Sulfide Scales Downhole in Well RN-22 Reykjanes High-temperature Area

Vigdís Hardardóttir^{1,*} and Nicole Hurtig² ¹ÍSOR Grensásvegur 9 108 Reykjavík, Iceland

²Colorado School of Mines, Dept. of Geology and Geol. Engineering, 1516 Illinois St., 80401 Golden, CO, USA

*corresponding author: vh@os.is

Keywords: Sulfides, scale, downhole, Reykjanes, high-temperature, pipelinesIceland, geothermal

ABSTRACT

Reykjanes is a high-temperature (270-310°C) seawater dominated geothermal area located on the southern tip of the Reykjanes peninsula SW-Iceland where the Atlantic Ridge comes on shore. Between 2006 and 2013, output maximum capacity dropped from 14 to 2 MWe in well RN22 as a result of scale formation and a decrease in pressure. Several attempts were made to clean the well from scales. Early attempts only reached down to a depth of ~670 m and showed relatively minor scaling. In 2013, scales were collected from the liner at 679–1647 m depth. Significant scales formed at a depth of ~1100 m depth where boiling is intense. Material collected from the bottom of the pipe is mainly composed of rounded fragments of sulfides, clusters of sulfides, mainly sphalerite, and rounded rock samples indicating that the material had fallen from the liner above. The material collected from the bottom of the pipe (liner, No. 79) amounts to ~0.48 m³, i.e. ~2000 kg. Calculated from the volume of the scales in the pipelines the thickness is ~1 mm if spread evenly over the 1100 m casing string. However, scales precipitated most where the boiling is intense (~1100 m depth), and in areas where pressure decreases. Another possibility is also intense precipitation of sulfides in the host-rock where the main feed points at ~1100 m are in the well. The GEM-selektor numerical simulation package was used to estimate the amount of minerals that can precipitate from the cooling ascending fluid and complement observations from well RN-22. Numerical simulations of cooling and decompression followed the PT fluid pathway observed at well RN-22 (320°C and 120 bar to 220°C and 23 bar) using an average downhole fluid composition. The equilibrated downhole fluid precipitates bornite, chalcopyrite and sphalerite upon cooling and decompression. Below 250°C and 38 bar, sulfide precipitation increases by one order of magnitude, which corresponds to observations from well RN-22. A total amount of to 0.86 g sulfides precipitate per 100 kg fluid. Mass balance calculations were used to scale the numerical simulations in terms of potential kilograms which can precipitate during geothermal energy production. In 2006 and 2007, production was at 1.9 and 3.1 M tones of water. Based on these production numbers and numerical simulations using the average downhole fluid we calculated that potential sulfide precipitation (16000-26000 kg) might be an order of magnitude higher than material collected in pipe No. 79.

1. INTRODUCTION

Variety of scale problems are associated with brine or seawater dominated geothermal systems such as reservoir formation plugging, well and line plugging, resulting in reduced steam-brine flow in production wells. Seawater dominated geothermal systems are affected by scaling problems include the Cerro Prieto field in Mexico (Ocampo-Diaz et al., 2005; Dean et al., 1992; Hurtado and Mercado, 1990), the Fushime field in Kyushu Japan (Akaku, 1990; Akaku and Yagt, 1988; Akaku and Nakatsuka, 2001) and the Reykjanes field in Iceland (Hardardóttir, 2011; Hardardóttir et al., 2010). Similar scaling problems are also observed at Ohaaki-Broadland in New Zealand (Simmons and Browne, 2000; Brown and Simmons, 2003), where fluids are less saline and at Salton Sea in USA, where fluids have a much higher salinity (Skinner et al., 1967; McKibben and Elders, 1985). The scales are of various compositions depending on their location and may even vary within the geothermal area. Calcite, amorphous silica, Fe-, Mg-, Ca-, Zn-silicates and sulfide phases are well known precipitates forming in Cerro Prieto, while the dominant scale in Fushime field is amorphous silica and galena. Predominant scale in Reykjanes is sphalerite, with minor chalcopyrite, and bornite at temperature > 220°C and galena together with amorphous silica at lower temperature (<219°C). In general, fluid composition is variable within geothermal areas, therefore scaling problems may vary between wells and geothermal fields. Here, we use numerical simulation to understand the processes resulting in sulfide precipitation and the amount of sulfides which precipitate from solution. We also use mass balance calculations to estimate potential kilograms of sulfides which can precipitate.

