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Scale Inhibition in Geothermal Plants in the Upper Rhine Graben: Analytical Details of Fluid and Scale Composition

S. Jähnichen[1], D. Degering[1], F. Heberling[2], A. Seibt[3], J. Scheiber[4] J. Mouchot[5], C. Buse[6]

[1] VKTA – Strahlenschutz, Analytik & Entsorgung Rossendorf e. V., Bautzner Landstr. 400, 01328 Dresden, Germany

[2] Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal, Hermann von Helmholtz Platz 1,
76344 Eggenstein-Leopoldhafen, Germany

[3] BWG Geochemische Beratung GmbH Neubrandenburg, Seestraße 7A, 17033 Neubrandenburg, Germany

[4] Bestec GmbH, Bismarckstr.19, 76870 Kandel, Germany

[5] Electricité de Strasbourg Géothermie, Bat Le Belem, rue de Lisbonne 5, 67300 Schiltigheim, France

[6] Geothermie Neubrandenburg GmbH, Seestraße 7A, 17033 Neubrandenburg, Germany

sabine.jaehnichen@vkta.de

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ABSTRACT

Deposition of minerals within the surface installations of geothermic plants of the Upper Rhine Graben is still a problem although - according to the state-of-the-art, sulfate based scales are successfully inhibited. In principle, the formation of scales can be reduced by addition of chemical inhibitors. However, the selection of an appropriate inhibitor depends on the composition of the scales. In order to learn more about scale formation and the effects of different inhibitors a monitoring program including characterization 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 formation processes. The effect of the individual inhibitors on the particular elements was evaluated by a comparative analysis of chemical, mineralogical and radiological data. As result it was found, that the different inhibitors caused different impacts on the distribution of lead species, arsenic and antimony within the scales.

1. INTRODUCTION

The performance of geothermal power plants is often limited by the deposition of scales. This deposition can be rinfluenced by addition of a chemical inhibitor. It should be take into account, that the selection of an appropriate inhibitor depends on the composition thermal water and the scales, and the operational parameters of the power plant (temperature, pressure). The (partial) elimination of scales formed in geothermal plants in the Upper Rhine Graben was 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.

According to the state-of-art sulfate scales are are successfully eliminated in all investigated geothermal sites. However, there are still scales being formed. At the outset of the investigation it was known that these scales consist of the elements lead (Pb), antimony (Sb) and arsenic (As), but information on the exact element speciation and mineralogical composition was scarce. Thus, the analytical part of the project was focused on the chemical, mineralogical and radiological characterization of scales and – in order to understand the process of scale formation – also on the respective analysis of the soluble and particulate fractions in the fluids. Altogether, fluids and scales from three different geothermal plants were sampled and analyzed. The investigation comprises a pure sulfate-inhibition period ("reference") and a period with application of various new inhibitors.

2. METHODS

2.1 Monitoring program with sampling conditions, sample preservation

On-site parameter (pH, conductivity, redox potential, temperature) were measured at production and injection side (Figure 1). Fluid samples were taken from both, production and injection, side. Sampling temperature was always adjusted to the respective injection temperature by cooling the production fluid. For analysis of elements, fluid was filtered over 0.45 µm and fixated by adding HNO_3. Samples for analysis of Ba, Sr were diluted with water (1:10, v/v) and for Si, sulfate (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 citric acid. For determination of ^{210}Pb fluids were filtered over 0.45 µm.

For analysis of particulate constituents (fluid particle) 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 the SUBITO pipe.

