

## Inhibition of scales in geothermal plants in Upper Rhine Graben: Monitoring of fluids and scales

Sabine Jähnichen<sup>1</sup>, Detlev Degering<sup>1</sup>, Andrea Seibt<sup>2</sup>, Julia Scheiber<sup>3</sup>, Justine Mouchot<sup>4</sup>,  
Christian Buse<sup>5</sup>, Frank Heberling<sup>6</sup>

<sup>1</sup> VKTA – Strahlenschutz, Analytik & Entsorgung Rossendorf e. V, Germany;

<sup>2</sup> BWG Geochemische Beratung GmbH Neubrandenburg, Germany;

<sup>3</sup> Bestec GmbH, Kandel, Germany;

<sup>4</sup> ES Géothermie Strasbourg, France;

<sup>5</sup> Geothermie Neubrandenburg GmbH, Germany;

<sup>6</sup> Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal, Germany.

**Keywords:** monitoring, scales, lead, antimony, arsenic.

### ABSTRACT

Precipitation of minerals within the surface installations of geothermic plants is still a problem although - according to the state-of-the-art - sulfate based scales are successfully inhibited. In order to learn more about scale formation and the effects of different inhibitors a monitoring program including characterisation of dissolved and particulate constituents of the fluids and a detailed analysis of scales was carried out. By addition of several kinds of inhibitors a remarkable mass reduction of scales was achieved indicating an influence on the scale forming processes.

### 1. INTRODUCTION

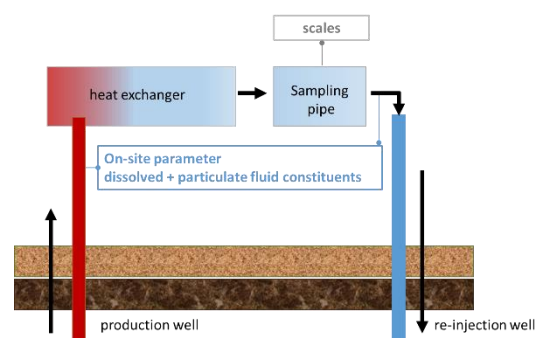
During the operation of geothermal plants in the Upper Rhine Graben the precipitation of minerals within the surface installations has been observed. In order to reduce the formation of such scales various measures have been initiated. In a first instance, sulfate inhibition has been applied. According to the state-of-the-art sulfate scales are now successfully inhibited in all of investigated geothermic plants. However, there have been still scales being formed. Based on their chemical and mineralogical analysis they consist mainly of lead (Pb), antimony (Sb) and arsenic (As). Investigations has been focused on a detailed characterization and quantification of scales within the context of monitoring the potentially scale forming elements in fluids. The (partial) elimination of these scales is the aim of a project funded by the German Federal Ministry for Economic Affairs and Energy (BMWi). Within the framework of this project – called SUBITO - several inhibitors or composites of inhibitors for scale reduction were tested.

### 2 METHODS

#### 2.1 Monitoring program with sampling conditions, sample preservation

On-site parameter (pH, conductivity, redox potential, temperature) were measured at production and re-injection well (Figure 1).

Fluid samples were taken from both, production and re-injection, side. Sampling temperature was always adjusted to the respective re-injection temperature by cooling the production fluid. For analysis of elements, fluid was filtered over 0.45 µm and fixed by adding HNO<sub>3</sub>. Samples for analysis of Ba, Sr were diluted with water (1:10, v/v) and for Si, sulfate also with water (1:50, v/v). For analysis of anions an untreated sample was used. For sulfide analysis samples were fixed by adding a mixture of NaOH, EDTA and ascorbic acid.



**Figure 1: Schema of monitoring program for sampling of fluid and scales.**

For analysis of particulate constituents (fluid particles) samples were obtained by in-situ filtration of a defined fluid volume. Thermal fluid was directly drawn from the system and run through a sampling device that holds the 3 µm membrane filters. Sampling was done at a constant pressure of 1 bar.

