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Evolution of Brine Geochemical Composition during Operation of EGS Geothermal Plants (Alsace, France)

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ABSTRACT

Geothermal energy has been a subject of great interest since the 1990’s in the Upper Rhine Graben, where the first European Enhanced Geothermal System (EGS) pilot site has been developed, in Soultz-sous-Forêts (SsF), France. The geothermal potential of this French-German Tertiary basin is the result of a thermal gradient anomaly coupled with a dense naturally fractured network, allowing the exploitation of hydrothermal brine circulating in the granitic reservoir. Thanks to the development of the EGS technology, two industrial geothermal plants in SsF and Rittershoffen (France) were commissioned in 2016 to produce electricity (1.7MWe) and superheated water for industrial needs (24 MWth), respectively. Other additional geothermal sites are presently under development in the Strasbourg area (Vendenheim and Illkirch, France), and other plants that benefited from the research done at SsF are operating on the German side of this Tertiary graben.

The SsF and Rittershoffen sites have experienced a successful continuous exploitation since their launch with a plant availability higher than 90%, allowing to characterize the chemical evolution of the geothermal brines during their operational phase. For this purpose, the geothermal fluids were regularly sampled and analyzed for physicochemical parameters, major and trace elements, radionuclide concentration and gas content and composition in order to monitor any potential impact of the exploitation phase on the fluid properties. The heat capacity, density and viscosity of the fluids were also measured in-situ once on the Rittershoffen fluid to obtain the actual physical parameters of this energy vector in the heat process. Data collected from 2016 to 2020 indicates a highly salted, Na-Cl brine, strongly enriched in important metals like lithium. During this period, more than 3 and 10 Mm^3 of geothermal brine circulated in the SsF and Rittershoffen sites, respectively and only minor variations were observed on the chemical composition of the fluids. Such observation means that long-term geothermal activity does not have a major impact on the reservoir composition. Considering the relative spatial proximity of the wells of both plants (<7 km), the chemical stability observed in the brines over time also suggests the sustainability of a geothermal co-exploitation activity in a fractured granite reservoir for energy needs. Moreover, the spatial homogeneity of the brine composition could be interpreted as a proxy of the significant size of the geothermal reservoir.

The new chemical data on Illkirch geothermal fluid appears consistent with the chemical features expected for an Upper Rhine graben brine produced from the granitic basement. However, additional analysis should be performed in the future to better characterize the brine composition in this area.

1. INTRODUCTION

1.1 Geothermal energy in the Upper Rhine Graben

The Upper Rhine Graben (UGR) extends from Basel (Switzerland) in the south to Mainz (Germany) in the north, over 300 km. The region benefited of important temperature anomalies, controlled by a thermal gradient locally over 100°C/km and organized along the NNE direction, which is also the direction of the graben border normal faults in the region. In the early 90’s, the first European geothermal research project of Soultz-sous-Forêts (SsF) was launched in the URG. It was based on the initial Hot Dry Rock (HDR) concept, where the goal was to create an artificial heat exchanger in the basement rocks by hydraulic fracturing (Genter et al., 2010). However, the results obtained after the drilling of the first well at SsF showed the presence of natural fluid circulation through the existing fracture network of the reservoir (Vidal and Genter, 2018). Since then, the development of the URG geothermal project was performed following the Enhanced Geothermal System (EGS) technology. This approach consists in exploiting the natural thermal brine circulation by improving the connection between the geothermal wells and the reservoir with various chemical, hydraulic and thermic treatments (Schill et al., 2017).

Over the last decades, several geothermal projects have been developed in the French, German and Swiss URG region. Today, in France, the geothermal plants of Rittershoffen and SsF are in operation, respectively for heat and power production, while in Germany, 3 plants are operational for power production. In addition, 2 projects (Vendenheim and Illkirch) are currently under development in the French side, close to Strasbourg, and several explorations permits for geothermal energy (6) and for lithium extraction (3) are in progress in Alsace (France).

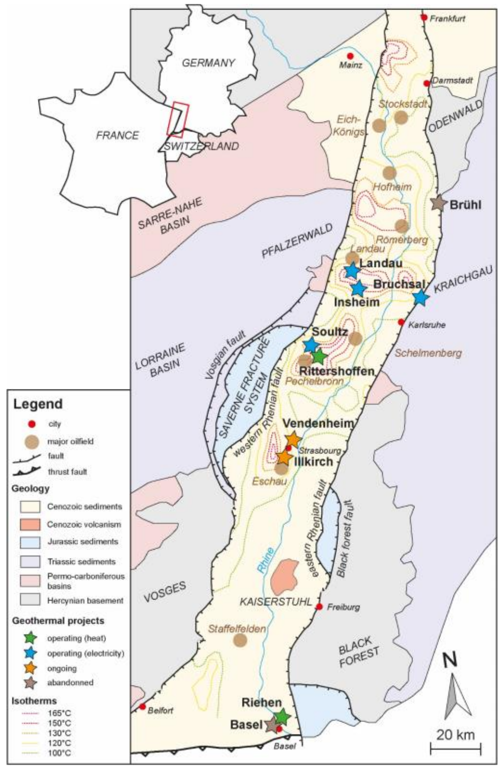

Figure 1 Map of the deep geothermal sites operating or under development in 2021 also representing the major oilfield and the isotherms at 2000 m depth (Glaas, 2021).

1.2 The geothermal plants in the French URG

Soultz-sous-Forêts

The Soultz-sous-Forêts geothermal project started in 1987 and is the cradle of the geothermal energy European research in granitic and fractured systems. After almost 30 years of research, the geothermal site is exploiting the fractured basement at 5 km depth, under commercial conditions, for the EEIG Heat Mining (Figure 2). The actual geothermal system is made of three wells: one production well named GPK-2 and two injection wells named GPK-3 and GPK-4 drilled at 5km in a granitic basement. The geothermal brine is produced at a temperature of 150°C, reaching the wellhead with a nominal flow rate of 30 kg/s provided by a downhole production Line Shaft Pump (Baujard et al., 2018). The installed gross capacity of the plant is about 1.7 MWe.

The geothermal brine is then flowing through a system of three consecutive double-pass tubular heat exchangers supplying heat to an Organic Ranking Cycle (ORC), in order to produce electricity. The geothermal brine is then fully reinjected at around 70°C, and the volume of reinjected brine is shared between the two injection wells, one third in GPK-4 and two third in GPK-3 without using reinjection pumps. The well-head overpressure in the surface infrastructure is regulated by the production pump and reaches about 23 bars to keep the dissolved gas in the brine. The reinjection temperature is linked to the conversion process. The geothermal plant has been successfully producing electricity since September 2016 under commercial conditions, with an availability rate about 90% for the last four years (Mouchot et al., 2019).

Figure 2 View of the Soultz-sous-Forêts (on the left) and Rittershoffen (on the right) geothermal sites.

Rittershoffen

The geothermal heat plant of Rittershoffen located in Northern Alsace (France) has been developed to supply heat to the industrial processes of a starch plant (Figure 2). This industrial user, located 15 km away, is connected to the plant via a transport loop and totals 100 MWth of thermal needs. The geothermal heat plant, with an installed capacity of 27.5 MWth, has been successfully providing an average of 22.5 MWth and 180 GWh/year of heat to this starch plant since June 2016.

The targeted reservoir is a Triassic fractured sandstone and the top of a fractured Carboniferous granite basement located at 2200 m depth (Duringer et al., 2019). The first well, GRT-1, was drilled in 2012 and the first testing results after drilling showed a low productivity index. A stimulation program, including thermal, chemical, and hydraulic stimulation, was therefore designed, and successfully performed in 2013 (Baujard et al., 2017). Induced micro seismicity activity related to the stimulation tests was very low and virtually undetectable for the surrounding population (Lengliné et al., 2017; Maurer et al., 2020). The second well, GRT-2, was drilled in 2014. Unlike GRT-1, GRT-2 had a very good initial productivity index during the testing phase after drilling and was therefore not stimulated (Baujard et al., 2017). The Rittershoffen geothermal power plant is classified as an EGS due to the stimulation program performed on GRT-1 but also because of the total reinjection of the discharged geothermal fluids in the reservoir inducing a micro-seismicity activity at reinjection side during geothermal exploitation (Maurer et al., 2020).

The geothermal heat plant was designed with a pressurized geothermal loop: a downhole line shaft pump pressurizes the geothermal brine in the surface equipment over the gas break-out pressure to prevent any Non-Condensable Gases (NCG) emission during operation (Ravier et al., 2017). The production wellhead temperature at GRT-2 reaches 170°C and the flowrate is regulated at 75-85 kg/s, according to the starch plant's heat demand. The geothermal heat is transferred to a secondary loop, containing fresh water, using several tubular heat exchangers and the brine is fully reinjected without additional pumps at 85°C into the injection well GRT-1. The Rittershoffen plant availability is higher 92% for the last four years (Mouchot et al., 2019).

Illkirch

Illkirch is a geothermal project located 5 km south from Strasbourg city, in Alsace (France). The doublet aims to produce electricity and heat for district heating network. The first well GIL-1 was completed mid-2019, reaching a final depth of 3800 mMD (3319 mTVD) in a deep-seated fractured Carboniferous granite (Glaas et al., 2021). The rig was then demobilized to integrate collected data and optimize second well plan.

