UNIVERSITY OF LEEDS

This is a repository copy of *Microstructural and chemical variation in silica rich precipitates at the Hellisheidi geothermal power plant.*.

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/85779/

Version: Accepted Version

Article:

Meier, DB, Gunnlaugsson, E, Gunnarsson, I et al. (3 more authors) (2014) Microstructural and chemical variation in silica rich precipitates at the Hellisheidi geothermal power plant. Mineralogical Magazine, 78 (6). 1381 - 1389. ISSN 0026-461X

https://doi.org/10.1180/minmag.2014.078.6.04

Reuse
Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher’s website.

Takedown
If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

White Rose
university consortium
Universities of Leeds, Sheffield & York

eprints@whiterose.ac.uk
https://eprints.whiterose.ac.uk/

Microstructural and chemical variation in silica rich precipitates at the Hellisheiði geothermal power plant

D.B. MEIER[1]*, E. GUNNLAUGSSON[2], I. GUNNARSSON[2], B. JAMTVEIT[3], C.L. PEACOCK[1], L.G. BENNING[1,4]

[1]Cohen Geochemistry Group, School of Earth and Environment, University of Leeds, Leeds LS2 9JT, United Kingdom

[2]Reykjavik Energy, 110 Reykjavik, Iceland

[3]Physics of Geological Processes, Department of Geoscience, University of Oslo, 0316 Oslo, Norway

[4]GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany

*Email: eedbm@leeds.ac.uk

Abstract

Precipitation of amorphous silica (SiO_2) in geothermal power plants, although a common factor limiting the efficiency of geothermal energy production, is poorly understood and no universally applicable mitigation strategy to prevent or reduce precipitation is available. This is primarily due to the lack of understanding of the precipitation mechanism of amorphous silica in geothermal systems.

In this study we present data about microstructures and compositions of precipitates formed on scaling plates inserted at five different locations into the pipelines at the Hellisheiði power station (SW-Iceland). Precipitates on these plates formed during 6 to 8 weeks of immersion in 120 or 60°C hot, fast flowing and silica supersaturated geothermal fluids (around 800 ppm of SiO_2). Although the composition of the precipitates is fairly homogeneous, with silica being the dominant component and Fe-sulphides as a less common phase, the microstructures of the precipitates are highly variable and dependent on the location within the geothermal pipelines. The silica precipitates have grown through aggregation and precipitation of silica particles that precipitated homogeneously in the geothermal fluid. We identified 5 main factors that may control the precipitation of silica: (1) temperature, (2) fluid composition, (3) fluid flow regime, (4) distance along flow path and (5) immersion time.

On all scaling plates, a corrosion layer was found underlying the silica precipitates indicating that once formed the presence of a silica layer likely protects the steel pipe surface against further corrosion. Yet silica precipitates influence the flow of the geothermal fluids and therefore can limit the efficiency of geothermal power stations.

Introduction

In geothermal power plants around the world the polymerization of monomeric silica and the formation and deposition of amorphous silica (SiO_2) precipitates on pipes and other fluid handling systems (most often termed scaling) has been identified as one of the most common problems limiting the efficiency of geothermal power stations (Gunnarsson and Arnórsson, 2003). Although amorphous silica precipitation in natural geothermal settings has been extensively studied (e.g., Mountain et al., 2003; Tobler et al., 2008), the processes that occur at the water-fluid handling equipment interfaces (e.g., scale formation on pipes) are far less well understood. A wide range of approaches to mitigate amorphous silica scale formation, such as pH control (e.g. Fleming and Crerar, 1982, Henley, 1983, Stapleton and Weres, 2011), dilution and acidification with steam condensate (Gunnarsson and Arnórsson, 2003) or the usage of (in)organic inhibitors (e.g.