2. REYKJANES GEOTHERMAL SYSTEM

Reykjanes is a high-temperature (270-310°C) seawater-dominated geothermal area which is located on the southern tip of the Reykjanes peninsula SW-Iceland where the Atlantic Ridge comes on shore (Fig.1). The Peninsula is constructed solely of volcanic rocks of both glacial and interglacial age as well as post-glacial lava flows (Jónsson, 1978; Sæmundsson et al., 2010). The volcanic rocks are of basaltic composition, ranging from picrite shield lavas through olivine tholeite shield lavas and fissure products with no intermediate or rhyolitic rocks. Surface manifestations of geothermal activity cover about 2 km² and are warm to hot ground, mud pools, steam vents, and hot springs.

The stratigraphy of the Reykjanes system is based on cuttings sampled at 2 m intervals during drilling. The main lithologies consist of hyaloclastite and breccias of reworked tuffaceous sediments to 1000 m depth interbedded with basaltic lava flows, and pillow basalts at greater depths (Björnsson et al., 1972a, b; Tómasson and Kristmannsdóttir, 1972; Franzson et al., 2002; Franzson, 2004). Some volcanic sedimentary horizons contain fragments of marine fossils (Richter et al., 2003; Jónsson et al., 2003). Dykes are common below ~1000 m depth and increase in abundance with depth. Franzson et al. (2002) and Franzson (2004) built a conceptual model of the volcanic stratigraphy. Below ~1200 m depth, the rocks consist largely of pillow basalt formed by submarine volcanic eruptions. As the depth of volcanic effusion became shallower, (i.e. lower pressure), gas exsolution in the magma increased and caused explosive reaction with the seawater, causing brecciation and formation of volcaniclastic material. Subsequent deposition of

shallow marine volcaniclastic sedimentary horizons occurred, as indicated by the marine fossil fragments. The sequence is capped by pillow basalts and subaerial basalt flows of post-glacial age (<120 m depth).

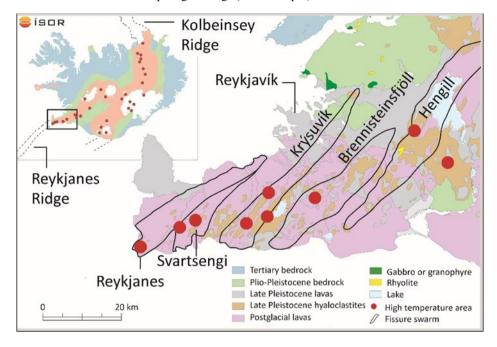


Figure 1: Geology map of Reykjanes Peninsula. Iceland in the inset showing the location of the Reykjanes Peninsula (modified from Sæmundsson et al., 2010).

The reservoir liquid in the Reykjanes high-temperature geothermal system has a salinity (NaCl \sim 3.2 wt%) like seawater (3.5 wt%), with a well inflow temperature between 275°C to 315° and a calculated pH of \sim 5.3 (Björnsson et al., 1972b; Bjarnason, 2002). As shown by Seyfried and Bischoff (1977), in seafloor hydrothermal systems (black smokers on the seafloor) and at Reykjanes, reaction of the heated seawater with the surrounding basalt results in removal of most of the SO₄-2 and Mg from the hydrothermal fluid and increases the concentrations of SiO₂, K and Ca compared to seawater (Björnsson et al., 1972b; Arnórsson, 1978; Kristmannsdóttir, 1984). Hardardóttir et al. (2009) collected fluids from 1350 to 1500 m depth from three wells in 2007 (RN-12, RN-19, RN-21). The average fluid composition is shown in Table 1. A liquid of essentially constant composition is thought to feed all the wells at Reykjanes. The composition of dissolved gases of this fluid is calculated based on the composition of surface-sampled liquids, corrected for vapor loss (Arnórsson et al., 1982; Henley et al., 1984; Bjarnason, 2002). The composition of dissolved elements such as Al, Si, Ca, K and metals (Cu, Zn, Pb, Ag and Au) were directly measured downhole at 1500 m depth (Table 1; Hardardóttir et al., 2009). The very low metal contents in the fluids sampled at the surface are interpreted to reflect deposition of metals during fluid ascent and boiling, based on the orders of magnitude higher metal concentrations measured in downhole samples. The liquids collected at 1350–1500 m depth and 284–295°C, contain 9–140 ppm Fe (154–2431 µM), 14–17 ppm Cu (207–261 µM), 5–27 ppm Zn (79–393 µM), 120–290 ppb Pb (0.6–1.4 µM), 1–6 ppb Au (6–31 nM) and 28–107 ppb Ag (250–960 nM).