GIL-1 well targets a regional fault zone, at the interface of the Triassic sandstone and the granitic basement (Richard et al., 2016; Edel et al, 2018). This fault zone is oriented approximately N-S and characterized by a vertical normal offset of approx. 800m. The open section of the well intersects the Triassic sandstone on the lower compartment (west side of the fault) over a vertical depth of around 170m and the granitic basement after crossing the fault at 2892 mMD (900 m open hole length in the granite). The rocks showed a high hydrothermal alteration around this fault zone, with high clay content and up to 50% carbonates (Glaas et al., 2021), but the well showed a limited productivity index. Thus, numerous production and injection tests as well as chemical and hydraulic stimulations were carried out to characterize as precisely as possible the reservoir behavior and increase the well connection to the reservoir. During the injection and stimulation tests, a low rate induced seismicity was observed. Temperature at TD was measured at 156°C (measured in the drill strings and not stabilized after drilling).

1.3 Geochemical characterization of the brine during operation

Several studies have focused on the characterization of the geochemical brine from the Upper Rhine Graben (Sanjuan et al., 2010, 2016, 2021 and Scheiber et al., 2012), providing a large database for major and trace elements concentrations, radionuclides and even isotopic signature. However, those data are mainly measured on the brine collected after the well drilling and development, while very few characterizations concern the geochemical evolution of the brine during several years of continuous operation.

Thus, the main goal of the present work is to complete the study already performed by Mouchot et al. (2018), by characterizing the chemical signature of the geothermal fluids over the initial operation phase of two sites, Rittershoffen and Soultz-sous-Forêts. For this purpose, a monitoring of physico-chemical parameters and analysis of major anions and cations as well as trace elements and radionuclides analysis were performed since 2016. Measurements of the gas fraction of the Rittershoffen brine and of the composition of the emissions of the plants are also presented. Those results will allow to evaluate the impact of the operational phase on the geothermal reservoir stability. Geochemical data obtained at SsF and Rittershoffen geothermal plants will be supplemented by the preliminary analysis of the Illkirch first well (GIL-1) fluids, and their comparison will allow to appreciate the regional variations of the reservoir.

In addition, physical features of the brine, such as the viscosity, the specific heat capacity and the density will be included in this study. The aim is to provide precise data on these parameters, which will be helpful to consolidate the initial hypothesis assumed for the design of the plant surface installation.

The intention of the paper is to evaluate the influence of sampling procedure on the analytical results by the comparison of major cations and anions and trace elements concentrations obtained by analysis of several laboratories.

2. MATERIAL AND METHODS

Several geochemical parameters were monitored on geothermal fluids and measured for the present study: pH, electrical conductivity, redox potential, major and trace elements concentration, radionuclide and Non-Condensable Gas (NCG) ratio and composition.

2.1 Brine monitoring

The monitoring of the brine of SsF and Rittershoffen was realized at least one per month on the injection and production wells since the beginning of the operational phase in 2016, with more than 100 data available up today. The measured parameters were pH, electrical conductivity (CE), temperature and redox potential (Eh). The analysis was performed on site by the operator of the plants (ES-Géothermie), in collaboration with the authors of this study or with external partners.

The pH, CE and Eh results appears particularly sensitive to plant operation, measurement conditions, sampling temperature and the selected equipment. By consequent, it was decided to present in this study only the data measured with the same device and at a temperature included between 60 ± 10°C (42 analyses for SsF and 32 analyses for Rittershoffen).

2.2 Sampling and analysis

Several samples of fluids were collected since the beginning of operation activity (2016) for SsF and Rittershoffen plants. Two sample of fluid were collected at Illkirch during a hydraulic test phase of GIL-1 (2019). The analyses were performed by external laboratories specially commissioned within the framework of several research projects (SUBITO, H2020 Geothermica-ZoDrEx and H2020 DESTRESS projects).

The thermophysical characterization of the fluid was performed only one on the fluid of the Rittershoffen plant with the analysis of the specific heat capacity, the viscosity and the density of the brine (Schröder et al., 2015). Parameters have been assessed under operating pressure and at production temperature, considering then monophasic geothermal fluid with the innovative device mentioned in Schroder et al., 2015.

The monitoring of the major cations and anions as well the trace elements of exploited geothermal sites is reglementary due at least 1 per year. In this study, one sample of the brine at the production and injection wells were collected for each year of exploitation, including one additional sample from the injection well of Rittershoffen obtained during the well test phase in 2014. Two sample of fluid from Illkirch were also collected during the well test phase of 2019 and analyzed for elementary composition. Sampling of the geothermal fluid is thanks to the use of a small heat exchanger, allowing cooling down the fluid to a fixer temperature (approximately 50°C). Different sampling procedure and sampling pretreatment were applied, depending on the laboratory commissioned. For laboratory 1 and 3, the sampling protocol included the filtration (0.45 µm) and conditioning (acidification) of samples on site. On the opposite, for laboratory 2, no filtration of the brine was operated, and the samples were stored in pre-acidified flasks. Laboratory 3, working within the SUBITO project, optimized the sampling and preservation procedure for the SsF and Rittershoffen sites. It concerns sampling temperature, start of sampling after reaching the equilibrium based on the measurement of pH, Eh, conductivity and temperature and preservation of samples (see also Jähnichen et al, 2019). Analysis has been performed by ion chromatography, ICP-OES and ICP-MS. Total Organic Carbon (TOC) and suspended matter (MES) have been measured only on 2020 samples. For analytical details concerning laboratory 3, see also Jähnichen et al., 2019.

The analysis of the gas fraction present in the brine was performed several times for the injection and production well of the SsF and Rittershoffen plants. NCG content was measured at the production and reinjection well heads, to monitor the Gas Liquid Ratio. Sampling is enables thanks to the use of a separator and the cooling device of the vapor phase to count only the NCG emissions. At Rittershoffen, the gas emissions were also characterized, through an important sampling campaign realized in 2019. For this purpose, the collection of gas samples was performed from several venting valves of the plant, located on the production line, on the heat exchanger, on the injection line and at the annular of the injection well (Figure 3). The sampling was realized by the operator (ES-Géothermie) during a period of transitory flowrate phase (177 m^3/h, instead of 300 m^3/h at nominal flowrate), allowing to maximize the degassing process. The gas analysis was performed by laboratory 3, including a large spectrum of analyzed gases using gas chromatography: CO_2, CH_4, N_2, O_2, H_2, He, Ar, H_2S and C_2H_6.

Radionuclides concentration were measured on the brine of SsF and Rittershoffen at the production and injection wells, several times since 2016. A large screening of the potential radionuclides was performed by gamma spectrometry, including: ^{238}U, ^{235}U, ^{231}Pa, ^{227}Ac, ^{234}Th, ^{230}Th, ^{227}Th, ^{228}Th, ^{228}Ra, ^{226}Ra, ^{224}Ra, ^{223}Ra, ^{210}Pb, ^{40}K. Unfortunately, Radon isotopes could not be analyzed, as no laboratory was identified to measure this radioactive noble gas properly in the high-pressure gas-fluid system of the hot brines. Radionuclides analyses were performed within the project SUBITO by laboratory 3 on filtered (0.45 µm) and acidified fluids. This laboratory uses for the correction of the appearing radioactive disequilibria in the brine samples to the date of sampling the method presented in Degering and Köhler (2011). In the present study, radionuclide data for the residues collected during filtration are also added.

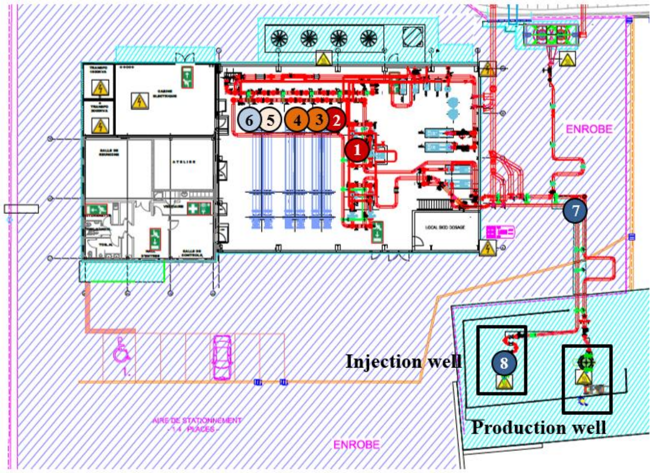

Figure 3 The layout plan of the Rittershoffen geothermal plant. The location of the gas samples collected from the venting valves are indicated by the circle symbols. Their colors represent the temperature of the brine, with red indicating hot fluid and blue for cold fluid (details are given in Table 7).

3. THERMOPHYSICAL PROPERTIES

One of the key parameters for dimensioning geothermal power plants is the thermal power of the brine. This variable is determined by the chemical and physical properties of the fluid, but also by considering specific-site conditions, such as mass flowrate, temperature and pressure. Parameters such as specific heat capacity, viscosity and density of the brine are thus generally assumed on the basis of theoretical estimation or laboratory studies. At Rittershoffen, the data used for the design of the heat exchangers were based on the work of Sharqawy et al. (2010), considering a brine of 100 g/L.