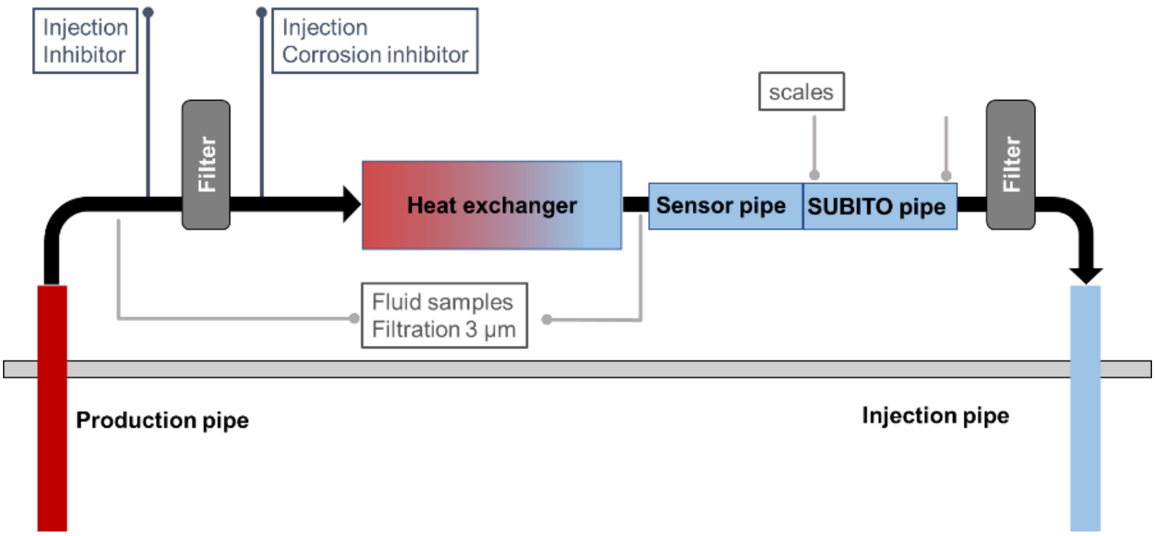

Figure 1: Schema of the monitoring program for sampling of fluid and scales within the SUBITO project.

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 ISO 17294-2. For scale analysis air-dried samples were digested by two steps, adding a mixture of HNO_3, H_2O_2 and HF for the first one and HBO_3 adding for the second step using for 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 $NaHCO_3/Na_2CO_3$ (1 mM, 3.2 mM) as eluent. Sulfide 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.

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_3, H_2O_2 and water for the first step, HNO_3 and HF for the second one and for the third HNO_3 and analysed by ICP-MS (see element analysis).

Scale samples were analysed according to their chemical composition after digestion with HNO_3, H_2O_2 and HF in a first and in a second step with HBO_3. 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). For XRF analysis of scales a handheld spectrometer (Spectro xSort) was used.

3. RESULTS

First, only the deposition of sulfate scales was inhibited by addition of a phosphonate-based inhibitor. This is the so-called “reference” period. As a result of the solid-phase analysis of the “reference” scales it turned out that they are dominated by Pb (see Figure 2, 3) in the form of PbS and Pb(0) (Haas-Nüesch et al. 2018). The dominance of Pb was confirmed by XRF measurements and by chemical analyses. In addition, these scales contain Sb and As as solid metals (Sb(0), As(0)). The ratio of radioactive ^{210}Pb to inactive Pb was constant in all scales of one geothermal plant, pointing to a consistent source of both components.

