phase brine in the thermo-elastic regime. The equations governing the THM coupling are developed from the reference book of Coussy (2004) and detailed in Vallier et al. (2019) for this study case. Here, the following assumptions have been made:

- The Cauchy stress tensor is constituted by the effective stress and the hydraulic stress.
- The thermodynamic flows are linearly related to thermodynamic forces. Most of the homogenized properties in Hooke's law, Darcy's law, and Fourier's law depend on porosity, fluid pressure and temperature.

One particularity of the THM model is that the brine rheology is taken dependent on temperature and/or fluid pressure. As an example, Fig. 4 illustrates the specific mass of pure water and brine and the brine viscosity as a function of temperature, and fluid pressure for the specific mass. Indeed, the brine rheology is extrapolated from experimental results for artificial brines at varying salinities (Zaytsev and Aseyev 1992; Kestin et al. 1981; Rowe and Chou 1970). The other relationships between fluid properties (thermal dilatation, heat capacity, thermal conductivity) and temperature are given in Vallier et al. (2019). The fluid under consideration is assumed to be a pure NaCl solution, with a mean specific mass content of 100 g/L (Magnenet et al., 2014; Genter et al., 2010).

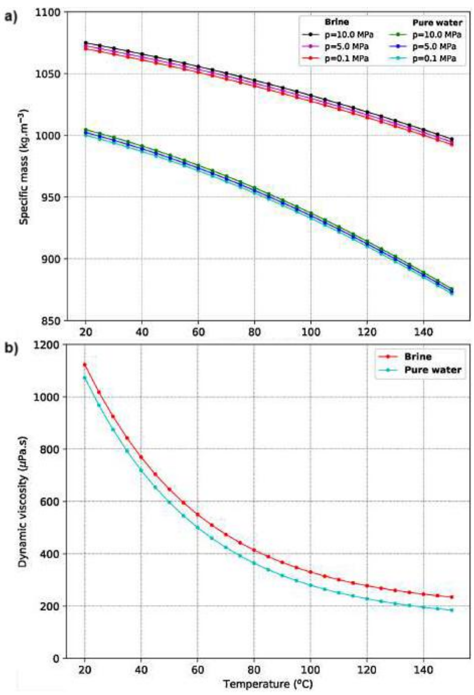

Figure 4: (a) The specific mass of pure water and brine as a function of temperature and fluid pressure, as deduced from the empirical correlation of Rowe and Chou (1970). (b) The fluid dynamic viscosity of pure water or brine depending on temperature, according to the experimental correlations of Kestin et al. (1981).

2.2.2 Finite element solving

The governing equations are solved by using the open-source finite element solver Code_Aster (EDF, 2016), in which specific developments were added to account for the heat sources induced by the radioactivity of rocks, the nonlinear brine rheology and the search for the stationary solutions. As illustrated in Fig. 5, the considered geothermal reservoir model is depicted as a two-dimensional vertical cross section of the horizontal units, which have been homogenized at the scale of a Representative Elementary Volume. Fig. 5 also illustrates the THM boundary conditions: (i) temperatures are maintained at a set value for the upper and lower boundaries. It should be noted that the lower boundary can also be set as a heat flow condition if the heat flow value is better constrained than the temperature at the studied geothermal site. The lateral boundaries are taken to be adiabatic; (ii) the value of atmospheric pressure is imposed on the upper boundary of the fluid pressure. The remaining boundaries are presumed to be impermeable; (iii) The normal component of the mechanical displacement is nil on the lower and lateral boundaries. The upper boundary is stress free.

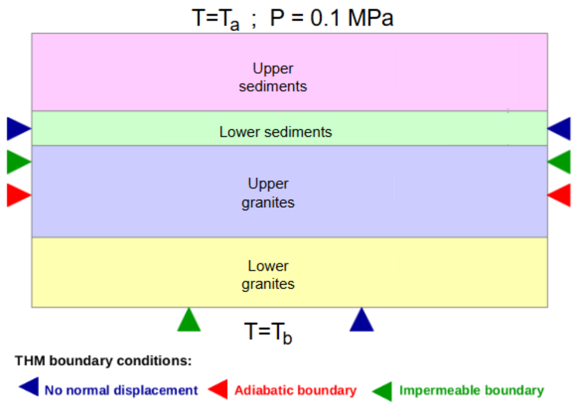

Figure 5: 2D model as a vertical cross-section, along with its associated THM boundary conditions. Ta and Tb are set temperatures deduced from experimental T-logs. The background colors correspond to the homogenized geological layers at a scale of 100 m.