2.1 Well RN-22 - background

Drilling of well RN-22 was completed in January 2006 down to 1680 m measured depth. The well has surface casing down to 74 m ($22\frac{1}{2}$ "), anchor casing down to 283 m ($18\frac{4}{8}$ "), production casing down to 720 m ($13\frac{3}{8}$ ") and a perforated/slotted liner from 679–1647 m. The well is directional, and the aim was to intersect the main up-flow reservoir, located below the Gunnuhver area (hot spring, Fig. 2). Steam feed zones are visible at 1100-1200 m depth and minor liquid feed zone at 1600 m depth (Mortensen et al. 2008; Sigurdsson, 2012).

Up on connection of RN-22 to the power plant in 2006, initial maximum output capacity was \sim 14 MWe with a longer-term capacity of \sim 10 MWe (Sigurdsson, 2012). The average wellhead pressure was 37.5 bar in the period 2006-2007 (Hardardóttir, 2014a, b). The output declined rather rapidly until early 2009 and since the pressure decline. Consequently, the well output has been more gradual with an estimated output of 2 MWe in May 2011 (Sigurdsson, 2012). In 2009, attempts were made to clean the well from scaling. However, the available drill string was not long enough to reach down to greater depth than \sim 670 m. The average wellhead pressure in 2009 was 28.3 bar (Hardardottir, 2011). Some scales were collected downhole in 2009 (see below). In May 2011, the well was disconnected from the power plant and a renewed attempt was made to clean well scaling. A third attempt to clean the well of scale was made in April 2013 by pulling out the liner revealing that nearly all the scale was found in the bottom part of the liner at the bottom of the well.

Table 1: Composition of surface fluids from RN-22, average composition of fluids collected at \sim 1500 m depth at Reykjanes and seawater.

			average at ~ 1500 m	
	RN-22	RN-22	depth ⁽¹⁾	Seawater (2)
Date	2006-11-15	2011-12-07	2007	
P at sampling bar	41.3	26		1
T at sampling [°C]	251	224	290	2
Fluid				
pH/°C	5.79/21.2	5.94/22.6	$4.7^{(3)}$	4-3.8
CO ₂ [ppm]	18.6	10	892(3)	101
H ₂ S [ppm]	4.76	0.7	89(3)	nd
NH ₃ [ppm]	1.55	1.31	$1.83^{(3)}$	na
B [ppm]	10	9.3	8	4.4
Ba [ppm]	12.4	12.1	11	0.02
SiO ₂ [ppm]	719.2	693	665	6
Na [ppm]	11777	11950	9390	10770
K [ppm]	1732	1750	1582	380
Mg [ppm]	1.83	1.65	5	1290
Ca [ppm]	2027	2000	1843	412
F [ppm]	0.23	0.21	$0.18^{(3)}$	1.3
Cl [ppm]	23100	23900	19166	19500
SO ₄ [ppm]	18.7	25.2	18.23 ⁽³⁾	2712
Al [ppm]	0.118	0.101	1.54	0.0004
As [ppb]	37.3	13.4	128	3.7
Co [ppb]	< 0.05	0.094	2	0.003
Cr [ppb]	0.792	0.692	59	0.3
Cu [ppb]	< 0.5	< 0.5	14884	0.0001
Fe [ppb]	1640	552	58000	0.055
Mn [ppb]	3080	1600	3000	0.0001
Mo [ppb]	2.14	22.1	21	10
Ni [ppb]	1.99	20.3	307	0.48
Pb [ppb]	1.81	< 0.3	234	0.003
Sr [ppb]	11500	11300	9390	8
Zn [ppb]	61.6	40.4	14971	0.5
TDS [ppm]	43250	40820	na	na
Gas				
CO ₂ [ppm]	8250	5140	na	na
H ₂ S [ppm]	339	170	na	na

⁽¹⁾ concentrations unnumbered are from Hardardóttir et al., (2009), (2) Bearman (1989), (3) calculated from WATCH2.4 see text; na: not analyzed; nd: not detected.