Amjad and Zuhl, 2008, Gallup, 2002, Gallup and Barcelon, 2005, Harrar et al., 1982) have been applied in various geothermal power plants. However, due to the large variations in geothermal fluid conditions, no single method for adequately mitigating silica scaling exists (Mroczek et al., 2011). One of the limits to developing a universally applicable mitigation approach is the lack of a fundamental understanding of the pathways and mechanisms of amorphous silica precipitation. This is partly due to the dearth of data on silica scale microstructures and compositions. In this study we investigated the microstructures and compositional characteristics of silica-dominated precipitates that formed in the pipes of the Hellisheiði geothermal power station in SW-Iceland.

Materials and methods

Silica precipitation was monitored using stainless steel scaling plates (5 x 2.5 cm) deployed at different points within the pipelines of the Hellisheiði geothermal power plant, but in all cases after the steam used for the production of electrical energy was separated (Fig. 1). The chemical composition and pH of the separated water at sampling point 1 is monitored at regular intervals by the power plant operators. The separated water is cooled and filtered before the pH is measured and sample aliquots are taken for the different analyses. For details of sample preservation and sampling containers see Arnorsson et al. (2006). The cations were analysed by ion chromatography (IC) at Reykjavik Energy while the anions were analysed by ICP-MS at the University of Iceland. The concentration of H_2S is measured by titration with mercury acetate using dithizone as an indicator (Arnorsson et al., 2006).

The plates were inserted into the path of the flowing geothermal fluid for 6 (plates 2, 3 and 4) or 8 weeks (plates 1 and 5). After removal from the separated water, the plates were first dried at room temperature on-site, and, after shipping to Leeds, they were again dried at 30°C for 24h before further analysis.

From one side of each plate some precipitates were scraped off using a plastic spatula and ground up using an agate mortar and pestle. The powder was analysed by X-ray diffraction using a Bruker D8 diffractometer (XRD, $CuK\alpha_1$; 2θ 5 – 90°; 0.01°/step) and the patterns were evaluated using the EVA software (Bruker, Version 3.0). The other side of the plates was coated with around 40 nm of gold and imaged using a field emission scanning electron microscope (FEG SEM, FEI Quanta 650 at 20 keV). Spot analyses and elemental mapping were performed using an energy dispersive spectrometer (EDS) and the AZtec software (Oxford Instruments, Version 2.2).

Results

The separated water from which precipitation occurred is a dilute, low ionic strength fluid with a high concentration of dissolved H_2S and a pH varying between 9.1 and 9.4 (Table 1). Depending on which production well is used, the waters contain between 700 and 800 ppm SiO_2 (Table 1). No data is currently available about solution compositions at the other sampling points.

After 6 to 8 weeks of immersion, all scaling plates showed visible signs of precipitation. Although the XRD analyses revealed silica as the dominant precipitate in all cases, the microstructures of the precipitates were highly variable (Fig. 2). Precipitation onto plate 1 occurred at 120°C due to its position directly before the heat exchanger (Fig. 1). The precipitates formed large (up to 1-2 mm) fan-shaped structures pointing towards the direction of the flow (Fig. 2 and 3A). The fans were composed of silica particles (~1-20 μm in diameter; Fig. 3F), while the rest of the plate was covered by individual silica spheres or idiomorphic Fe-sulphides (Fig. 4C). The precipitates on plate 2 formed immediately after the heat exchanger (Fig. 1) at 60°C. They formed wave-shaped structures, oriented parallel to the flow (Fig. 2), again composed of larger, weakly aggregated silica spheres. These were overlying a film of smaller silica particles forming aggregates up to 50 μm (Fig. 3B). Plate 3 was located immediately before mixing the geothermal fluid with steam condensate fluid (Fig. 1), and was characterised by the least amount of silica precipitates (Fig. 2 and 3C). The precipitates on plate 4 consisted of individual or connected flakes of a dark grey precipitate (Fig. 2 and 3D), which was composed of very small (< 1 μm) angular Fe-sulphide aggregates and (0.1 μm) spherical silica particles (Fig. 3D; XRD results revealed mackinawite, greigite and pyrrhotite). The metal between the flakes was covered by spherical silica particles (0.1 to 0.5 μm in size) and idiomorphic, columnar sulphur crystals several micrometres in length. Plate 5 was characterised by the highest amount of precipitates and was densely covered by grey, ridge-shapes, oriented perpendicular to the flow (Fig. 2). These ridges (Fig. 3E) were composed of individual, small silica spheres (0.1 to 0.5 μm) that occasionally were interspersed with larger, smooth silica particles (up to 10 μm in diameter).