2.2.3 Inversion method and model validation

In order to validate the approach, the key petrophysical parameters are assessed from an inversion of the observed temperature and stress-depth profiles. The THM model is used as the forward model in this process. The inversion is carried out using the Parameter ESTimation code (PEST) (Doherty, 2005). PEST employs a standard resolution approach based on a Levenberg-Marquardt algorithm, which minimises the L2-norm of the difference between the model and observations with respect to a chosen set of key parameters. It is important to note that the PEST deterministic inversion procedure is sensitive to the initial conditions, such as the prior distributions of the rock properties. However, the prior distributions are well constrained thanks to the databases from the Rittershoffen and Soultz sites. Nevertheless, in the event that the targeted geothermal reservoir is not characterised by a well-constrained database, it may be necessary to establish an inversion process that is less sensitive to the prior distributions of rock properties. In this study, the key parameters adjusted during the inversion are: permeability, thermal conductivity and elastic moduli (i.e., Young's modulus and Poisson's ratio).

3. PRACTICAL TOOLS FOR GEOTHERMAL EXPLORATION IN NEW ZEALAND

3.1 Linking of surface data to reservoir temperature

The objective of the THM model is here to function as a predictive tool for new geothermal projects during the exploration phase in various contexts, including the URG or New Zealand.

Fig. 6 illustrates the built relationship between surface thermal gradient and reservoir temperature with regard to different values of cap rock depths. The depth of the cap-rock can be assumed from preliminary geological studies and the thermal gradient measured at the near-surface can be deduced from the early-stage exploration phase. However, the reservoir temperature is a key parameter for any geothermal exploitation but its value is not easily accessible during the exploratory phase. The near surface thermal gradient measured and the assumed cap rock depth would provide an approximate value of this key parameter. Knowing the value of the reservoir temperature would thus help to assess the viability of the geothermal reservoirs. Furthermore, relationships are being established between the heat flux measured at the surface and the data available at depth. In the future, these abacuses could serve as a significant decision-making tool for new geothermal projects in the URG or in New Zealand.

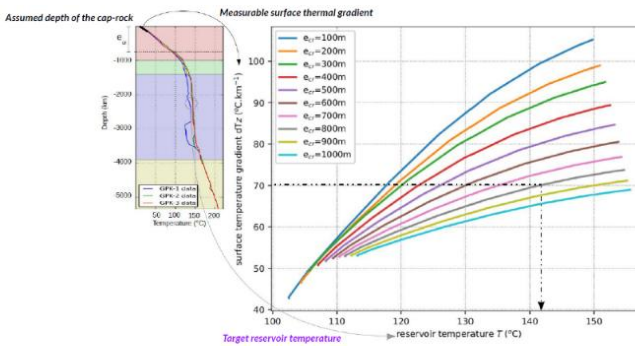

Figure 6: Link between the measurable surface thermal gradient and the key reservoir temperature value according to the assumed hydraulic roof depth (ecr).

3.2 Use of geophysical data from exploration phase

Geophysical campaigns are a commonly employed method during the exploratory phase of geothermal projects, with the objective of characterizing the geothermal reservoirs and their associated hydrothermal circulation. The THM model has been demonstrated to facilitate the characterization process through the generation of simulated geophysical outputs. This paper presents a case study derived from geophysical campaigns in the URG and detailled in Vallier et al. (2020).

Fig. 7a illustrates the comparison of spatial distributions between the local Bouguer anomalies and the isotherms in the URG (Baillieux et al. 2014; Rotstein et al. 2006). The gravimetric anomalies appear to be spatially correlated with the thermal anomalies. The THM model aims to provide new insights into the relationship between the gravimetric and thermal data. In order to do so, the simulated gravimetric signal is generated from the distribution of the simulated relative variation of the total homogenized specific mass.

Fig. 7b shows the comparison of the spatial variations between the simulated gravity signal and surface heat flow from the hydrothermal circulation. The oscillations in the gravity signal show an anti-phase relationship with the surface heat flux. This finding lends further support to the notion of a correlation between the gravimetric and thermal anomalies. In the future, the THM model will facilitate the characterization of geothermal reservoir within the context of gravimetric surveys. The model's future development aims to inverse geophysical observations, such as gravimetric, but also MT campaigns, Insar data and ambient noise tomography (Abdelfettah et al., 2018; Lehujeur et al., 2018). This could be easily applicable to the geophysical campaigns for the ongoing and future exploration phase in New Zealand.