2.1.1 Scales in RN-22

Scales were collected during various maintenance brakes and efforts were made to increase production output of well RN-22. Detailed descriptions of the scales collected in 2007, 2011 and 2013 are summarized in Hardardóttir (2011, 2014a, b, Table 2). Here, we provide a brief overview of the different scales collected during the course of this study.

At the maintenance brake in 2007, the surface pipelines upstream of the orifice plate were coated by sulfides scales composed of mainly sphalerite, minor chalcopyrite and bornite and traces of galena. The pipelines downstream of the orifice plate, where the pressure drops to 22 bar, were heavily clogged by predominantly sphalerite (Fig. 3).

In 2009, the scales were collected from depths of 141 to 669 m. The most abundant mineral (90%) was sphalerite followed by chalcopyrite. Magnetite is found in the upper part and decreases with depth until it is hardly seen in the deepest sample. Wurtzite is identified in the upper samples and its occurrence increases with depth. Similarly, chalcopyrite abundance also increases with depth. Hematite and pyrite are observed and bornite is seen in the top part of the well scaling.

X-ray diffraction of downhole scales collected in September 2011 revealed hematite and magnetite with a bulk composition of 90% oxides (Fe and Ca). The sample is probably a drill lube with trace of sulfides (Zn, Cu, Pb).

The scales from the workover in April/May 2013 were located nearly entirety in the bottom liner pipe (No. 79) \sim 12.7 m long at \sim 1634–1647 m depth. Traces of scales were also seen in other locations (1051 m, 1064 m, 1076 m, 1088 m, 1586 m 1610 m 1647 m) and consisted of clinochlore, sphalerite/wurtzite, magnetite, pyrite and chalcopyrite identified by XRD. The scale accumulated in pipe No. 79 are composed primarily of sulfides, mainly sphalerite with minor amount of rock fragments and flakes of metals originating from the liner string above. Chalcopyrite and pyrite are also found (Table 2, Hardardóttir, 2014a).

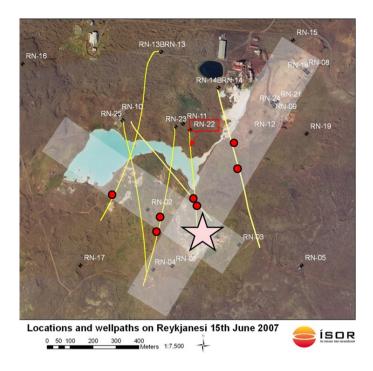


Figure 2. Locations of drillholes at Reykjanes, as of June 2007. Yellow lines show the traces of deviated wells. Two main upflow zones are indicated by the shaded quadrangles, and the star represents the principal focus of upflow at Gunnuhver hot spring Red dots are locations of the major inflow zones of the deviated wells projected to the surface (from Hardardóttir 2011).



Figure 3: Well RN-22 downstream of the orifice plate, at the maintenance brake in 2007; pipeline is heavily clogged by mainly sphalerite.

Table 2: Scales precipitated in well RN-22 Reykjanes.

Mineral	Chemical name	Mineral	Chemical name
Sphalerite	(Fe,Zn)S	Amorphous silica	SiO_2
Wurtziate	(Fe,Zn)S	Magnetite	Fe_3O_4
Chalcopyrite	$CuFeS_2$	Hematite	Fe_2O_3
Bornite	Cu ₅ FeS ₄	Clinochlore	clay mineral
Galena	PbS		
Pyrite	FeS ₂		

3 METHODS

The geochemical simulations of the behavior of RN-22 fluid was carried out using GEM-Selektor v.3.5 (http://gems.web.psi.ch/GEMS3/), which is based on the Gibbs energy minimization method (Karpov et al., 2002, 2001; Kulik et al., 2013). We thermodynamically model the precipitation of sulfides during cooling and decompression in well RN-22 to quantify sulfide well scaling.