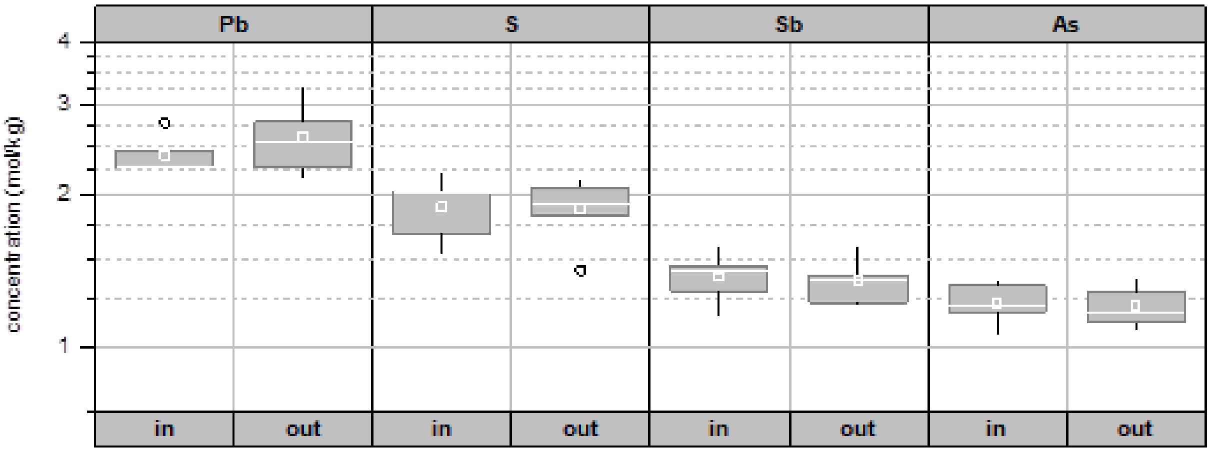

Figure 2: Pb, S, Sb and As in reference scales, data from ICP-MS measurements. Each for inlet (in) and outlet (out) of the SUBITO pipe. Boxplot with mean, median, 25, 75% percentile.

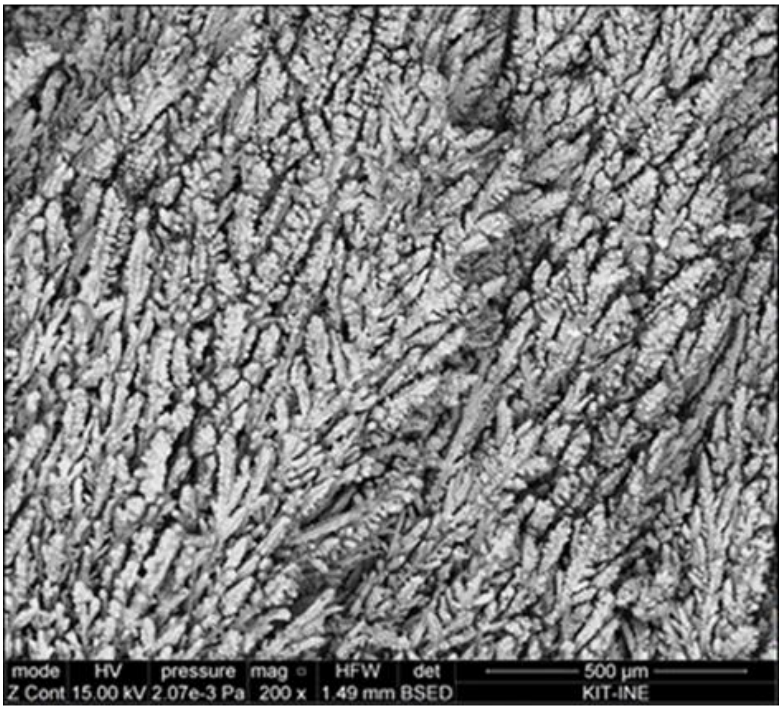

Figure 3: SEM image for scales from "reference" period. Dendrites containing Pb, S, Sb and As.

Fluids are highly mineralized with around 100 g/L of total dissolved solids. Among the three scale-forming elements (Pb, Sb, As) the most prominent one was As in all investigated fluids (Figure 4). One order of magnitude lower in concentration was Pb followed by even lower Sb. When compared to the ratio of the elements Pb, Sb, As in scales it can be concluded that the deposition of Pb and Sb is favoured compared to the deposition of As (compare Figure 2 and Figure 4). Parts of the scales consist of PbS. Consequently, it was a matter of particular interest to analyze sulfide in fluids. However, sulfide in fluids was always below the detection limit.