Scale samples were taken from a defined area of 10 cm x 15 cm from both, the inlet and the outlet, of a pipe.

#### 2.2 Analysis

Cations and elements were determined by Inductively coupled plasma-mass spectrometry (ICP-MS; Element 2, Thermo Fisher Scientific) according to DIN EN IS 17294-2. For scale analysis air-dried samples were digested by two steps, adding a mixture of HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and HF for the first one and HBO<sub>3</sub> adding for the second step using for both a microwave equipment (ETHOS.lab). Metrohm ion chromatography systems (882 Compact IC plus, 930

Compact IC flex) with both, conductivity and UV detection, were used for determination of dissolved anions according to DIN EN ISO 10304-1 (D 20). Analysis was performed on Metrosep A Supp 5 columns of different length at a temperature of 30°C using a mixture of NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> (1 mM, 3.2 mM) as eluent. Sulphide was determined polarographically by 797 VA Computrace (Metrohm) according to Metrohm Application Bulletin 199/3d.

Gamma ray spectrometry measurements were performed in the underground laboratory Felsenkeller (Niese et al 1998) on several low-level spectrometry systems using HPGe detectors of 20 ... 90 % relative efficiency.

For detailed information of all methods used see also Jähnichen et. al. (2016).

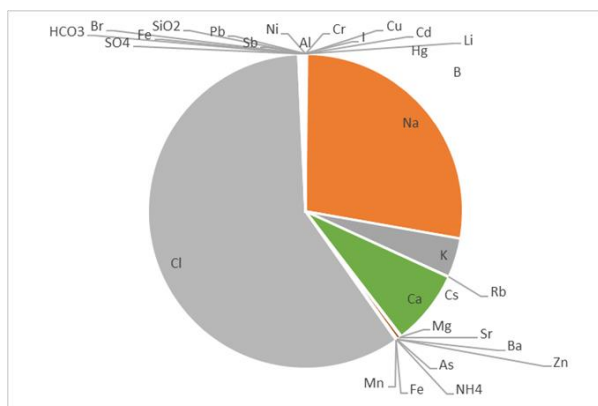
The amount of particulate matter obtained during filtration was determined by differential weighting of the filter membranes. The particles themselves were analysed by SEM-EDX in regard to their geochemical composition, size, and structure, Geochemical bulk composition of all particulate matter on said filter membranes was also determined using SEM-EDX. In addition, particle samples were digested by three steps adding HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and water for the first step; HNO<sub>3</sub> and HF for the second one and for the third HNO<sub>3</sub> and analysed by ICP-MS (see element analysis).

Scale samples were analysed according to their chemical composition after digestion with HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and HF in a first and in a second step with HBO<sub>3</sub>. Analysis was performed as well by ICP-MS (see element analysis). For all experimental details of solid-phase investigations (XRD, SEM-EDX, XANES) see Haas-Nüesch et al. (2018).

### 3 RESULTS

#### 3.1 Monitoring of fluids

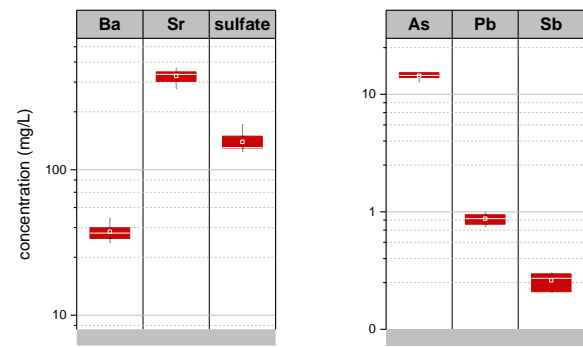
Fluids are dominated by Na, Ca, K and chloride with a total ion concentration of about 100 g/L (see Figure 2).