As uncertainties may exist between estimation and real data, thermodynamic properties of the brine were determined at Rittershoffen during the operation of the geothermal plant. The results show a geothermal fluid with a specific heat capacity varying from 3878 to 3738 J/kg.K, a viscosity of included between 2.1 and 4.1 m^2/s and a density between 967 and 1035 g/L. As expected, the specific heat capacity increase with temperature, while viscosity and density decrease for hottest fluids. When comparing the data obtained by laboratory analysis on operational fluids with the estimation used for the design of the geothermal plant, the results appears consistent, confirming the accuracy of the surface installation design.

Table 1 The physical characteristics measured on two brine samples of the Rittershoffen geothermal plant. PW = Production Well; IW = Injection Well. The estimated parameters are from Sharqawy et al. (2010).

	PW			**IW**			**Estimated parameters**	
Pressure (bars)	26.0	25.9	26.3	26.0	26.3	26.0		
Temperature (°C)	171	168	168	86	86	85	80	90
Specific heat capacity (J/kg.K)	3878			3738			3742	3747
Viscosity (m^2/s)		2.1			4.1		4.4	4.0
Density (g/L)			967			1035	1031	1038

4. PHYSICO-CHEMICAL PARAMETERS

SsF brine shows a pH included between 5.05 and 5.60 and a CE between 107 and 128 mS/cm over the 4 years of exploitation (Figure 4). Similar values are measured for Rittershoffen fluids, with a pH between 5.00 and 5.77 and a CE between 96 and 126 mS/cm (Figure 4). The presented data includes measurements of fluids from both the production and injection wells, and no major changes are observed in the physico-chemical parameters.

It is interesting to note that slightly lower pH values are measured for Rittershoffen in 2020, corresponding a change in the sensor equipment used for analysis. Redox values are negative, with value included between -45 and -20 mV. Temperature represents the temperature during the analysis of the fluids, which are adjusted to 60 ± 10°C.

pH and CE of Rittershoffen and SsF fluids are consistent with previous analysis (Sanjuan et al., 2010, 2016, Scheiber et al., 2015) and with the values expected for the URG granitic reservoir (Sanjuan et al, 2016). Negative redox potential corresponds to anoxic conditions representative of the geothermal reservoir. The stability of the physico-chemical parameters observed since 2016 indicates that the operational phase only has minor impact on the reservoir features, without important consequences on its chemistry.

Similarly, the stability of the fluid between the production and injection well witnesses the lack of impact of the operational conditions, such as no significant degassing and neither oxygen input through the equipment.

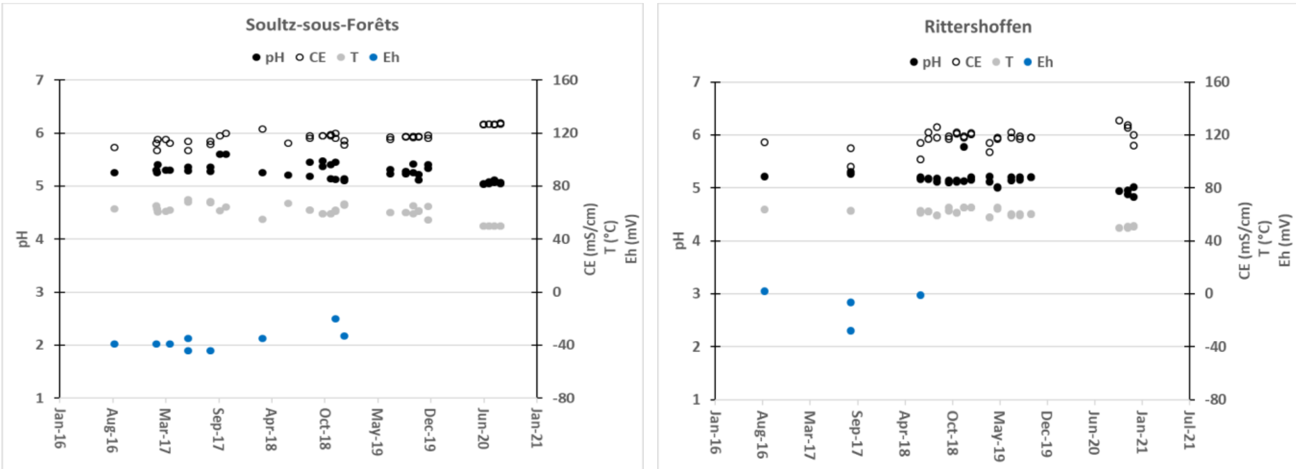

Figure 4 The pH, electrical conductivity (CE), temperature (T) and redox potential (Eh) monitoring during the first years of operation (2016 – 2020) for SsF and Rittershoffen geothermal plants.

5. CHEMICAL CHARACTERIZATION

5.1 Major and trace elements

Concentrations of cations and anions as well of trace elements composition of SsF and Rittershoffen fluids are summarized in Table 2 and Table 3, respectively. In addition, a supplementary database is supplied in Appendix 1, in order to provide a complete geochemical screening of the fluids.

Geothermal fluids of Rittershoffen and SsF plants are Na-Ca-Cl brines, with important concentrations of K. As already showed by several studies (Sanjuan et al., 2010, 2016, 2021), this composition corresponds to a typical geothermal fluid circulating in the basement reservoir of the URG (Figure 5). The concentration of those major ions is almost identical between the two geothermal sites and no significant variations are observed over the operational phase, neither at the production nor at the injection well (Figure 6, Appendix 2).

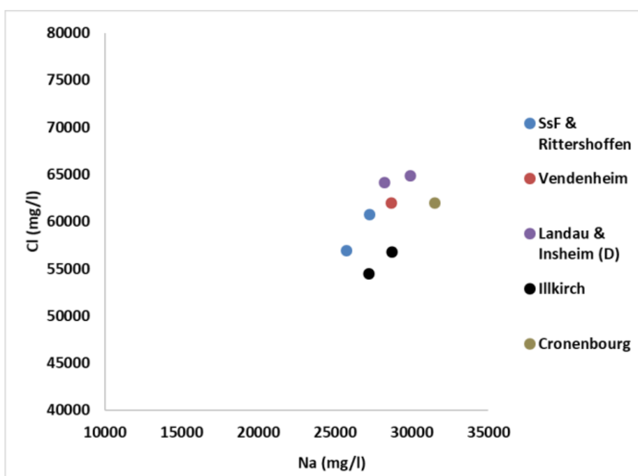

Figure 5 Na-Cl concentration of different geothermal brines from the Upper Rhine Graben. Landau, Insheim and Cronenbourg data are from Sanjuan et al. (2016), Vendenheim date are from Sanjuan et al. (2021), SsF and Rittershoffen are mean values of the database presented in this study.

Among the other elements composing the chemical signature of the Rittershoffen and SsF fluids, some constituents reach concentration of hundreds ppm, in particular: Sr, Br, SO_4, SiO_2, Li and Mn. Those elements show very consistent content between SsF and Rittershoffen sites, with stable concentration all along the first 4 years of operation (Figure 7). However, when comparing the mean concentrations at SsF and Rittershoffen of several elements, differences could be highlighted between the two sites, in particular for low-concentrated elements (Appendix 1 and Appendix 2).

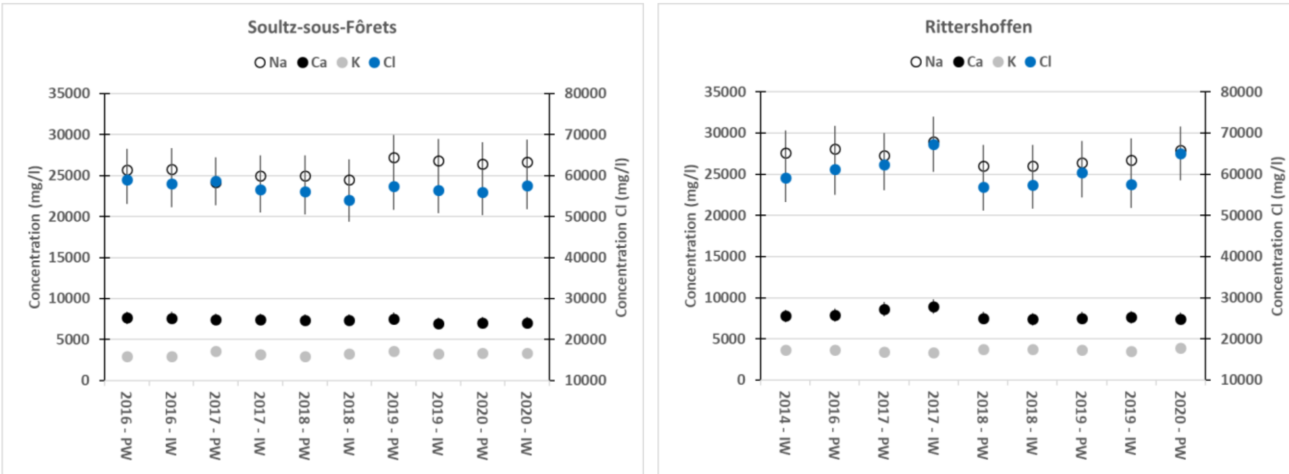

Figure 6 Major ion concentrations in brine samples collected since 2014 at the injection and production wells (namely IW and PW) of the SsF and Rittershoffen geothermal plants. The measurement uncertainty corresponds to ±10%.