References to the thermodynamic data sets for minerals, aqueous species and gases used in the numerical simulations are summarized in the Mines2018 database (Gysi, 2017; http://tdb.mines.edu/). The activity models and equations of state are summarized in the TSolMod library class (Wagner et al., 2012) implemented in GEM-Selektor. The reference state is 25 °C and 1 bar. The standard state for all solids was that of a pure phase and for gases was that of an ideal gas at 1 bar. The PVT properties of the major gases were determined using the Peng-Robinson-Stryjek-Vera (PRSV) equation of state assuming ideal mixing. The activity model used for aqueous species was the extended Debye-Hueckel equation with NaCl as the background electrolyte and extended term parameters calibrated for the NaCl-KCl-NaOH-KOH system. Thermodynamic properties of aqueous species were corrected for pressure and temperature using the revised Helgeson-Kirkam-Flowers (HKF) equation of state or fitted to new experimental data using logarithmic equilibrium constants and implemented in to the GEMS Mines2018 database. A sub-regular solid-solution model for Au-Ag alloys (White et al., 1957) was introduced as user-defined temperature-dependent equations for calculating the activity coefficients of Au and Ag in electrum.

3.1 Simulation set-up

We present two types of simulations: 1) system equilibrium calculations at elevated temperature and pressure to calculate a thermodynamically stable fluid using the measured composition of RN-22 fluid sampled at depth (Table 3, EQ-Fluid) the flushing model, which cools and decompresses this high PT-fluid for quantifying sulfide precipitation (Fig. 4). The PT-fluid pathway (Fig. 4) was modeled after measured temperatures and pressures in well RN-22. The fluid starts out as a single-phase fluid at the bottom of the well, which cools and decompresses upon ascent starting to boil around 270°C at 1100 m depth. The fluid further cools and decompresses along the saturation water vapor pressure curve to temperature 220°C and a pressure of ~23 bar at the well head.

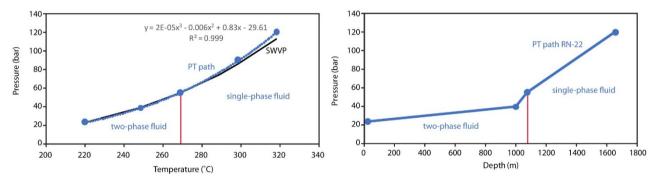


Figure 4: a) Left. PT-path for well RN-22, which is used for the flushing model, the fluid enters the two-phase field at ~270°C. SWVP = saturation water vapor pressure. b) Right. Pressure plotted as a function of depth showing data points for well RN-22 used to build the PT-path.

Table 3: Starting conditions

Element	EQ-FL ^a	RN-Fluid ^b	%°
Al [ppm]	0.0002	1.54	0
C [ppm]	144	243	59
Ca [ppm]	1825	1843	99
Cl [ppm]	19381	19166	101
F [ppm]	0.74	0.18	404
Fe [ppm]	12.4	58.3	21
K [ppm]	1593	1582	101
Mg [ppm]	5.28	5.42	97
Na [ppm]	9487	9390	101
S [ppm]	76.3	92.9	82
Si [ppm]	268	310	86
Ag [ppb]	57.1	57.2	100
Au [ppb]	0.36	3.03	12
Cu [ppb]	1809	14884	12
Mo [ppb]	0.0004	20.6	0
Pb [ppb]	236	234	101
Zn [ppb]	15031	14971	100

^a equilibrated fluid using GEM-Selektor at 320°C and 130 bar.

^b average downhole fluid calculated from measured RN-fluid.

^c calculated by dividing 100 by RN-Fluid 2007 and multiplying by EQ-FL.

4. RESULTS

4.1 System equilibrium model: 320°C, 130 bar

To calculate a thermodynamically stable input fluid for numerical simulations we used an average fluid composition measured by Hardardóttir et al. (2009) in 2007. The average fluid composition (RN-Fluid 2007; Table 3) is based on measured element concentrations of the high-temperature downhole fluid for major and trace metals. The dissolved gas content of RN-Fluid 2007 is calculated using WATCH2.4 (Arnórsson et al., 1982) based on the average composition of liquid and gases collected at surface from well RN-22. The input fluid (Table 1; EQ-FL) was iteratively calculated by alternately changing redox conditions, pH and temperature to reach optimal conditions where most of the elements occur as dissolved aqueous components. Modeled dissolved metals, major elements and gases were compared to the measured average fluid composition (RN-Fluid 2007; Table 3).