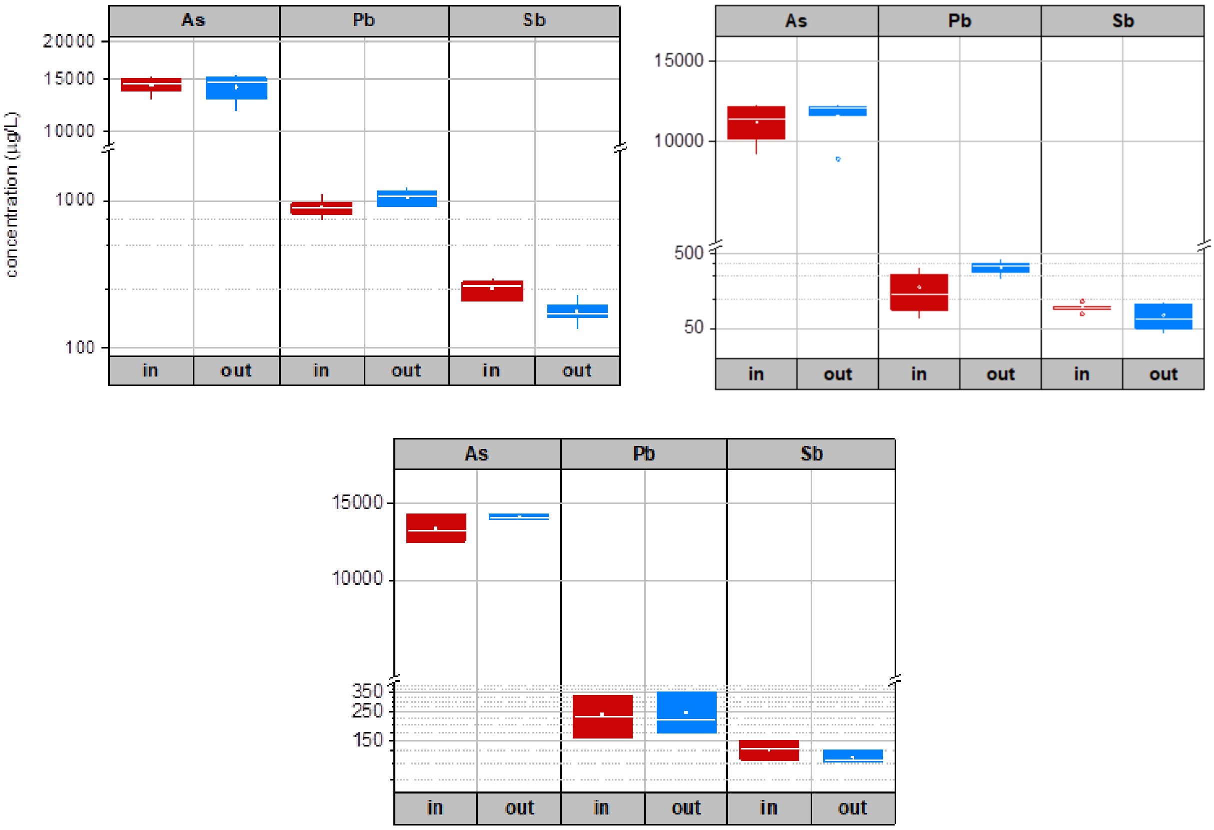

Figure 4: As, Pb, Sb in fluids for the three investigated geothermal plants, each concentration for production (in) and injection (out) side. Boxplot with mean, median, 25, 75% percentile. Data from ICP-MS measurements. Note the logarithmic scale of y axis.

In the context of scale deposition, the particulate concentration and radionuclide content in fluids were monitored. By the analysis of ^{210}Pb activity the Pb concentration in fluids was verified, during the investigation the specific ^{210}Pb activity was constant. Concerning the dissolved concentrations of elements in fluid especially a variation of Pb and Sb was observed.

Main elements within the particulate fraction in the fluid were Cu, Ca, S and - during the application of phosphonate based inhibitors - P at the sampling point near to the injection side (Figure 5). Compared to other elements Pb, Sb, As had only a minor proportion on particulate element content. 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 6). The increase of Pb in particles was confirmed by ICP-MS data (Figure 5).