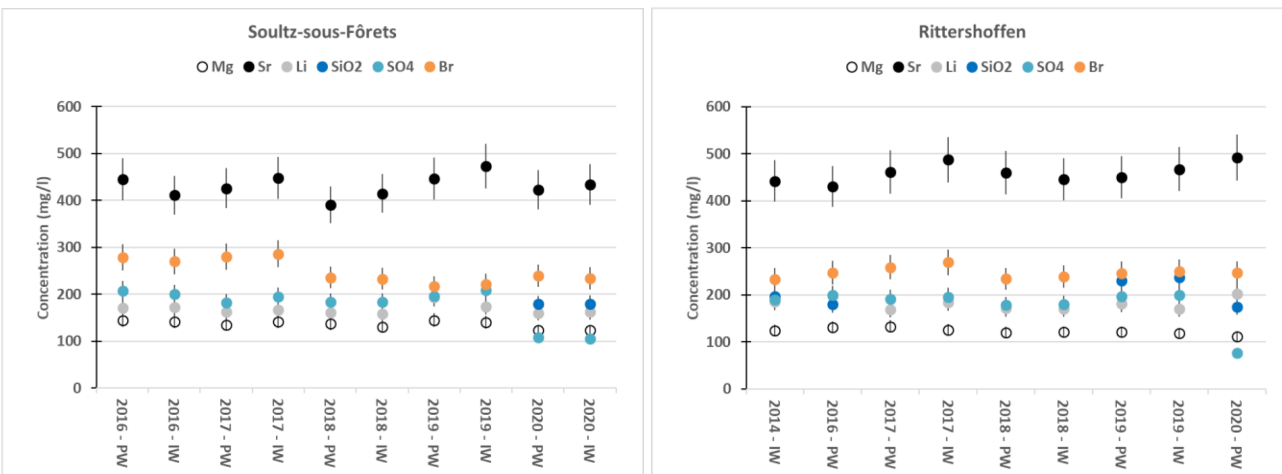

Figure 7 Selected constituents in brines collected since 2014 at the injection and production wells (namely IW and PW) of the SsF and Rittershoffen geothermal plants. The measurement uncertainty corresponds to ±10%.

The homogeneity of the chemical signature of the brine at the production and the injection well indicates that geothermal fluid circulation in the surface equipment does not significantly affect the composition of the fluids, despite the existence of corrosion, scale formation and degassing processes in the installations (Mouchot et al., 2018 and 2019). Only minor variations are observed on Pb and Sb concentrations, over time and between the production and the injection wells. As Pb and Sb are among the main elements presently composing the scales deposited in the SsF and Ritterhosffen installations (Mouchot et al., 2018), those variations could reflect the efficiency of the inhibitor treatment. However, Pb and Sb concentration are not systematically higher at the injection well and varies at the production well over time. Those observations suggest that complex processes are involved in the elementary variations of the fluid composition, potentially including processes occurring in the reservoir and/or the well, and not only in the surface equipment. However, the absence of sensitive geochemical modification of the fluid highlights that corrosion and scale processes are today well controlled by the site operator, thus allowing to limit their impacts on the projects, in term of costs, efficiency and operability of the plants.

Extrapolated at the reservoir scale, this observation means that geothermal activities do not have strong impacts on the chemical composition of the geothermal reservoir at SsF and Rittershoffen. Such an assumption is confirmed by the data obtained for the present study, where the fluid composition shows strong stability over time, for both Rittershoffen and SsF sites. Based on those conclusions, it should be highlighted that the achieving of stable geochemical brine along with operation is not only the consequence of the geothermal context, but also the fruit of a proper project management policy, aiming to minimize the impact on the natural exploited system.

Table 2 Brine composition of the SsF geothermal plant during the first years of operation (2016 – 2020). PW = Production Well; IW = Injection Well.

Date		15/11/2016		31/05/2017		18/09/2018		19/10/2018		09/01/2019		05/02/2020	
Sample		PW	IW	PW	IW	PW	IW	PW	IW	PW	IW	PW	IW
Analysis		Lab 3	Lab 3	Lab 3	Lab 3	Lab 3	Lab 3	Lab 2	Lab 2	Lab 3	Lab 3	Lab 1	Lab 1
Na	mg/l	25700	25800	24200	25000	25000	24500	21400	22500	27200	26800	26400	26700
Ca	mg/l	7630	7610	7430	7420	7360	7340	6380	6140	7540	6950	7020	7030
K	mg/l	2940	2940	3620	3200	2960	3240	3830	3670	3570	3240	3360	3350
Cl	mg/l	59000	58000	58600	56600	56100	54100	41100	44000	57400	56470	55940	57490
Mg	mg/l	145	142	135	142	137	131	46	46	145	140	123	123
Sr	mg/l	445	411	426	448	391	415	615	594	446	473	422	434
Li	mg/l	171	172	163	167	161	159	354	226	193	174	160	163
SiO_2	mg/l							73	81			179	180
SO_4	mg/l	207	200	182	195	183	183	210	202	196	209	108	106
Br	mg/l	279	270	280	286	236	233	230	233	217	222	240	234
Mn	mg/l	19	19	16	17	17	17	3	3	18	17	17	17
NH_4	mg/l	23	23	23	23	24	25	22	22	26	24	23	24
As	mg/l	9	9	10	12	11	12	8	9	12	12	10	10
Ba	mg/l	29	28	26	24	23	24	24	23	27	26	26	22
Cs	mg/l	14	15	14	15	14	14	17	16	16	15	14	13
Rb	mg/l	24	24	23	24	23	22	30	27	25	24	23	23
Si	mg/l	53	97	92	88	91	94	34	38	100	95		
B	mg/l	35	36	41	45	37	37			39	36	38	39
Fe	mg/l	32	30	29	32	30	30	4	4	31	32	26	27
Zn	mg/l	2.8	2.8	2.6	2.8	2.9	3.0	0.2	0.2	1.9	3.0	2.8	2.7
P	mg/l	3.2	4.0	5.4	3.8	4.0	4.1			4.1	4.0		0.1
F	mg/l	4.0	4.1	3.9	4.1	2.1	2.5			4.8	4.9	1.3	1.2
I	mg/l	1.8	2.0	1.5	2.4	1.4	1.5			1.4	1.1	1.6	1.6
Cu	mg/l			0.003	0.003	0.004	0.003			0.002			
Hg	mg/l			0.0003	0.0003	0.0004	0.0004			0.0001			
Pb	mg/l	0.10	0.21	0.15	0.31	0.26	0.37	0.02	0.06	0.33	0.36	0.11	0.16
Cd	mg/l	0.01	0.01	0.02	0.02	0.02	0.02			0.01	0.01	0.01	0.01
Sb	mg/l	0.07	0.07	0.10	0.07	0.10	0.11	0.04	0.04	0.12	0.08	0.06	0.06
Al	mg/l	0.06	0.06	0.05	0.05	0.06	0.05			0.06	0.06	0.05	0.05
Cr	mg/l	0.015	0.013	0.00	0.00	0.00	0.00			0.00	0.00		
U	mg/l	0.00001	0.00001	0.00002	0.00004					0.00002	0.00001		
Ni	mg/l	0.0006	0.0000	0.0025		0.0010	0.0009			0.0014	0.0014	0.0011	0.0010
HCO_3	mg/l											197	188
COT	mg/l											0.9	1.5

Table 3 Brine composition of the Rittershoffen geothermal plant during the well test phase (2014) and the first years of operation (2016 – 2020). PW = Production Well; IW = Injection Well.

Date		07/10/2014	24/08/2016	05/04/2017		27/02/2018		02/04/2019		04/11/2020
Sample		IW	PW	PW	IW	PW	IW	PW	IW	PW
Analysis		Lab 3	Lab 3	Lab 3	Lab 3	Lab 3	Lab 3	Lab 3	Lab 3	Lab 1
Na	mg/l	27600	28100	27300	29000	26000	26000	26400	26700	27960
Ca	mg/l	7790	7930	8640	8920	7530	7410	7520	7640	7450
K	mg/l	3710	3670	3470	3370	3790	3780	3650	3550	3890
Cl	mg/l	59100	61200	62400	67250	56900	57400	60400	57500	65030
Mg	mg/l	124	131	133	126	120	121	121	118	111
Sr	mg/l	442	430	461	487	460	446	450	467	492
Li	mg/l	186	198	169	184	171	170	181	170	203
SiO_2	mg/l	197	180					231	238	175
SO_4	mg/l	190	199	192	196	178	180	197	199	76
Br	mg/l	233	247	259	269	234	239	246	250	247
Mn	mg/l	17	18	18	17	17	17	17	18	18
NH_4	mg/l	28	25	25	25	28	27	27	26	26
As	mg/l	13	13	13	13	13	14	14	14	13
Ba	mg/l	10	21	22	24	22	22	23	22	19
Cs	mg/l	16	16	16	17	17	16	16	16	16
Rb	mg/l	27	27	27	29	27	27	27	27	28
Si	mg/l		84	89	101	97	95	108	111	
B	mg/l	42	42	41	41	42	36	50	49	40
Fe	mg/l	35	33	34	33	31	29	33	29	25
Zn	mg/l	3.3	3.2	2.3	2.4	3.6	3.7	3.9	3.9	3.6
P	mg/l		13.0	4.4	4.4	5.0	5.3	0.2	0.4	3.8
F	mg/l		4.3	5.4	5.2	3.1	3.0	6.1	5.4	
I	mg/l	2.3	1.7	2.3	1.6	1.4	1.7	1.5	1.4	
Cu	mg/l	0.000	0.003	6.300	0.292	0.003	0.004	0	0	0.001
Hg	mg/l									
Pb	mg/l	0.19	0.25	0.84	0.70	0.16	0.35	0.23	0.17	0.24
Cd	mg/l		0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.01
Sb	mg/l	0.06	0.13	0.16	0.15	0.11	0.11	0.15	0.10	0.11
Al	mg/l		0.05	0.04	0.05	0.03	0.03	0.04	0.05	0.02
Cr	mg/l		0.00	0.00	0.00	0.01	0.01			0.05
U	mg/l					0.00004	0.00002			
Ni	mg/l	0.0109	0.0014	0.0598	0.0115	0.0013	0.0016	0.0010	0.0011	0.136
HCO_3	mg/l	157	180							173
COT	mg/l									0.5
MES	mg/l									67.8

Table 4 Brine composition of the Illkirch geothermal well GIL-1 during the well test phase (2019). Analysis were performed by an additional external laboratory.