At 290°C, quartz solubility was significantly lower compared to observed Si contents in the measured downhole fluid at Reykjanes. Increasing the temperature to 320°C improved dissolved Si concentrations to better match observations from measured fluid compositions. The redox potential of the fluid was adjusted by adding either $O_{2(aq)}$ or $H_{2(aq)}$ to the system and observing mineral stability, pH and the ratio of redox sensitive S and C aqueous species ($H_2S_{(aq)}$, SO_4^{2-} , $CO_{2(aq)}$, $CH_{4(aq)}$, etc.). For redox sensitive elements such as Au, Mo, Fe and Cu increasing the oxygen fugacity affects the element solubility, whereas the element concentrations of Ag, Pb and Zn are not affected (Fig. 5). Above $\log f_{02} = -32$, H_2S becomes a minor compound, which contradicts observations and measured fluid composition. Starting conditions were chosen to be around $\log f_{02} = -36$ to -32 at a pH of ~4.7. The equilibrated starting fluid matches element concentration of Ca, Cl, K, Mg, Na, S, Si, Ag, Pb and Zn (~80-100%) and shows a deviation for elements such as Al, C, Fe, Au, Mo and Cu (~0-60%) compared to the average downhole fluid collected in 2007 (Table 3).

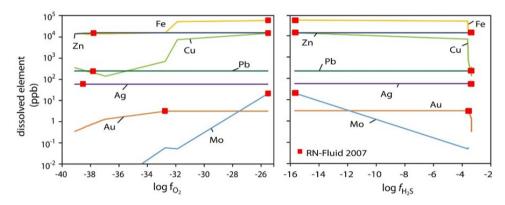


Figure 5: System equilibrium model at 320°C and 130 bar, showing element solubility as a function of increasing O₂ fugacity and decreasing H₂S fugacity. The red boxes represent the conditions at which modeled element concentrations match the measured average RN-Fluid 2007.

4.2 Single-pass flushing model: cooling and decompression from 320 to 220°C

In the single-pass model, we simulate the evolution of a single batch of fluid during cooling and decompression and record the amount of precipitated minerals and dissolved elements in solution (Figs. 6 and 7). The first single-pass model shows cooling of 1 kg fluid (Fig. 6 left panel) and the second model shows cooling of 100 kg of fluid (Fig. 6 right panel) between 320 and 220°C. A total amount of to 0.86 g sulfides precipitate per 100 kg fluid. Below 250°C and 38 bar, sulfide precipitation increases by one order of magnitude. Minor amounts of molybdenite and electrum form along the entire PT-path way. Bornite precipitates at elevated temperatures above 290°C amounting to 0.15 g per 100 kg fluid and is the least abundant Cu-bearing sulfide. Chalcopyrite precipitates subsequently between 290 and 240°C amounting to 0.2 g per 100 kg fluid. Finally, sphalerite starts to precipitate at 250°C and increases in abundance with decreasing temperature and pressure. Sphalerite is the major sulfide with 0.5 g per 100 kg fluid.

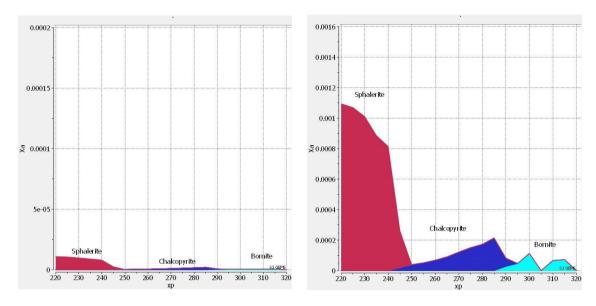


Figure 6: x-axis: temperature (°C); y-axis: moles of minerals precipitated. a) Top left. Single-pass model for 1 kg fluid precipitating bornite, chalcopyrite and sphalerite b) Top right. Single-pass model for 100 kg fluid precipitating bornite, chalcopyrite and sphalerite.

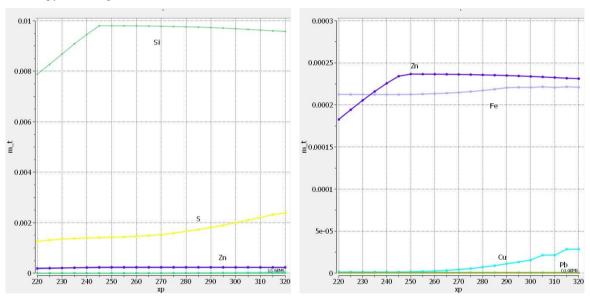


Figure 7: a) x-axis: temperature (°C); y-axis: mol/kg of dissolved elements. b) x-axis: temperature (°C); y-axis: mol/kg of dissolved elements, zoom into Figure (a).