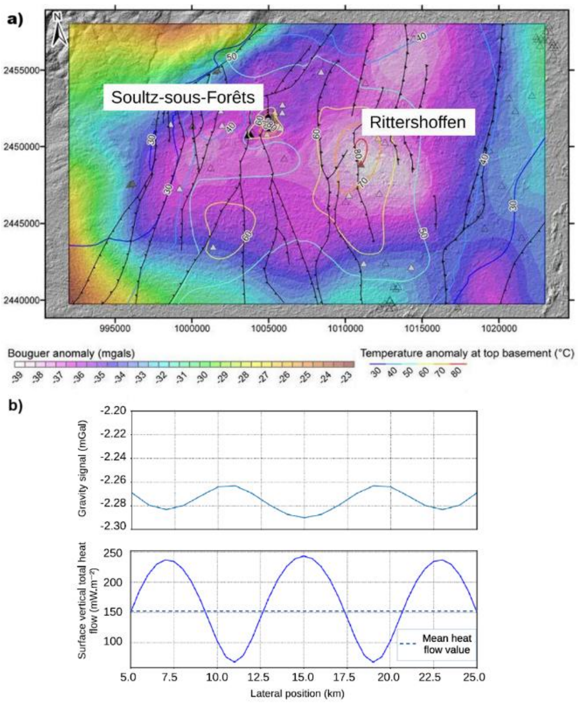

Figure 7: (a) Bouguer anomalies compared to temperature anomalies in the Soultz area (adapted from Baillieux et al., 2014). (b) Above: simulated gravimetric profile deduced from the simulated relative variation of the total homogenised specific mass. Below: profile of the simulated vertical surface heat flow. The dotted line corresponds to the mean heat flow value.

3.3 Determination of key brine properties

There is a limited amount of research that has focused on the role of brine rheology in large-scale hydrothermal circulation. However, it is crucial to quantify its impact in order to characterize the geothermal potential and ways to enhance it through stimulations. This is particularly pertinent in the context of "Super Hot" geothermal projects in New Zealand, where a significant range of temperatures is explored and the brine rheology change during reservoir exploitation. Fig. 8 illustrates the role of the fluid rheology on the geothermal potential, especially the impact of the brine: (a) thermal dilatation, (b) heat capacity, (c) viscosity and (d) thermal conductivity.

The geothermal potential is sensitive to changes in brine thermal dilatation, but is particularly influenced by variations in brine viscosity (cf. Fig. 6.a and 6.c). This suggests that the thermal anomaly and hydrothermal circulation are highly sensitive to fluid viscosity. Consequently, it is imperative for future geothermal modelling in the exploration phase of 'Super Hot' contexts to accurately constrain the rheology laws governing changes in brine viscosity with temperature.

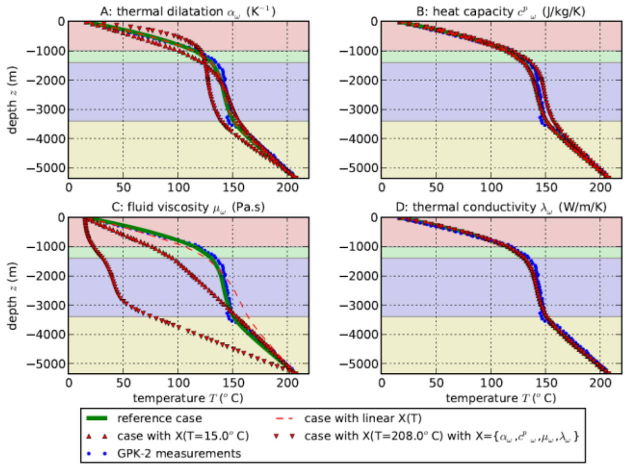

Figure 8: Simulated temperature-depth profiles for each fluid property X. The reference case is shown in green, the models with X(T=15°C) in the "up" triangle, the models with X(T=208°C) in the "down" triangle, and the models with a linear law X(T) in red. The background colors correspond to the homogenized layers.