Date		**19/05/2019**	**16/05/2019**
Na	mg/l	27200	28700
Ca	mg/l	4080	3860
K	mg/l	5920	6320
Cl	mg/l	54500	56800
Mg	mg/l	191	147
Sr	mg/l	224	235
Li	mg/l	173	188
SO_4	mg/l	400	430
Br	mg/l	320	340
Mn	mg/l	10	6
NH_4^+	mg/l	19	21
As	mg/l	2	2
Ba	mg/l	5	5
Cs	mg/l	13	15
Rb	mg/l	218	228
Si	mg/l	41	40
B	mg/l	33	35
Fe	mg/l	0.5	0.2
Pb	µg/l	50	76
Al	µg/l	310	291
S	mg/l	849	162
COT	g/l	2.6	1.2
MES	mg/l	517	467

Illkirch geothermal brine also shows very similar Na-Cl concentrations (Table 4), confirming a typical URG fluid signature (Figure 5). However, K, Ca as well as several minor elements present slightly different content than, for example, SsF and Rittershoffen fluids. The higher K concentration (roughly 5 000 ppm instead than 3 500) could be explained by a contamination of the brine by the K-Cl drilling mud, presenting K concentration of almost 21 g/l. Indeed, important mud losses occurred during Illkirch first well drilling. This scenario is consistent with the unusual dark color of the fluid and its high suspended matter and organic carbon content, totally unexpected for a geothermal brine. Based on the chemical composition of the brine and the mud, and on the respective produced, injected and loss volumes, it was estimated that the produced brine contained 10 to 30% of mud, which was still present in the well and the close reservoir during the hydraulic production test phase, when the samples were collected. In contrast, the chemical signature deviation for other elements is likely not the result of anthropic artefact induces by operational, sampling or analytical conditions.

It is interesting to notice that, for several elements, such for example Ca and SO_4, brines of the URG present a distinct signature, with one group formed by the fluids collected in the wells located in the center of the basin (Strasbourg region) and a second group composed by the fluids issued from projects located more in the North of the URG (Figure 1 and Figure 8). A similar trend could be observed for several elements, including Li, even if the Cronenbourg fluid composition does not always fit with the one of the Illkirch and Vendenheim wells (Figure 8).

The similar composition between all the geothermal fluids from the URG is an indicator of their common geological origin. Until now, the geothermal brine exploited for heat and power production in the region are issued from a geothermal reservoir located at the granitic basement interface, whose permeability is provided by the fracture network and by secondary porosity of the granitic matrix (Genter et Traineau, 1992). In addition to their geological origin, the chemical homogeneity of the brines in the URG might also be interpreted as the result of a large-size geothermal reservoir, where fluids migrate across dozens of kilometers, allowing the uniformization of their geochemical signature. The URG conceptual model, consisting in water circulation through the granitic basement and the overlying sedimentary horizons (Buntsandstein, Muschelkalk, Keuper) was demonstrated by Le Carlier et al. (1994), using a modelling approach based on lithological and geophysical studies. In the present study, those results are for the first time confirmed by chemical data, using brine composition from different projects in the URG obtained over several years of operation.

However, the variations observed among SsF and Rittershoffen brine for very low-concentrated elements, but also the discrepancy in the fluid composition between the wells located in the Strasbourg region and those farthest north suggest more complex behavior for mass transfer. Sanjuan et al. (2016) already proposed that hot fluids circulate through a NE-SW oriented fault system from the deep center of the graben sedimentary basin to SsF, Rittershoffen, Landau and Insheim sites, located at the graben's NW borders. Up to the authors, the discrepancies observed in the conservative chemical species between the geothermal sites located in the North and those located more southern in the Strasbourg area like Cronenbourg (Illkirch and Vendenheim wells did not exist at the time of Sanjuan et al., 2016) tend to indicate that there are no direct N-S hydraulic connections between these sites. More recently, Glaas (2021) suggests that the permeability distribution observed at Illkirch (Strasbourg area) highlights a new conceptual model of reservoir, where fluids are not directly circulating in the fault zone located at the interface between the Mesozoic sediments and the Paleozoic basement, but deeper in the granitic fracture network. Chemical data collected on the fluids of Rittershoffen, SsF and Illkirch wells confirms this interpretation and suggests the existence of local circulation paths, potentially connected to major permeable faults for Rittershoffen and SsF but to secondary fracture network in the Strasbourg region as proposed by Glaas (2021).

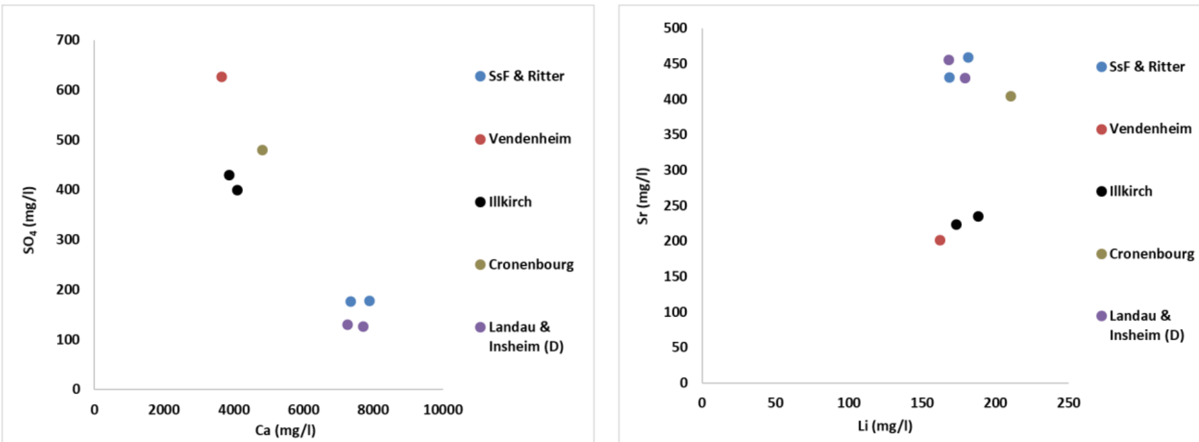

Figure 8 Ca-SO4 and Li-Sr concentration of different geothermal brines from the Upper Rhine Graben. Germany (Landau and Insheim) and Cronenbourg data are from Sanjuan et al. (2016), Vendenheim date are from Sanjuan et al. (2021), SsF and Rittershoffen are average values of the database presented in this study.

5.2 Radionuclides

Brines of SsF and Rittershoffen geothermal plants showed concentrations of the following radionuclides above the detection limit of the applied analytical method: ^{226}Ra and ^{210}Pb from the ^{238}U decay series, ^{228}Ra and ^{224}Ra from the ^{232}Th decay series and ^{40}K (Table 5, Figure 9). The lack of data for ^{40}K in sample from 2020 is not due to major change in fluids composition: the analysis of this radionuclides was simply not planned in the analytical offer for this sample. The radionuclides detected in the brine also correspond to those deposited in the different scale types formed in the installation during operation. Radium isotopes are accumulated in the barium sulfates which were the dominating phases during the circulation phases before the operation of the plants, when no chemical treatment was applied to prevent scales formation and/or deposition (Scheiber et al., 2012, Cuenot et al., 2013, Haas-Nüesch et al., 2018). At this time Pb-rich metal sulfides containing ^{210}Pb occurred to a minor extent. Since the beginning of operation, scale and corrosion inhibitors are used at SsF and Rittershoffen geothermal plant to control secondary minerals deposition, which are currently only formed of PbS and Pb(0) (Haas-Nüesch et al. 2018, Jähnichen et al. 2019). Moreover, scales also contain As and Sb, as presented in Mouchot et al. (2018).

Enhanced concentrations of the radium isotopes are common for saline fluids; they are predominantly released from mineral surfaces by α-recoil processes (Degering et al., 2016). As a consequence, the ^{228}Ra/^{226}Ra activity ratio is strongly correlated to the Th/U content ratio of the aquifer rock and may serve as a fingerprint of the aquifer. ^{210}Pb is a decay product of the ^{222}Rn content of the fluid whereas ^{40}K as part of the natural potassium isotope composition reflects the K concentration in the brine.

Generally, the radionuclide contents are stable over time and the ^{228}Ra/^{226}Ra ratio is comparable to values obtained for geothermal fluids from similar sites in this region (Degering et al., 2016). The radionuclides concentration in the fluid is comparable between production and injection wells for both sites. This observation means that: i) no important dissolution of radioactive secondary minerals deposited in the installation occurs during fluid circulation in the surface equipment (Scheiber et al., 2012 and Cuenot et al., 2013) and ii) the scales formed in the surface equipment do not significantly trap radionuclides from the fluid.