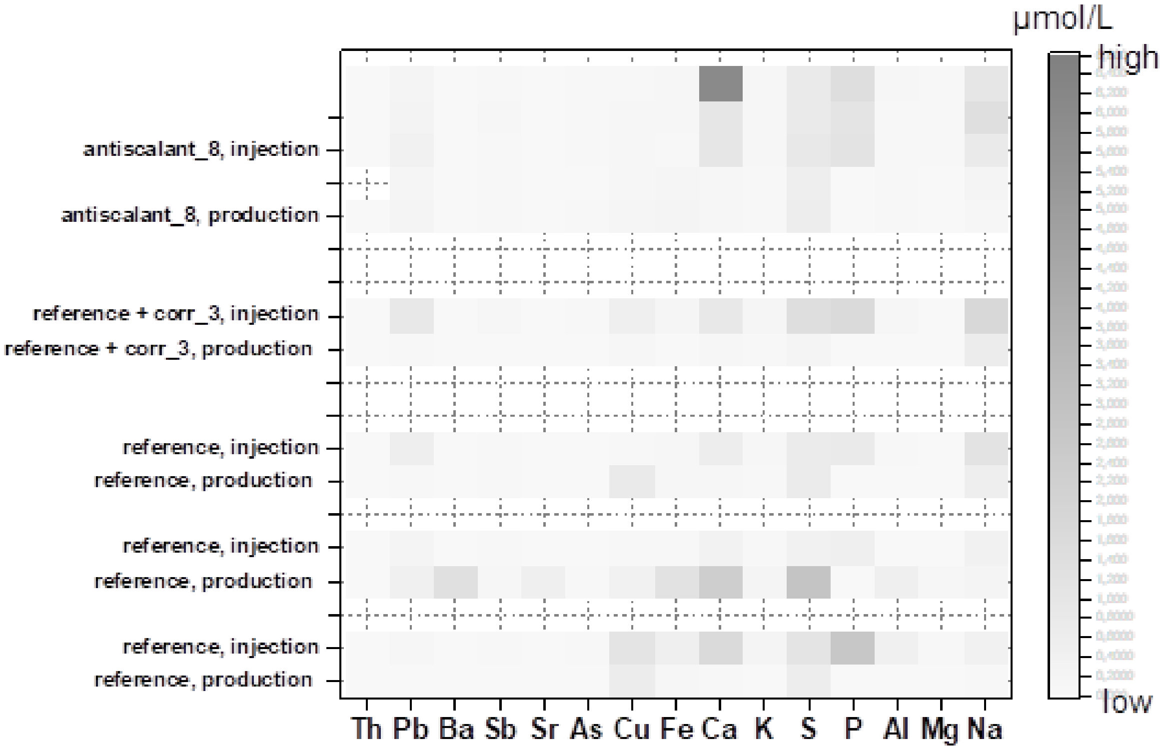

Figure 5: Element concentrations in particles, sepearted from the fluid from the production and injection side, respectively by filtration > 3 µm. Antiscalant with dispersing and anti-corrosive properties. Sampling and analysis for antiscalant with replicates for production side (2 replicates) and for injection side (3 replicates).

