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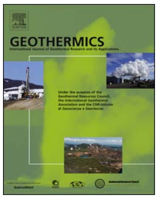

Mineralogical characterization of scalings formed in geothermal sites in the Upper Rhine Graben before and after the application of sulfate inhibitors

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ABSTRACT

Scale formation processes in the surface installations of geothermal power plants may have a negative effect on power plant performance. In addition, scales formed within the geothermal water circuit frequently accumulate natural radionuclides. Consequently, scale formation may lead to radiation dose rates, which are of radiological concern, and deposits, which may have to be disposed as radioactive waste. In order to minimize these problems and to foster geothermal power plant availability, it is of major interest to understand scale formation processes and to develop methods for their inhibition. One important pre-requisite towards this goal is a sound mineralogical and geochemical characterization of the formed material.

Geothermal brines at sites in the Upper Rhine Graben are in general highly mineralized and become, upon cooling in the heat exchanger, supersaturated with respect to sulfate solid-solutions, e.g. $(Ba,Sr)SO_4$, and other mineral phases. Some geothermal power plants very successfully tested the application of sulfate scaling inhibitors. Here we present mineralogical analyses of scale samples from geothermal power plants in the Upper Rhine Valley deposited in absence and presence of sulfate scaling inhibitors. Solid samples are investigated using wet-chemistry (after digestion), XRPD, SEM-EDX, XPS, EA-IRMS, Raman spectroscopy, and XANES (for explanation of abbreviations, see main text).

Samples of scales deposited in the absence of a sulfate scaling inhibitor mainly consist of two phases. The largest part is made up of a barite type $(Ba,Sr,Ca)SO_4$ solid-solution. Traces of Ra occurring in the scaling are assumed to be incorporated in the barite type solid solution. Further minor phases are sulfide phases, either an X-ray amorphous nano-particulate phase or galena (PbS).

Since the application of the sulfate inhibitor, sulfate minerals are no longer detectable in the scale samples. Subsequent scalings are Pb-dominated and consist mainly of galena (PbS), elemental lead (Pb), arsenic (As) and antimony (Sb). As and Sb are likely present as a nanocrystalline intermetallic mixed compound ((Sb, As) or $Pb_3(Sb,As)_2S_3$). The absence of barite-type minerals demonstrates the success of the application of the sulfate inhibitor. The precipitation of elemental Pb, As, and Sb, which are more noble than iron, may enhance the corrosion of mild steel pipes in the geothermal water circuit. Elution tests and oxidation of the scalings upon storage at atmospheric conditions demonstrate that proper disposal of the toxic heavy metal and metalloid containing scalings may be challenging.

1. Introduction

The western part of the Upper Rhine Graben (SW Germany, NE France) is a tertiary rift system showing a geothermal anomaly with a high temperature gradient and temperatures up to 130 °C at 1500 m depth (Dezayes et al., 2015). In the last decades, several geothermal projects started to access the deeper part of the reservoir. The encountered geothermal brines are highly mineralized (Sanjuan et al., 2016). Decreasing pressure and temperature at the production well and in the heat exchanger leads to mineral precipitation in the surface and

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subsurface installations of geothermal plants. Especially sulfate minerals with minor amounts of sulfides are encountered (Scheiber et al., 2014; Nitschke et al., 2014). The application of sulfate inhibitors efficiently reduces the amount of sulfate scales in the pipes. The geothermal site in Soultz-Sous-Forêts as an example, very successfully tested the application of a phosphonic acid based inhibitor (Scheiber et al., 2013; Scheiber et al., 2015). However, instead of sulfate dominated scales, ~3–5 mm thin brittle black scales are now forming at pipe walls in the surface installations, consisting of PbS, elemental Pb, As, Sb and minor oxide minerals. The deposition of sulfides and elemental lead in geothermal plants is a known phenomenon (Scheiber et al., 2013; Bressers et al., 2014). It is of concern due to the toxicity of Pb, As, and Sb, and due to the presence of ^{210}Pb and its daughter nuclides in the scales, which are consequently classified as NORM (Naturally Occurring Radioactive Material).

A detailed mineralogical and chemical characterization of the deposited material is an obligatory pre-requisite, to understand or predict the precipitation of these minerals out of the highly saline brine, and to develop tailored strategies to prevent their formation, e.g. with appropriate inhibitors. In this context this study reports detailed mineralogical and geochemical analyses based on various analytical methods, investigating six scale samples formed before and after the addition of sulfate scaling inhibitors to highly saline geothermal systems in the Upper Rhine Graben.

2. Sample origin

In the frame of this study, six scale samples (A–F) were investigated. They originate from three geothermal power plants in close proximity to each other. Samples A and B (in the following termed sulfate scalings) were collected before the application of a sulfate scaling inhibitor, the four samples C–F (in the following termed sulfide scalings) were deposited in the presence of an inhibitor. The geothermal sites in the Upper Rhine Graben and the composition of the produced geothermal brines are described in detail in (Sanjuan et al., 2016). Concerning the chemical composition of the produced brines, the geothermal plants in the Upper Rhine Graben are fairly similar. The average composition with respect to major- and scale forming ions after (Sanjuan et al., 2016) is depicted in Fig. 1.