Once verified the radioactive composition of the brine, it may be relevant to question if they are present in the fluid as dissolved ions or if they are mainly carried by the minerals still present in the brine as solid phase (< 0.45 µm). To face this issue, results are compared between the analysis of the brine and the correspondent filtration residues, on samples collected at the SsF production and injection wells. The data obtained with this approach shows that the particles residues filtered from the brine are only poorly enriched in radionuclides: no trace of K-40, Ra-228 and Ra-224 were detected, while Ra-226 is present at concentration of one magnitude order less than in the brine (Figure 10, Table 5). Only 210-Pb concentration are very similar between the brine and the particles phase. However, the results obtained on the filtration residues obtained from SsF over a year of exploitation (2017) shows that 210-Pb and 226-Ra concentration might vary of one magnitude order (Figure 11).

Table 5 Brine radionuclide composition of the SsF and Rittershoffen geothermal plants during the first years of operation (2016 – 2020). PW = Production Well; IW = Injection Well.

Date	Site	Sample	^{210}Pb	^{228}Ra	^{226}Ra	^{224}Ra	^{40}K	^{228}Ra/ ^{226}Ra	Analysis
			Bq/l	Bq/l	Bq/l	Bq/l	Bq/l		
05/04/2017	Rittershoffen	PW Not filtered	28 ± 4	37.1 ± 1.8	48.6 ± 2.3	24.6 ± 1.7	112 ± 7	0.76 ± 0.05	Lab 3
05/04/2017	Rittershoffen	IW Not filtered	24.3 ± 2.7	38.4 ± 1.8	52.4 ± 2.6	25.1 ± 1.7	106 ± 7	0.73 ± 0.05	Lab 3
13/06/2018	Rittershoffen	PW	7.5 ± 1.0	34.2 ± 1.3	52.6 ± 2.5	23.8 ± 2.1	105 ± 6	0.65 ± 0.04	Lab 3
13/06/2018	Rittershoffen	IW	11.4 ± 1.0	33.9 ± 1.3	51.0 ± 2.5	24.1 ± 2.2	101 ± 6	0.67 ± 0.04	Lab 3
02/04/2019	Rittershoffen	PW	8.4 ± 1.0	33.5 ± 1.3	52.9 ± 2.6	26.2 ± 2.6	107 ± 7	0.63 ± 0.04	Lab 3
02/04/2019	Rittershoffen	IW	6.0 ± 1.0	31.7 ± 1.2	47.9 ± 2.4	25.9 ± 2.7	104 ± 6	0.66 ± 0.04	Lab 3
04/11/2020	Rittershoffen	PW	20.9	28.4	47.5	37.5		0.60	Lab 1
16/11/2016	SsF	PW Not filtered	< 4.4	24.4 ± 0.9	33.4 ± 1.5	22.0 ± 1.7	101 ± 5	0.73 ± 0.04	Lab 3
16/11/2016	SsF	IW Not filtered	5.6 ± 1.1	23.1 ± 0.9	31.1 ± 1.4	19.0 ± 1.5	99 ± 5	0.74 ± 0.04	Lab 3
31/05/2017	SsF	PW	6.7 ± 1.5	31.7 ± 1.3	44.3 ± 2.2	27.3 ± 2.4	102 ± 6	0.72 ± 0.04	Lab 3
30/05/2017	SsF	IW	6.4 ± 1.1	34.1 ± 1.4	47.4 ± 2.3	28.6 ± 2.8	104 ± 6	0.72 ± 0.04	Lab 3
22/08/2017	SsF	PW	6.1 ± 1.6	27.5 ± 1.1	39.2 ± 1.6	21.2 ± 2.0	101 ± 6	0.70 ± 0.04	Lab 3
22/08/2017	SsF	IW	8.3 ± 1.2	24.9 ± 1.0	33.1 ± 1.7	19.1 ± 2.0	100 ± 6	0.75 ± 0.05	Lab 3
11/06/2018	SsF	PW	5.8 ± 1.2	23.0 ± 1.0	31.2 ± 1.6	17.2 ± 1.7	98 ± 6	0.75 ± 0.05	Lab 3
12/06/2018	SsF	IW	10.0 ± 1.3	22.9 ± 0.9	30.3 ± 1.5	17.4 ± 1.7	101 ± 6	0.76 ± 0.05	Lab 3
09/01/2019	SsF	PW	6.7 ± 1.4	24.8 ± 1.0	31.7 ± 1.6	18.3 ± 1.8	101 ± 7	0.78 ± 0.05	Lab 3
09/01/2019	SsF	IW	6.6 ± 1.4	25.3 ± 1.0	34.3 ± 1.7	19.5 ± 1.9	101 ± 7	0.74 ± 0.05	Lab 3
05/02/2020	SsF	PW		16.2	17.4			0.93	Lab 1
05/02/2020	SsF	IW	11	24.6	35.9	28.8		0.69	Lab 1
31/05/2017	SsF	Filtration residue (PW)	4.9 ± 0.5	0.10 ± 0.04	0.19 ± 0.04		< 0.29	0.53 ± 0.21	Lab 3
30/05/2017	SsF	Filtration residue (IW)	3.0 ± 0.4	< 0.13	0.33 ± 0.06		< 0.36	< 0.39	Lab 3
22/08/2017	SsF	Filtration residue (PW)	1.12 ± 0.15	< 0.052	0.021 ± 0.006			< 2.5	Lab 3
22/08/2017	SsF	Filtration residue (IW)	0.43 ± 0.08	< 0.040	0.021 ± 0.007			< 2.0	Lab 3

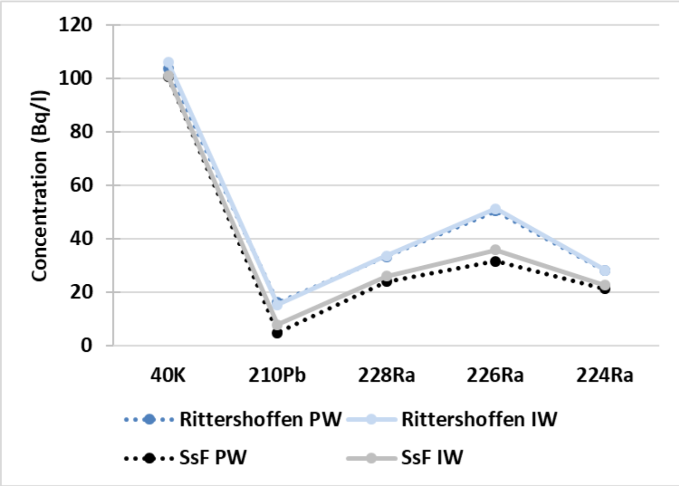

Figure 9 Mean value for radionuclide concentration in brine samples collected during the operation phase (2016-2020) at the injection and production wells of the SsF and Rittershoffen geothermal plants.

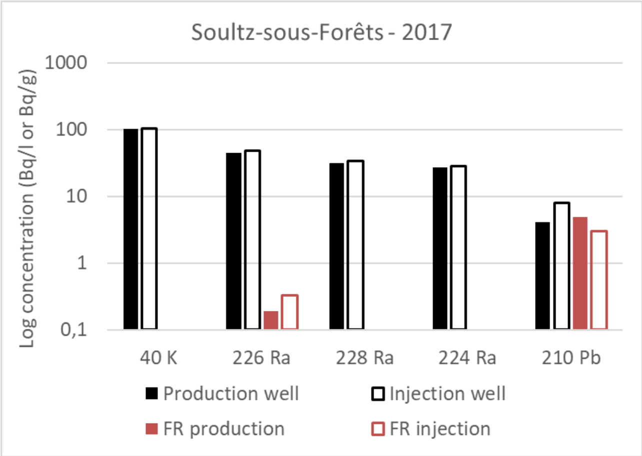

Figure 10 Comparison of radionuclide concentration of brine and filtration residues (FR) of SsF geothermal plant.

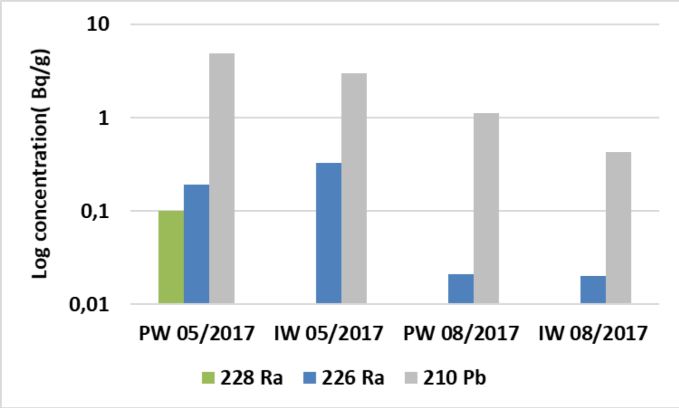

Figure 11 Comparison of radionuclide concentration of the filtration residues in the production (PW) and injection (IW) wells of SsF geothermal plant in 2017.