**Figure 2: Ion composition of a fluid from the Upper Rhine Graben.**

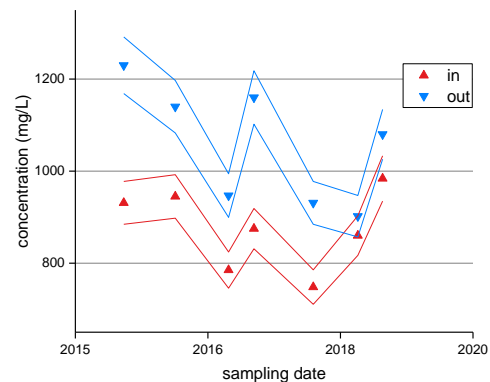
Relating to scale formation the following ions are matter of particular interest: Ba, Sr and sulfate as well as Pb, As, Sb. Fluid concentrations of Ba, Sr, sulfate

and As are in the mg-range, concentration for Pb and Sb are considerable lower (Figure 3).



**Figure 3: Concentrations in fluid of potentially scale-forming elements from samples taken at the production side (boxplots with mean, 25%, 75% percentile).**

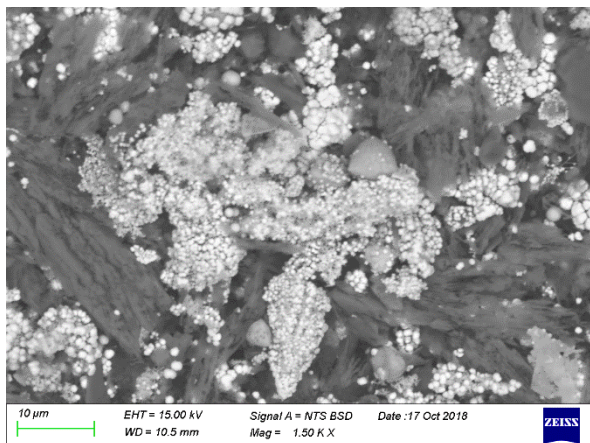
In order to evaluate the scale formation process fluid samples before and after passing the heat exchanger were investigated. Compared to samples from the production well samples from the re-injection side stands out from higher Pb concentrations (Figure 4). This phenomenon was similarly observed for another investigated geothermal plant. For all other ions no such remarkable differences between production and re-injection well were found. Fluid sampling and analysis was performed repeatedly, however variations over the time lie for most of the ions within the measurement uncertainty. Sulphide concentration in fluids was below the detection limit.



**Figure 4: Pb concentration in fluid from production (in) and re-injection (out) well. Measured value with uncertainty.**

In addition to the dissolved components of the fluids the particulate ones were analysed. The main components of particles are S, Ca, Fe, Cu, Pb, Si and during time of the injection of a phosphor-based inhibitor P on the filters from re-injection side. Less dominant elements are As, Sb, Sr and Ba. Among the scale-forming elements an increase of Pb on filters from production to re-injection side was remarkable (based on analysis with ICP-MS). Based on SEM-EDX data particles from the production side can be related more to reservoir particles like quartz and feldspar as

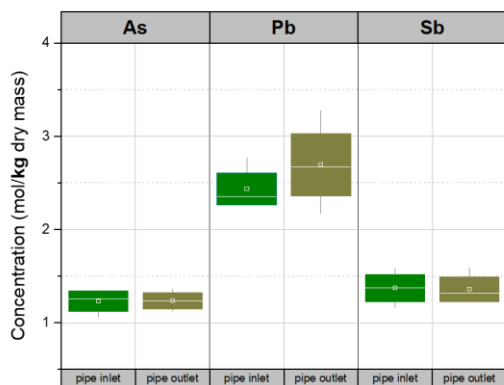
well as baryte and iron oxides. After passing the heat exchanger at the re-injection side a shift towards particles containing Pb and Sb, As was observed (Figure 5) consistently to the results based on ICP-MS data.