Along the rim of some plates, a clear morphological (Fig. 4A) and compositional (Fig. 5) layering was revealed. Underlying the silica precipitates (Fig. 4B and Fig. 5) was a layer composed of fine-grained, often idiomorphic Fe-sulphides (Fig. 4C and Fig. 5). In some areas even the corrosion of the stainless steel plates was observed in the form of rosette-shaped Fe-oxides (Fig. 4D). Based on the shape of the mineral phase, this was most likely hematite. Due to the small amount of these Fe-sulphides and Fe-oxides on the plates, a definitive mineralogical identification or quantification was not feasible.

Discussion

The results from our study of precipitates formed on scaling plates immersed in the fast flowing geothermal waters in the pipes of the Hellisheiði geothermal power station revealed that the microstructures and compositions of precipitates varied considerably along the flow path. Distinct microstructures that span from fan-shaped to wave-like to individual flakes or even ridge-shaped precipitates were observed. The dominant phases present on the scaling plates were amorphous silica, Fe-sulphides and rarely Fe-oxides. Silica was present as spherical nanoparticles, which form by homogeneous nucleation (Tobler et al., 2009, Tobler et al., 2013) from the supersaturated geothermal fluids that contained around 800 ppm of silica. Our data indicate that once the particles that form in solution come into contact with the scaling plates (or for that matter the pipe surfaces) they are deposited. Monomeric silica will also continuously polymerise, cementing the particles together to form larger and larger clusters (Angcoy and Arnorsson, 2010). The iron phases (Fe-sulphides and Fe-oxides) largely represent corrosion products. The Fe could be sourced either from the plates or pipes themselves or from the geothermal fluid and when combined with H_2S from the geothermal fluid they would precipitate as Fe-sulphides, and upon oxidation likely transform to Fe-oxides.

The observed variations in composition and microstructures are the result of differences in physico-chemical conditions in the power plant pipelines. Although our data so far cannot fully explain all observations, we have identified five parameters that all play a crucial role in controlling the precipitation regimes and modes of amorphous silica deposition on our scaling plates. These are:

(1) Variation in temperature: An increase in temperature results in faster polymerisation rates of monomeric silica and hence an increased rate of amorphous silica nanoparticle formation (e.g. Alexander, 1954, Kitahara, 1960, Tobler et al., 2013). At higher temperatures this effect could be counterbalanced by the higher solubility of amorphous silica and the resulting decrease in supersaturation (Gunnarsson and Arnórsson, 2000, Makrides et al., 1980).

(2) Variation in fluid composition: The composition of the geothermal fluid is crucial for the composition of the phases formed on the scaling plates. For example the dominant phases on plate 4, which formed immediately after the addition of steam condensate to the geothermal fluid (Fig 1.), were Fe-sulphides. In this case, the precipitation of Fe-sulphides was enhanced locally because of the mixing with steam condensate. The concentration of dissolved iron in the steam condensate is marginally higher than in the separated water (personal communication from power plant operators). Hence, when the Fe-rich steam condensate mixes with the H_2S from the geothermal fluid this may result in the very fast precipitation of Fe-

sulphides. The addition of condensate also decreased the concentration of silica and dilutes the geothermal fluid. Lower supersaturation of silica combined with reduced ionic strength of the geothermal fluid results in slower precipitation of silica (Fleming, 1986, Icopini et al., 2005). This may in part explain the smaller amount of amorphous silica on plate 4 compared to all the other plates.