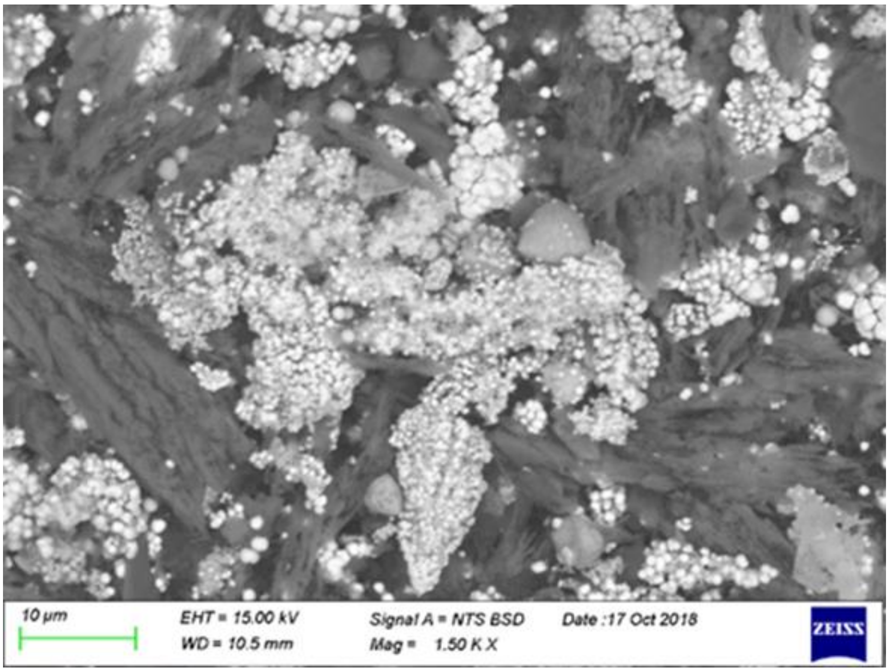

Figure 6: Fine grained Pb-rich scales (light grey) found on the re-injection side of a plant. Scales also contain Sb and As.

Several inhibitors - antiscalants with dispersing properties and corrosion inhibitors - were applied in the geothermal plants during the investigations. As result of inhibition the mass of scales was considerably reduced (see Scheiber et al. 2019). Inhibition had moreover an influence on the content and the relative fractions of Pb, As, Sb, and Ba within the scales. Beyond the mass reduction a strong impact on the PbS to Pb(0) ratio was observed. The ratio PbS to Pb(0) was determined by XRD (for example see Figure 7) and estimated by a stoichiometric calculation based on concentrations of Pb and S from ICP-MS data (Figure 8). Both approaches led to consistent results.

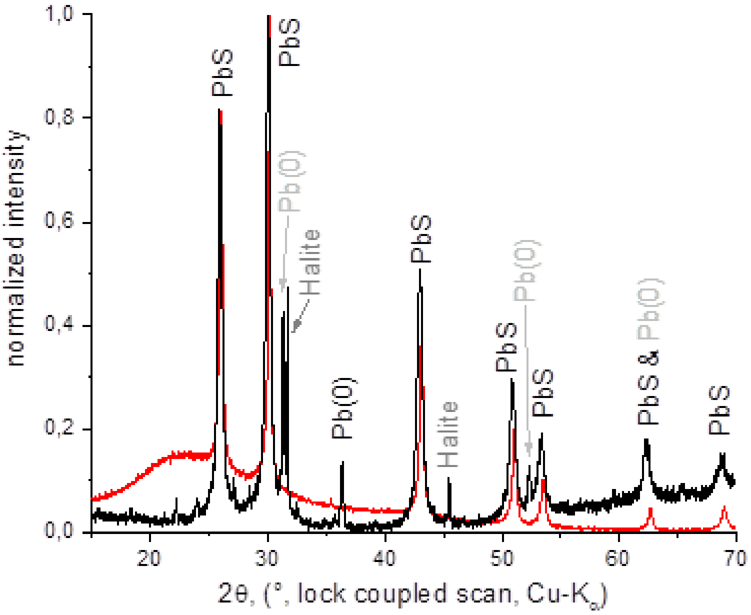

Figure 7: Exemplary powder diffraction data of scaling samples with Galena (PbS) as only mineral constitutent (red) or mixed Galena, Lead (Pb(0)), and Halite (black).