5. DISCUSSION

Hardardottir (2014a) calculated the volume of scales formed in well RN-22 (Table 4). The volume of the material in pipe No. 79 is \sim 0.48 m³, which is equal to 1968 kg using an average density for sulfides of 4.1 g/cm³. If all material precipitates as scale in the well starting from the boiling surface to the wellhead and is spread evenly an average thickness is calculated in Hardardóttir (2014a). Boiling starts at \sim 1100 m depth, because that is the location of the major feed-point. To simplify all the calculations the inside radius is given as 13.3 cm, which is the average of the slotted liner and the production casing. From these calculations the scale thickness is estimated to be \sim 1 mm if spread evenly over the 1100 m casing string. If boiling occurs at 1200 m depth, calculations give a scale thickness of \sim 0.96 mm. This thin scaling would not affect the production of the well but could explain why down-hole logging hardly measured any scale at all in the well.

The amount of scales calculated based on the amount of produced water and simulated sulfide precipitated (Table 5) are more substantial compared to observed scales. However, the total flux of Zn is roughly double the amount of precipitated sulfide from the simulations, indicating that only a portion of the Zn is precipitated in the high temperature part of the well.

Table 4: Parameters of well RN-22

Inside diameter	ф	r
Slotted liner (m)	0.221	0.110
Production casing (m)	0.311	0.156
Average (m)	0.266	0.133
Total liner length (m)	1190	
Liner pipe length average (m)	12.5	
Volume of scale deposits (m ³)	0.48	

Table 5: Mass balance calculations of precipitated sulfide in simulations

Year	Water produced ^a	Simulated sulfide precipitated ^b	Volume of sulfide	Total mass balance of Zn ^c	Coating spread along pipe ^d
	Mt	kg	m^3	kg	mm
2006	1.89	16065	3.91	28295	469
2007	3.1	26350	6.42	46410	769

^a Production water from well RN-22; ^b Simulated sulfide precipitated in the high temperature part of the well scaled using mass balance; ^c Scaled Zn mass balance using the average downhole concentration of 14.97 ppm Zn; ^d sulfide scale coating if evenly spread over the entire well casting using the amount of precipitated sulfides from the numerical simulations.

6. CONCLUSIONS

Well RN-22 was drilled in 2005 into the main up flow of the Gunnuhver reservoir with a slotted liner between 679-1647 m depth. The maximum output capacity declined from initially ~14 MWe in 2006-2007 to 2 MWe in 2011, correspondingly the wellhead pressure decreased from 37.5 to 28 bar as a result of massive sulfide scaling. Scales from surface pipelines collected in 2007 showed that the pipeline downstream of the orifice plate was heavily clogged by sulfides. In 2009, 2011 and 2013, attempts were made to clean the well from scaling. In 2009 the scales were collected between 150 and 670 m depth and consisted of mainly sphalerite (90%), followed by chalcopyrite. No sulfide scales were collected in the year 2011. The scales collected in 2013 were nearly all found in the last pipe (No. 79, part of the liner) between 1634 -1647 m depth. The dislocated scales consist mainly of sphalerite, chalcopyrite and mud (mainly clinochlore, very fine-grained sphalerite/wurtzite). After the work over and removal of the scaling in the liner in 2013 the production testing showed increased capability of 4 MWe and wellhead pressure around 20 bar.

The simulated sulfide mineralogy consisting of sphalerite, chalcopyrite and bornite is similar to the observed mineralogy of the well scales. Further, the simulations reveal a high temperature bornite zone, followed by a chalcopyrite zone at 250-280°C and finally a sphalerite zone below 250°C. Sulfide precipitation is one order of magnitude greater at temperatures below 250°C and dominated by sphalerite. The numeri cal simulations and observations from well RN-22 indicate that within the production well there will be zones of increased well scaling as a function of the cooling and ascent of the fluid.

Mass balance calculations show that scaled amounts of sulfides precipitated in numerical simulations exceed the observed volume of the material in pipe No. 79 by one order of magnitude. The difference between observation and numerical simulation could indicate that not all the scaling material was collected from the liner during its removal from the well. Alternatively, it is worth to carefully consider the total flux of metals and better understand the elevated concentrations of metals in the sampled downhole fluid. These elevated metal concentrations could also be indicative of local remobilization and saturation conditions of the fluid within the well, and thus might not be a true indicator for the total metal flux in the geothermal production well.