Based on the data obtained with this approach, several observations could be inferred concerning the radionuclides origin in the fluid and in the particles fraction:

- Potassium, as seen by the ^{40}K data, is predominantly dissolved in the fluid and is not detected in the solid phase > 0.45 µm.
- Radium is also enriched in the fluid as dissolved species, as the activities of Ra isotopes on the filter are small compared to the concentrations in the fluid.
- Furthermore, the $^{228}Ra/^{226}Ra$ ratio of the filters is smaller than that of the fluid. One explanation could be the occurrence of small rock particles, catched by the filter, with a Th/U ratio different from that of the main aquifer rock which is responsible for the radium ratio in the brine. However, at this stage, this hypothesis appears in contrast with the conceptual model of the reservoir, where the same primary and secondary mineral assemblages were observed for the different geothermal sites (Genter and Traineau, 1992, Vidal et al., 2018, Glaas et al., 2021). Alternatively, the particles fraction observed in the filter could correspond to remobilized barium sulfate scale deposits from the well with an age of several years. Because of their different half-lifes (^{228}Ra 5.75 yrs, ^{226}Ra 1600 yrs) the $^{228}Ra/^{226}Ra$ activity ratio decreases in the scales with time.
- ^{210}Pb contents of the filters comparable to that of the brine suggest that ^{210}Pb is not only dissolved in the brine, but also carried by particles > 0.45 µm. This holds particularly for the Rittershoffen samples, where ^{210}Pb concentrations of unfiltered samples were generally higher. As for Ra, also in this case scale particles, may be responsible: mainly composed of PbS, scales could enter the fluid by physical erosion during fluid circulation (Mouchot et al., 2018). Such hypothesis could also explain the important variability observed for ^{210}Pb of the residues on the two plant over exploitation, as the facility of peeling scales off may vary depending on the hydraulic conditions and the scale treatment applied, which was different between the two sampling periods.

5.3 Sampling strategy

Fluid chemical composition was measured by 3 different laboratories using mass-spectrometry equipment. By comparing data from the different laboratories concentrations from laboratory 2 stands out with lower or higher values (Figure 12). Such a deviation could be attributed to the sampling procedure, the preservation and to the analysis (including method, sample preparation, equipment used, but also experience in handling and analysis of highly saline brines). Even if not all the subtractors were used to work with complex matrix such as the fluid of this study, they all performed accredited analysis, which make difficult to question the measurement protocol. On the opposite, the sampling procedure and sample conditioning for the 3 laboratories was very different: laboratories 1 and 3 filtered the fluids on site, directly after the sampling, then conditioned the brine manually with different acids and different dilutions, while laboratory 2 did not filter the brine, which was sampled by the plant operator and conditioned in pre-acidified flasks nor did it apply any other pretreatment. The present results thus highlight the importance of the sampling protocol and sample conditioning on site directly after sampling, even for routine analysis of highly mineralized brines (Jähnichen et al., 2016).

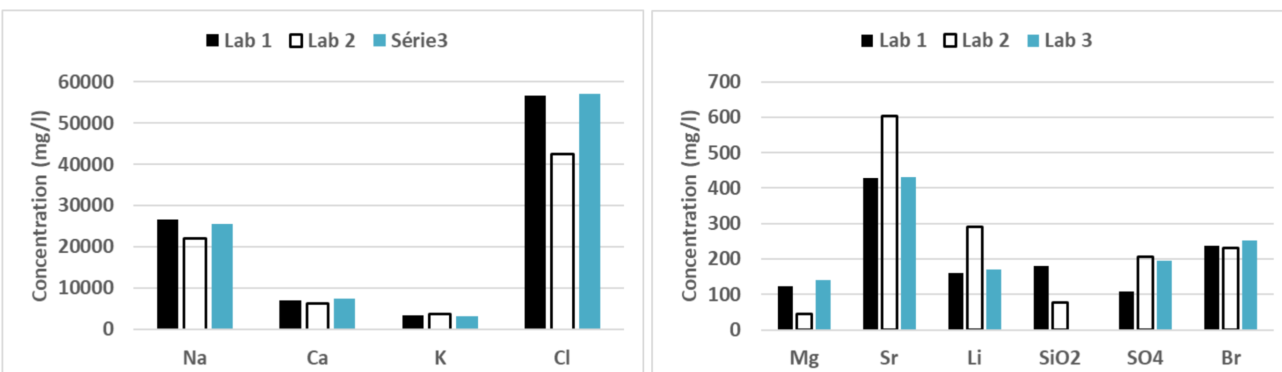

Figure 12 Comparison of the results obtained from 3 different laboratories for brine collected at the SsF geothermal plant. The concentrations correspond to mean of all the data presented in this study.

6. GASES

SsF and Rittershoffen geothermal fluids have a very similar gas/fluid ratio, even if the gas fraction is systematically lower for brine at SsF (1.0 Nm^3/m^3) compared to Rittershoffen (1.15 Nm^3/m^3, Table 6). The composition of the gas fraction contained in the brine is very close for the two sites (Table 6, Figure 13), basically consisting of CO_2 (88-93%), N_2 (5-10%), CH_4 (2%) and other gas at trace amounts (He, Ar, Figure 14). The only significant difference is nitrogen concentration, which is systematically lower at SsF.

It is interesting to note that no variations could be observed in the gas content and composition between the production and the injection well. This observation indicates that, during nominal flow phases such as those where the samples were collected, only minor degassing occurs in surface installation. No variations are also detectable over the 4 years of the operational phases, suggesting that geothermal activities do not induce depressurization of the reservoir, neither at the project scale, nor at a regional scale, potentially induced by the interferences between the two operational sites.

Table 6 Gas content and composition of the brine at the SsF and Rittershoffen geothermal plants during the first years of operation (2016 – 2019).

Date	Site	Sample	Gas/fluid ratio (Nm^3/m^3)	CO_2	CH_4	N_2	He	Ar
				%	%	%	%	%
23/08/2016	SsF	2016 PW	1.0	91	2	7	0.3	0.13
03/04/2019	SsF	2019 PW	1.0	88	2	9	0.3	
03/04/2019	SsF	2019 IW	1.0	89	2	8	0.3	
24/08/2016	Rittershoffen	2016 PW	1.2	90	2	7	0.3	0.15
23/08/2017	Rittershoffen	2017 PW	1.2	89	2	10		
13/06/2018	Rittershoffen	2018 PW	1.2	88	2	10		
09/10/2019	Rittershoffen	2019 PW	1.1	88	2	9		
23/08/2017	Rittershoffen	2017 IW	1.2	89	2	10		
09/10/2019	Rittershoffen	2019 IW	1.1	93	2	5		

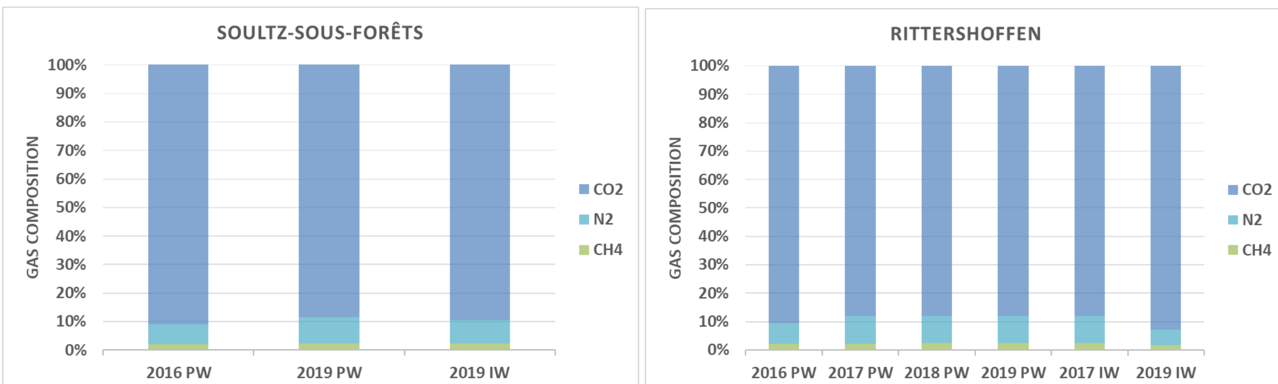

Figure 13 Composition of the gas phase of the brine collected at the injection and production wells (namely, IW and PW) at the SsF and Rittershoffen plants during the first years of operation (2016 – 2019).

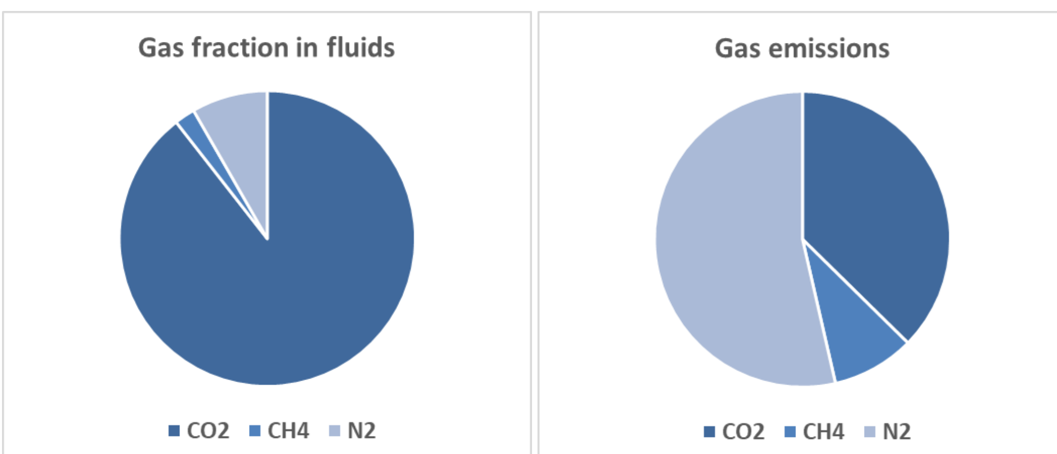

Figure 14 The mean values for composition of the gas fraction in the fluids (left) and of the venting valves emissions (right) for the Rittershoffen plant.