During application of the reference inhibitor (Figure 8, left) all scale samples were dominated by PbS accompanied by more or less Pb(0). The ratio PbS to Pb(0) was almost constant when a corrosion inhibitor was added. This combination of inhibition caused a slight decrease of As, Sb contents. Scales in another geothermal plant contained as well PbS, Pb(0) and As, Sb (Figure 8 right). However, the ratio PbS to Pb(0) was stronger shifted to PbS during application of the reference inhibitor (reference 2, here another phosphonate based inhibitor was applied). Due to application of different antiscalants with dispersing properties obviously more Pb(0) was detected. The addition of different corrosion inhibitors caused an increase of PbS compared to Pb(0). Concerning the other scale forming elements - Sb and As - it is obvious that their concentrations were lower than those of Pb. All inhibitors had an influence on As and only a minor effect on Sb. Moreover, for all inhibitors can be stated that Ba concentration within the scales decreased up tp 2 mass%.

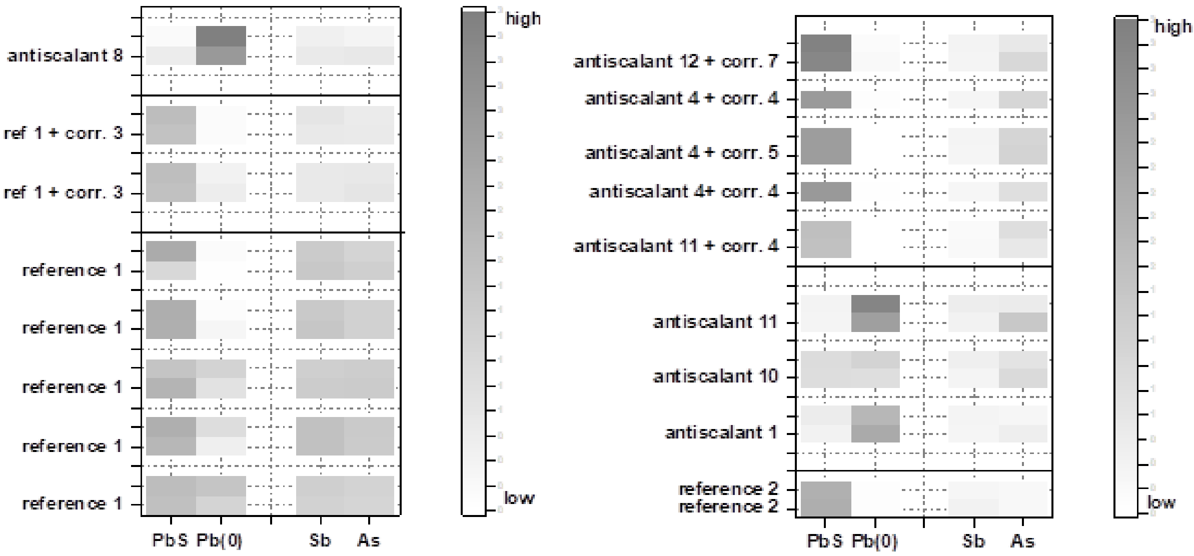

Figure 8: PbS, Pb(0), Sb, As in scales, example for two of the three investigated geothermal plants, each concentration pair refers to samples from inlet(in) and outlet (out) of the SUBITO pipe. Concentrations in µmol/kg scale. PbS and Pb(0) were calculated based on Pb and S concentration. PbS to Pb(0) ratio confirmed by XRD. Reference and reference 2 phosphonate based inhibitors. Corr. Inh. – different corrosion inhibitors, antiscalant – different antiscalants.

4. CONCLUSION

During the investigation antiscalants with dispersing properties, corrosion inhibitors, and the combination of both have been applied. A reduction of the mass of the scales by at least factor 2 compared to the reference was observed for all investigated inhibitors. Moreover, all inhibitors had an influence on the content and the relative fractions of Pb, As, Sb, and S within the scales. In more detail, antiscalants with dispersing properties mainly reduced PbS concentrations, whereas corrosion inhibitors strongly reduced the elemental lead species Pb(0). The addition of corrosion inhibitors had a slightly decreasing effect on Sb. The effect on As is ambiguous and consequently of interest for more detailed examination.

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