(3) Fluid flow regime: Fan shaped structures like those on plate 1 have recently been modelled by Hawkins et al. (2014). The authors used fluid dymanic modelling approaches and simulated the surface growth processes in a geothermal pipeline in the presence of nonhomogeneous and nonlaminar flow. They found that the competition between advection and diffusion (Péclet number) and the turbulence characteristics (Reynolds number) define the exact geometry of the precipitates. The microstructures found on plate 1 (Fig. 2 and 3a) are matched by the modelling results thus confirming that fluid flow indeed plays a dominant role. However, why this microstructure was only observed on plate 1 (120˚C, before heat exchanger) is not yet clear and further, time resolved immersion experiments that are in progress hope to address this.

(4) Distance along flow path: The precipitation of silica is affected by the distance between a spot, where the physico-chemical conditions in the power plant pipelines change drastically and the location of the scaling plate. An example is the effect of cooling the geothermal fluid from 120˚C to 60˚C in the heat exchanger: This temperature drop affects the polymerisation rate and it has been shown that it may take up to 3 hours to

reach steady state again (Tobler et al., 2013). Hence, the precipitation conditions where plate 2 is located are different from the conditions further downstream where plate 3 is located. Another example are the differences between plate 4 and plate 5. The addition of steam condensate enhances precipitation of Fe-sulphides (see above) onto plate 4. As plate 5 is located several hundred meters further downstream, the geothermal fluid at plate 5 had more time to react to the physico-chemical disturbance and re-equilibrate. Thus at plate 5 amorphous silica becomes again the prime precipitate

(5) Immersion time: The amount of time the scaling plates are immersed in the geothermal fluid will have an effect on the amount of precipitates and probably on the microstructures formed. In this study, we only studied the precipitation after 6 to 8 weeks but precipitation has been monitored since commissioning of the Hellisheiði power station in 2006. However, the rates of precipitation are not known. Thus in order to investigate precipitation and the evolution of microstructures as a function of time, additional time resolved experiments are in progress.

Despite our detailed evaluation of the microstructures and compositions of the precipitates on the individual plates, the exact contribution of the individual factors mentioned above remains unclear.

All precipitates were made up of different layers (Fig. 4 and 5): (1) the stainless steel metal plate that in some cases was partly oxidised to Fe-oxides, (2) the corrosion layer composed primarily of Fe-sulphides and (3) the main precipitation layer dominantly composed of spherical amorphous silica and, in the case of plate 1 and 4, Fe-sulphides. The precipitation of amorphous silica (and Fe-sulphides on plate 4), the corrosion of the plates and the related formation of Fe-sulphides are likely concurrent processes starting both as soon as the plates are immersed in the geothermal fluids. However, the Fe-sulphide corrosion layer was in most cases concealed under the silica precipitates, suggestion that before a protective amorphous silica layer could form, metal corrosion dominated. Once the precipitation layer became more continuous, further corrosion was passivated or at least slowed down by the amorphous silica (and Fe-sulphides on plate 4) layer. Thus, on the one hand, the precipitation of amorphous silica is indeed limiting the efficiency of geothermal power production by reducing the flow of the geothermal fluid through the system (Gunnarsson and Arnórsson, 2003) but, on the other hand, its deposition in thin, variable structured layers helps limit the corrosion of the steel pipes. To explore this passivation effect, a longer-term (12 month) time-resolved scaling plate exposure study is already underway.