Among the gases that were systematically analyzed, H_2S was always measured below the detection limit (DL, < 0.05 %). This result questions about the origin and formation mechanisms of the scales deposited in the installation, which are today mainly composed of metallic sulfides (Mouchot et al., 2018, 2019). Based on a dedicated study, no bacteriological activity was detected in the surface installation, which thus exclude the possibility to form Sulphur by bio-oxidation of sulfates present in the fluids. Haas-Nüesch et al. (2018) suggest that sulfide scales are the results of electrochemical processes, namely corrosion, occurring during operation. However, data collected during this study show that geothermal fluid may contain up to 64 mg/L of S (Appendix 1) and this concentration appears enough, based on a mass balance approach, to explain the whole Sulphur amount deposited in the installation.

The gas emissions of the venting valve at Rittershoffen geothermal site have, as expected, the same gas composition than the gas fraction of the brine, but in different proportions (Table 6, Table 7, Figure 14Figure 13). CO_2 is thus less predominant (30 to 60 %), with on the opposite, higher concentration of N_2 (27 to 66 %) and CH_4 (7 to 10%). Such a distribution reflects the Henry law for gas dissolution in fluid, predicting that N_2 has lower solubility than CO_2 and CH_4. Nitrogen is thus the first gas released during degassing in the plant. On the other side, based on Henry constant, CO_2 is the more soluble gas, which explain the highest concentration in the fluid compared to the atmospheric emissions.

The gas composition of the plant emissions changes with the temperature, with CH_4 and N_2 proportions increasing with lowering temperatures (Table 7, Figure 15). Based on Henry law, gases are more soluble in the water at colder temperature..

Table 7 Composition of the gas emissions at the Rittershoffen geothermal plant. The point number (N) correspond to the symbols of Figure 3.

Date	Site	Sample	Point N	T	P	CO_2	CH_4	N_2
				°C	Bars	%	%	%
18/11/2019	Rittershoffen	Production line	1	167	23.8	41	9	51
18/11/2019	Rittershoffen	HEX 1S	2	167	23.8	41	9	51
18/11/2019	Rittershoffen	HEX 4S	3	136	23.4	36	9	55
18/11/2019	Rittershoffen	HEX 5S	4	136	23.4	34	9	57
18/11/2019	Rittershoffen	HEX 8S	5	127	23.1	34	9	57
18/11/2019	Rittershoffen	HEX 12S	6	90	23.1	25	10	66
18/11/2019	Rittershoffen	Injection line	7	86	5.3	66	7	27
09/10/2019	Rittershoffen	Well head	8	85	16	31	10	59
18/11/2019	Rittershoffen	Well annular	8	86	1.4	31	10	59

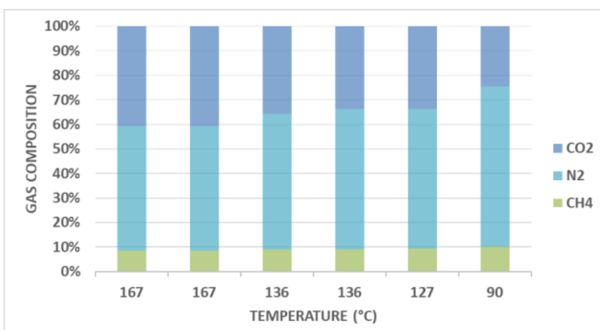

Figure 15 Evolution of the gas emissions with temperature (stable pressure and flowrate) at the Rittershoffen geothermal plant.

7. CONCLUSION

After four years of operation, a large geochemical fluid dataset has been collected for SsF and Rittershoffen geothermal plants located in the Upper Rhine Graben. The main goal of this study was to better characterize the geothermal fluid composition versus time discharged from fractured reservoirs and to evaluate its impact of the operational phase during exploitation in terms of scaling or other physico-chemical processes.

Geochemical data collected at the production and injection wells indicates that geothermal exploitation does not induce significant changes on the fluid composition over time. Similarly, modification of the fluid due to interferences between proximal geothermal plants (<10km) are not observed during the first years of operation. The similarity between fluid collected in SsF and Rittershoffen plants indicates a homogeneous origin of the fluid, potentially issued from a large-size fractured reservoir. The composition of the gas phase present in the fluid and the atmospheric emissions also confirm those conclusions. The geochemical discrepancies observed between the fluids of the geothermal plants located in the North of the URG and those from wells around the Strasbourg area tend to be an indication of the existence of preferential circulation paths in the graben, where the permeability distribution would be controlled by different geological structures.

This study presents the first and unique data existing at this day for thermodynamic parameters of the URG geothermal brines. By consequent, future industrial projects on the region may rely on this dataset for surface installation design and dimensioning. In addition, important and stable concentrations of strategic metal resources as lithium were measured for both SsF and Rittershoffen over more than 4 years. At this stage, Li appears as a critical resource for the future industrial development, with proved risks on the supply chain. The data collected during this study thus allow to validate the interest for geothermal co-valorization industrial projects, aiming to exploit jointly different resources present in the fluids, and may be used to better define the development strategies for this sector.

The results obtained in this work also open new perspectives on important operational issues, as the corrosion and scaling processes. Indeed, the lack of H_2S in the gas phases and of microbiological activity in the installation, confirms that the formation of PbS and other metallic sulfides scales could not be induced by the bio-reduction of sulfates present in the fluids. Metallic-sulfides formation is likely controlled by complex processes, including complex electro-chemical reaction and thermodynamic reactions.

This conclusion, but also the results obtained on the gas phase composition, which vary as a function of pressure and temperature, indicates the importance to better understand the studied system, composed of both the geothermal reservoir and the surface installation. Developing numerical approaches might thus be helpful to characterize and understand the different processes controlling scale formation and degassing.

Finally, the present work allowed to assess the importance of the analytical approach in the monitoring of a geothermal site. Accurate and precise chemical data are necessary to properly operate a geothermal site and their acquisition is strongly tributary of the sampling and analysis protocols. By consequent, analytical partners for complex matrix such as URG geothermal brine should be attentively selected.

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ANNEXES

Appendix 1: Detailed geochemical composition for brine sample of Soultz-sous-Forêts and Rittershoffen

Date		**05/02/2020**	**05/02/2020**	**04/11/2020**
Site		**SsF**	**SsF**	**Rittershoffen**
Sample		**PW**	**IW**	**PW**
S	mg/L	64	64	
Ti	mg/L	<0.001	<0.001	
Th	mg/L	<0.001	<0.001	<0.001
NH4	mg/L	23	24	26.3
NO3	mg/L	<5	<5	<5
NO2	mg/L	<0.01	<0.01	<0.01
Sulfites	mg/L	20	<4.0	<1
Co	µg/l	2.5	2.4	5.5
Ag	µg/l	<0.01	<0.01	0.5
V	µg/l	<0.001	<0.01	1.4
Mo	µg/l	4.2	4.1	8.3
Se	µg/l	<0.1	<0.001	1.4
Be	µg/l	37.8	37.1	26.7
Bi	µg/l	<0.5	<0.5	<0.5
Ta	µg/l	<0.001	<0.001	
W	µg/l	25.4	26.0	24.7
Zr	µg/l	<5	<5	<5
In	µg/l	0.16	0.27	0.56
Re	µg/l	0.26	0.21	<0.5
Sc	µg/l	0.62	0.65	1.38
Ga	µg/l	<1	<1	<1
Ge	µg/l	45.4	47.6	57.2
Rh	µg/l	0.24	0.30	1.16
Pd	µg/l	7.1	7.0	<0.5
Hf	µg/l	<0.0001	<0.0001	1.98
Os	µg/l	<0.005	<0.005	<0.5
Ir	µg/l	<0.006	<0.006	<0.5
Pt	µg/l	<0.007	<0.007	<0.5
Au	µg/l	<0.008	<0.008	<0.5
Dy	µg/l	0.28	0.31	<0.1
Er	µg/l	0.15	0.12	<0.1
Eu	µg/l	0.38	0.36	0.29
Gd	µg/l	0.25	0.27	0.13
Ho	µg/l	0.06	0.05	<0.1
Lu	µg/l	0.01	0.02	<0.1
Pr	µg/l	0.18	0.19	<0.1
Sm	µg/l	0.18	0.19	<0.1
Tb	µg/l	0.05	0.04	<0.1
Tm	µg/l	0.02	0.02	<0.1
Y	µg/l	1.5	1.8	1.4
Yb	µg/l	0.97	0.11	<0.1
Ce	µg/l	1.6	1.7	0.7
Nd	µg/l	0.64	0.65	0.30
La	µg/l	1.1	1.1	0.6

Appendix 2: Detailed geochemical comparison of brine from Soultz-sous-Forêts and Rittershoffen geothermal plants

The concentrations used in the following graphs are an average of all the data present in this study for each site.