Samples A and B originate from two different geothermal sites. Both scales were deposited inside a heat exchanger. Samples were taken after regular cleaning work from canisters containing the removed scaling material. According to γ-spectroscopic measurements the specific activity of sample A (about 1900 Bq/g) is dominated by ^{226}Ra, ^{210}Pb and ^{228}Ra (Köhler, 2013).

Samples C-F were collected at a third geothermal plant at four time intervals: sample C was taken first (t_0), sample D at t_0 + 126 days, sample E at t_0 + 253 days, and sample F at t_0 + 420 days. The samples were taken at one specific location in the water circuit from a pipe wall on the cold side (60 °C) of the heat exchanger. Two different ways of sampling and storing were chosen: 1. ambient conditions (C, D, part of E and F) and 2. under anoxic conditions (argon glove box) in order to minimize the oxidation of the samples for the purpose of assessing the oxidation state of As, Pb and Sb by means of X-ray absorption near edge spectroscopy (pieces of E and F). Samples E and F were taken two and one day after a regular shut-down of the geothermal plant, but with the pipes only emptied and opened just before sampling. They were placed in an argon bag immediately after sampling and rapidly transferred to an argon glove box, where they were stored until the XANES measurements.

3. Analytical methods

Scale samples are analyzed 1) after digestion by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Element 2, Thermo Scientific), Ion Chromatography (IC, Metrohm 930 IC Flex) for Cl measurements according to DIN EN ISO 10304-1 (D 19), and Infrared Spectroscopy (IR) for TOC measurements according to DIN EN 1484, and 2) directly in solid state by X-ray powder diffraction (XRPD, Bruker D8 Advance diffractometer), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray fluorescence measurements (SEM-EDX, FEI Quanta 650 FEG environmental SEM), X-ray photoelectron spectroscopy (XPS, ULVAC-PHI VersaProbe II), Isotope Ratio Mass Spectrometry (IRMS, IsoPrime, GV Instruments) coupled to an Elemental Analyzer (EA, HEKAtech), and Raman spectroscopy (BRUKER Senterra Raman microscope). Raman spectra were measured with depolarized laser beams at 532 nm (5 mW) and 785 nm (25 mW) excitation wavelengths, respectively. X-ray absorption near edge spectroscopy (XANES) is employed to assess the oxidation state of As (As-K edge, 11867 eV), Pb (Pb-L_{III} edge, 13035 eV) an Sb (Sb-L_{III} edge, 4132 eV) in the scale samples. XANES measurements are performed at the INE-Beamline for actinide science at ANKA (Rothe et al., 2012). XRD patterns were semi-quantitatively evaluated using the Bruker software DIFFRAC·EVA and TOPAS 4.2. For XANES data handling the IFEFFIT software package (Ravel and Newville, 2005) was used. All results reported in terms of percent refer to atom-percent or mole fractions. Thermodynamic model calculations are performed using PhreeqC 3 (Parkhurst and Appelo, 2013) and the ThermoChimie

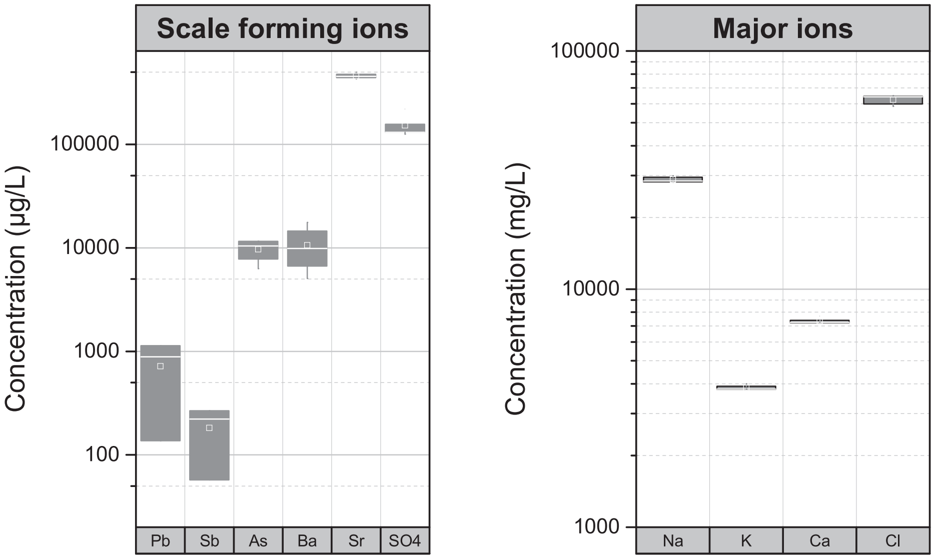

Fig. 1. Average chemical composition of the geothermal brines in the Upper Rhine Valley, with respect to scale forming and major ions (after Sanjuan et al., 2016).