4. CONCLUSION

A THM model of the deep geothermal reservoir has been developed, based on a simplified, large-scale geological model homogenized at a representative elementary volume of 100 meters. It is hypothesized that regional faults have a negligible impact on natural hydrothermal convection, in contrast to the local, well-connected fracture network. The model has been validated by inverting the measured temperature and stress-depth profiles from the Soultz site in the URG. Following validation, the model has been capable of providing useful tools and insights for any exploration phase of geothermal projects, whether for EGS or 'Super Hot' systems in New Zealand:

• Abacuses establishing a relationship between measurement easily obtainable in the preliminary phase (i.e., near surface heat flux and geothermal gradient measured) and key results such as the reservoir temperature.

• Integration of geophysical data (i.e., gravimetry, magneto-telluric, Insar data, Ambient noise tomography) in modelling process in order to characterize the geothermal potential in the exploration phase.

• New insights into the impact of brine rheophysics, with a particular focus on brine viscosity and thermal dilatation, on geothermal potential. This is of particular importance for 'Super Hot' systems in New Zealand.

ACKNOWLEDGEMENTS

This work was done under the framework of the LABEX ANR-11-LABX-0050-G-EAU-THERMIE-PROFONDE and benefited from a state funding managed by the French National Research Agency (ANR) as part of the "Investments for the Future" program. It had also been funded by the EGS Alsace Grant from ADEME. I would like to express my profound gratitude to my PhD directors, Jean Schmittbuhl, Christophe Fond and Vincent Magnenet, and my supervisor for their invaluable contributions to our collaborative efforts on the THM modelling for Soultz and Rittershoffen. Moreover, I would like to thank Christoph Clauser, Albert Genter, Clément Baujard, Thomas Kohl, Chrystel Dezayes, David Bruhn, Nima Gholizadeh Doonechaly, Bernard Sanjuan, Benoit Valley, Judith Sausse, Philippe Jousset, Dominique Bruel, Eva Schill, Patrick Baud, Mike Heap, Luke Griffiths, Alexandra Kushnir, Olivier Lengliné, Coralie Aichholzer, Philippe Duringer and François Cornet for very fruitful discussions.

REFERENCES

Abdelfettah, Y., Sailhac, P., Larnier, H., Matthey, P. D., Schill, E. (2018). Continuous and time-lapse magnetotelluric monitoring of low volume injection at Rittershoffen geothermal project, Northern Alsace-France. Geothermics, 71, 1-11.

Aichholzer, C, Duringer, P, Orciani, S, Genter, A, 2016. New stratigraphic interpretation of the Soultz-sous-Forêts 30-year-old geothermal wells calibrated on the recent one from Rittershoffen (Upper Rhine Graben, France). Geother. Energy 4 (1), 13.

André, L, Vuataz, F, 2005. Simulated evolution of reservoir properties for the Enhanced Geothermal System at Soultz-sous-Forêts: the role of hot brine–rock interactions. 13th Workshop on Geothermal Reservoir Engineering Stanford University, 283-290.

Baillieux P, Schill E, Abdelfettah Y, Dezayes C. Possible natural fluid pathways from gravity pseudo-tomography in the geothermal fields of Northern Alsace (Upper Rhine Graben). Geotherm Energy. 2014;2(1):16.

Cornet FH, Bérard T, Bourouis S. How close to failure is a granite rock mass at a 5 km depth? Int J Rock Mech Mining Sci. 2007;44(1):47–66.

Coussy O. Poromechanics. Chihester: Wiley; 2004.

Dezayes C, Chevremont P, Tourlière B, Homeier G, Genter A, 2005. Geological study of the GPK4 HFR borehole and correlation with the GPK3, borehole (Soultz-sous-Forêts, France). BRGM/RP-53697-FR. Technical Report, BRGM.

Doherty, J., 2005. PEST: Model independent parameter estimation. www.pesthomepage.org.

EDF R. Code_Aster Open Source, general FEA software. 2016. http://www.code-aster .org.

Evans, K, Genter, A, Sausse, J, 2005. Permeability creation and damage due to massive fluid injections into granite at 3.5 km at Soultz: 1. borehole observations. J. Geophys. Res.: Solid Earth 110, B4.

Evans K, Valley B, Häring M, Hopkirk R, Baujard C, Kohl T, Magel T, André L, Portier S, Vuataz F. Studies and support for the EGS reservoirs at Soultz-sous-Forêts. Centre for Geothermal Research CREGE CHYN: Technical report; 2009.

Fagan, C.J, Wilson, C. J. N, Spinks, K. D, Browne, P. R. L, Simmons, S.F (2006). Stratigraphy, hydrothermal alteration and evolution of the Mangakino geothermal system, Taupo Volcanic Zone, New Zealand. In Proceedings 28th New Zealand Geothermal Workshop.