Conclusion

Our results provide the first detailed description of silica-rich precipitates in pipes from the Hellisheiði power station. The microstructure and composition of the precipitates vary considerably depending on the ambient physico-chemical conditions in the power plant pipelines. However, exactly how and why particular physico-chemical conditions lead to a variety of microstructures in the silica precipitates is still unclear. Nevertheless, this study presents important findings which, combined with fluid chemical data, information about fluid flow and longer term scaling plate immersion experiments, will allow us to derive the first comprehensive model for silica precipitation in geothermal systems and this information will potentially help reduce silica scaling in geothermal power plants.

Acknowledgments

The authors would like to acknowledge the help of the staff at the Hellisheiði power station, especially Einar Örn Thrastarson, for their support with emplacing and removing the scaling plates from the pipes. The authors are also thankful to Richard Walshaw and Lesley Neve, University of Leeds, for their assistance with SEM and XRD analyses, respectively. Comments by several members of the Cohen Geochemistry group at Leeds, by Thomas Rinder (Associate Editor Mineralogical Magazine for this special issue) and three anonymous reviewers have greatly helped improve this manuscript. This research was made possible by a Marie Curie grant from the European Commission in the framework of the MINSC ITN (Initial Training Research network), Project number 290040.

References

Alexander, G. (1954) The polymerization of monosilicic acid. Journal of the American Chemical Society, **76**, 2094-2096.

Amjad, Z. and Zuhl, R. (2008) An evaluation of silica scale control additives for industrial water systems. Paper No. 08368, CORROSION Conference & Expo, NACE International, Houston TX, USA.

Angcoy, E. and Arnorsson, S. (2010) An Experiment on Monomeric and Polymeric Silica Precipitation Rates from Supersaturated Solutions. Proceedings of the World Geothermal Congress, Bali, Indonesia.

Arnórsson, S., Bjarnason, J. Ö., Giroud, N., Gunnarsson, I., & Stefánsson, A. (2006) Sampling and analysis of geothermal fluids. Geofluids, **6(3)**, 203-216.

Fleming, B. and Crerar, D. (1982) Silicic acid ionization and calculation of silica solubility at elevated temperature and pH application to geothermal fluid processing and reinjection. Geothermics, **11,** 15-29.

Fleming, B. A. (1986) Kinetics of reaction between silicic acid and amorphous silica surfaces in NaCl solutions. Journal of Colloid and Interface Science, **110**, 40-64.

Gallup, D. L. (2002) Investigations of organic inhibitors for silica scale control in geothermal brines. Geothermics, **31,** 415-430.

Gallup, D. L. and Barcelon, E. (2005) Investigations of organic inhibitors for silica scale control from geothermal brines–II. Geothermics, **34,** 756-771.

Gunnarsson, I. and Arnorsson, S. (2000) Amorphous silica solubility and the thermodynamic properties of $H_4SiO_4°$ in the range of 0° to 350° C at P_{sat}. Geochimica et Cosmochimica Acta, **64,** 2295-2307.

Gunnarsson, I. and Arnorsson, S. (2003) Silica scaling: The main obstacle in efficient use of high-temperature geothermal fluids. International Geothermal Conference, Reykjavik, Iceland, 30-36.

Harrar, J., Locke, F., Otto Jr., C.H., Lorensen, L., Monaco, S. and Frey, W. (1982) Field tests of organic additives for scale control at the Salton Sea geothermal field. Old SPE Journal, **22,** 17-27.

Hawkins, C., Angheluta, L. and Jamtveit, B. (2014) Hydrodynamic shadowing effect during precipitation of dendrites in channel flow. Physical Review E, **89,** 022402.

Henley, R. (1983) pH and silica scaling control in geothermal field development. Geothermics, **12,** 307-321.

Icopini, G. A., Brantley, S. L. and Heaney, P. J. (2005) Kinetics of silica oligomerization and nanocolloid formation as a function of pH and ionic strength at 25 C. Geochimica et Cosmochimica Acta, **69**, 293-303.

Kitahara, S. (1960) The polymerization of silicic acid obtained by the hydrothermal treatment of quartz and the solubility of amorphous silica. The Review of Physical Chememistry of Japan, **30**, 131-137.