**Figure 5:** Fine grained Pb-rich scales (light grey) found on the re-injection side of a plant. Scales also contain Sb and As.

### 3.2 Monitoring of scales

Main elements in scales are Pb, Sb and As (see Figure 6). The percentage of sulphur pointed to the deposition of sulphur containing compounds. Samples from the inlet and the outlet of the pipe do not show any remarkable differences. Based on a combination of solid-phase investigations of these scales it is now known that the scales consists of PbS and Pb(0) (see Haas-Nüesch et al. 2018). Most of As and Sb were reduced to the elemental species as well. The percentage of Ba was very low indicating a successful inhibition of BaSO<sub>4</sub> precipitation. Moreover, the accumulation of Pb was detectable through an enhanced level of radioactive <sup>210</sup>Pb with an average activity of 8000 Bq per g of dry mass scales.



**Figure 6:** Concentrations of Pb, As, Sb in scales. Boxplot with mean and 25%, 75% percentile.

### 3.3 Inhibition of scalings

Several different inhibitors have been tested during the investigations (see also Mouchot et al. 2019, Scheiber et al. 2019). Due to the application of inhibitors a mass reduction of the total scale was observed (see Scheiber et al. 2019).

Moreover, the proportion of the scale-forming elements was changed. A detailed evaluation of all data are still in progress.

### 3. CONCLUSIONS

Scales, which were formed after the successful inhibition of the BaSO<sub>4</sub> precipitation, has been characterised. They consists of PbS, Pb(0) and As, Sb mostly as As(0) and Sb(0). In order to reduce the precipitation or deposition of these scales several inhibitors has been tested. Due to the application of these new inhibitors a reduction of the total mass of scales was observed. Moreover, the proportion of the main constituents switched, a detailed evaluation concerning this issue is still in progress.

### REFERENCES

- Jähnichen, S., Czeslik, U., Degering, D., Seibt, A.: Monitoring of saline fluids from geothermal plants: Special aspects of sampling, sample preservation and analysis. Proceedings of the European Geothermal Congress 2016, Strasbourg, France.
- Haas-Nüesch, R., Heberling, F., Schild, D., Rothe, J., Dardenne, K., Jähnichen, S., Eiche, E., Marquardt, C. Metz, V., Schäfer, T.: Mineralogical characterization of scalings formed in geothermal sites in the Upper Rhine Graben before and after the application of sulfate inhibitors, *Geothermics* 71 (2018) 264–273.
- Metrohm Application Bulletin 199/3d: Polarographic determination of sulfide and sulfite.
- Mouchot, J., Scheiber, J., Florencio, J., Seibt, A., Jähnichen, S.: Scale and Corrosion control program, Example of two geothermal plants in Operation in the Upper Rhine Graben, Proceedings of the European Geothermal Congress 2019, Den Hague, Netherlands.
- Niese, S., Köhler, M., Gleisberg, B.: Low - level counting techniques in the underground laboratory “Felsenkeller” in Dresden, *Journal of Radioanalytical and Nuclear Chemistry* 233 (1–2) (1998), 167–172.
- Scheiber, J., Seibt, A., Jähnichen, S., Degering, D., Mouchot, J.: Combined Application of Inhibitors for Scale and Corrosion Mitigation: Lessons Learned, Proceedings of the European Geothermal Congress 2019, Den Hague, Netherlands, (2019)..

Water quality - Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of selected elements including uranium isotopes (ISO/DIS 17294-2:2014); German version EN ISO 17294-2:2014.

Water quality - Determination of calcium and magnesium - Atomic absorption spectrometric method (ISO 7980:1986); German version EN ISO 7980:2000.

Water quality - Determination of dissolved anions by liquid chromatography of ions - Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate (ISO 10304-1:2007); German version EN ISO 10304-1:2009.

### **Acknowledgements**

We acknowledge the financial support by the German Federal Ministry for Economic Affairs and Energy (BMWi) through the collaborative project SUBITO (0325790A).