Genter A, Evans K, Cuenot N, Fritsch D, Sanjuan B. Contribution of the exploration of deep crystalline fractured reservoir of Soultz to the knowledge of enhanced geothermal systems (EGS). Comptes Rendus Geosci. 2010;342(7):502–16.

Huenges E, Ledru P. Geothermal energy systems: exploration, development, and utilization. Hoboken: Wiley; 2011.

Jain C, Vogt C, Clauser C. Maximum potential for geothermal power in Germany based on engineered geothermal systems. Geothermal Energy. 2015 ; 3(1):15.

Kestin, J., Khalifa, H., Correia, R., 1981. Tables of the dynamic and kinematic viscosity of aqueous NaCl solutions in the temperature range 20-150 °C and the pressure range 0.1-35 MPa. J. Phys. Chem. Ref. Data 10 (1), 71-88.

Lehujeur, M., Vergne, J., Schmittbuhl, J., Zigone, D., Le Chenadec, A., EstOF Team. (2018). Reservoir imaging using ambient noise correlation from a dense seismic network. Journal of Geophysical Research: Solid Earth, 123(8), 6671-6686.

Magnenet, V, Fond, C, Genter, A, Schmittbuhl, J. Two-dimensional THM modelling of the large scale natural hydrothermal circulation at Soultz-sous-Forêts. Geotherm Energy. 2014;2(1):17.

Pribnow D, Schellschmidt R. Thermal tracking of upper crustal fluid flow in the Rhine Graben. Geophys Res Lett. 2000;27(13):1957-60.

Rotstein Y, Edel JB, Gabriel G, Boulanger D, Schaming M, Munschy M. Insight into the structure of the Upper Rhine Graben and its basement from a new compilation of Bouguer Gravity. Tectonophysics. 2006;425:55-70.

Rowe, AM, Chou, JCS. Pressure–volume–temperature-concentration relation of aqueous sodium chloride solutions. J Chem Eng Data. 1970;15(1):61-6.

Rustandi, D, Zarrouk, S.J, Luketina, K.M (2016). The Mangakino geothermal system: Resource evaluation. In Proceedings the 38th New Zealand Geothermal Workshop.

Sanjuan, B, Pinault, J, Rose, P, Gerard, A, Brach, M, Braibant, G, Crouzet, C, Foucher, J, Gautier, A, Touzelet, S, 2006. Geochemical fluid characteristics and main achievements about tracer tests at Soultz-sous-Forêts (France). EHDRA Scientific Conference 1–13.

Sanyal SK, Butler SJ, Swenson D, Hardeman B. Review of the state-of-the-art of numerical simulation of enhanced geothermal systems. Trans Geotherm Resourc Council. 2000;28:181-6.

Sausse, J, Dezayes, C, Dorbath, L, Genter, A, Place, J, 2010. 3D model of fracture zones at Soultz-sous-Forêts based on geological data, image logs, induced microseismicity and vertical seismic profiles. Comptes Rendus Geosci. 342 (7), 531–545

Schaming, M, Grunberg, M, Jahn, M, Schmittbuhl, J, Cuenot, N, Genter, A, Dalmais, E, 2016. CDGP, the data center for deep geothermal data from Alsace. EGU General Assembly Conference Abstracts. volume 18 9897.

Tomac I, Sauter M. A review on challenges in the assessment of geomechanical rock performance for deep geothermal reservoir development. Renewable Sustain Energy Rev. 2017; 1:1.

Vallier B, Magnenet V, Schmittbuhl J, Fond C. Thermo-hydro-mechanical modeling of hydro-thermal convection at Rittershoffen geothermal reservoir (France). In: EGU general assembly conference abstracts, vol. 1. 2018.

Vallier B, Magnenet V, Schmittbuhl J, Fond C. Large scale hydro-thermal circulation in the deep geothermal reservoir of Soultz-sous-Forêts (France). Geothermics. 2019;78:154–69.

Vallier, B, Magnenet, V, Schmittbuhl, J, Fond, C (2020). THM modeling of gravity anomalies related to deep hydrothermal circulation at Soultz-sous-Forêts (France). Geothermal Energy, 8, 1-21.

Zaytsev, I.D, Aseyev, G.G, 1992. Properties of Aqueous Solutions of Electrolytes. CRC Press.