Makrides, A. C., Turner, M. and Slaughter, J. (1980) Condensation of silica from supersaturated silicic acid solutions. Journal of Colloid and Interface Science, **73**, 345-367.

Mountain B. W., Benning L. G., and Boerema J. (2003) Experimental Studies on New Zealand Hot Spring Sinters: Rates of Growth and Textural Development. Canadian Journal of Earth Sciences, **40**, 1643-1667.

Mroczek, E., Graham, D. and Bacon, L. (2011) Silica Deposition Experiments: Past Work and Future Research Directions. Proceedings International Workshop on Mineral Scaling in Geothermal Environments, Manila, Philippines. 51-58.

Stapleton, M. and Weres, O. (2011) Recent Developments in Geothermal Scale Control. Proceedings International Workshop on Mineral Scaling in Geothermal Environments, Manila, Philippines. 69-76.

Tobler, D. J., Stefansson, A. and Benning L.G. (2008) In-situ grown silica sinters in Icelandic geothermal areas. Geobiology, **6,** 481-502.

Tobler, D. J., Shaw, S. and Benning, L.G. (2009) Quantification of initial steps of nucleation and growth of silica nanoparticles: An in-situ SAXS and DLS study. Geochimica et Cosmochimica Acta, **73,** 5377-5393.

Tobler, D. J., Shaw, S. and Benning, L.G. (2013) The in-situ and time resolved nucleation and growth of silica nanoparticles under simulated geothermal conditions. Geochimica et Cosmochimica Acta, **144**, 156-168.

Table 1. Chemical composition of the separated water at sampling location 1 (Fig. 1; before the heat exchanger, 120 °C). Data represent average values of measurements between September 2012 and January 2014 (n = 4). The variations in pH and concentration are due to the use of different production wells, tapping different parts of the aquifer, at different points in time.

Fig. 1. System schematic of the Hellisheiði geothermal power station indicating the five points where the scaling plates were immersed (marked by stars). The geothermal fluid at depth being at up to 300°C is flowing up through production wells. In the steam separator the pressure is released and the geothermal fluid boils, separating the steam (used for the production of electrical energy) from the fluid. The remaining geothermal fluid (also called separated water) is passed through a heat exchanger where it heats up cold groundwater to be used for space heating. Some tens of meters further along the flow path, the geothermal fluid is mixed with steam condensate to dilute it before re-injecting some hundreds of meters further downstream (full details and schematics of the processes happening in a geothermal power plant are available at http://www.or.is/vinnsluras).

Fig. 2. Photographs of the scaling plates after immersion in the geothermal fluid for 6 (plates 2,3 and 4) and 8 weeks (plate 1 and 5) respectively.. The precipitates on each plate show distinct microstructures from fan-shaped (1) to wave-like (2) to thin films (3) and to dark flakes (4) or even ridge-shaped (5) precipitates.

Fig. 3. FEG-SEM images showing the different microstructure of the precipitates on the scaling plates. The microstructures on plate 1 (A), plate 2 (B), plate 3 (C) and plate 5 (E) are formed by the aggregation of silica particles (F). On plate 4 (D) the precipitates are dominated by Fe-sulphides.

Fig. 4. (A) Different layers at the edge of plate 5 showing the top layer composed of amorphous silica spheres, aggregated to form delicate structures (B). The silica layer covers a layer of Fe sulphides (C) most likely a corrosion product of the scaling plate while underneath this layer the metal of the scaling plate (D) was oxidised to Fe-oxides.

Fig. 5. Elemental maps of the layers on plate 5 described in Fig. 4 with the top precipitation layer showing primarily Si that overlies the Fe-sulphide layer (Fe and S maps) and the metal plate (Fe map). Dark areas on the Au map indicate areas where the topography of the sample resulted in a poor EDS signal. These areas will be dark in all elemental maps.