REFERENCES

- Akaku, K.: Geochemical study on mineral precipitation from geothermal waters at the Fushime field, Kyushu, Japan, *Geothermics*, v. 19, (1990), 455–467.
- Akaku, K., and Nakatsuka, K.: Chemical equilibrium models for the fluids in the Fushime geothermal system: Isoenthalpic and isothermal boiling, *Proceedings*, 26th Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, California, January 29–31, (2001). SGP-TR-168.
- Akaku, K., and Yagt, M.: Mineral precipitation from the saline geothermal water of the Fushime Area Kyushu, Japan: The precipitation process of anhydrite. *Proceedings*, 10th New Zealand Geothermal Workshop (1988), 229–234.
- Arnórsson, S. (1978). Major element chemistry of the geothermal sea-water at Reykjanes and Svartsengi, Iceland: *Mineralogical Magazine*, 42, 209–220.
- Arnórsson, S., Sigurdsson, S., and Svavarsson, H.: The chemistry of geothermal waters in Iceland. I. Calculation of aqueous speciation from 0°C to 370°C. *Geochimica et Cosmochimica Acta*, **46**, (1982), 1513–1532.

- Bearman, G., ed.: Ocean Chemistry and Deep-Sea Sediments. Pergamon, London, (1989), 134p.
- Bjarnason, J.: Reykjanes elements in geothermal brine and steam 1971-2001 (in Icelandic with English abstract): Report No. OS-2002/038, 69 p. http://www.os.is/gogn/Skyrslur/OS-2002/OS-2002-038.pdf
- Björnsson, S., Arnórsson, S., and Tómasson, J.: Economic evaluation of Reykjanes thermal brine area, Iceland: *The American Association of Petroleum Geologists Bulletin*, **56**, no. 12, (1972a), 2380-239.
- Björnsson, S., Arnórsson, S., and Tómasson, J.: Exploration of the Reykjanes thermal brine area: *Geothermics*, Special Issue 2, 2, part 2, (1972b), 1640-1650.
- Brown, K. L., and Simmons S. F.: Precious metals in high-temperature geothermal systems in New Zealand. *Geothermics*, 32, (2003), 619–625.
- Dean, T., McKibben, M.A., and Ruiz, M.C.: Sulfide scaling in Cerro Prieto geothermal wells. *Geothermal Resources Council Transactions*, 16, (1992).
- Franzson, H.: The high-temperature system at Reykjanes (in Icelandic), Iceland GeoSurvey, ÍSOR-2004/012, (2004), 68p.
- Franzson, H., Thordarson, S., Bjornsson, G., Guðlaugsson, S.Th., Richter, B., Friðleifsson, G.Ó., and Thorhallsson, S.: Reykjanes high-temperature field, SW-Iceland. Geology and hydrothermal alteration of well RN-10. *Proceedings*, 27th Workshop on Geothermal Reservoir Engineering. Stanford University, (2002), 233–240.
- Gysi: Numerical Simulations of CO₂ sequestration in basaltic rock formation: Challenges for optimizing mineral fluid reactions. Pure Appl, Chem. v 89, (2017) 591-596 p.
- Hardardóttir, V.: Metal-rich Scales in the Reykjanes Geothermal System, SW Iceland: Sulfide Minerals in a Seawater-dominated Hydrothermal Environment. PhD thesis. University of Ottawa, (2011), 288 p.
- Hardardóttir, V.: Scales Collected during work over 2013 from well RN-22, Reykjanes. Iceland GeoSurvey, ÍSOR-2014/032, (2014a), 41 p.
- Hardardóttir, V.: Sulfide Scaling, well by well review. Iceland GeoSurvey, ÍSOR-2014/033, (2014b), 119 p.
- Hardardóttir, V., Brown K. L., Fridriksson Th., Hedenquist J.W., Hannington M.D., and Thorhallsson S.: Metals in deep liquid of the Reykjanes geothermal system, southwest Iceland: Implications for the composition of seafloor black smoker fluids. *Geology*, **37**, *no* 12, (2009), 1103–1106.
- Hardardóttir, V., Hannington, M., Hedenquist, J., Kjarsgaard, I., and Hoal, K.: Cu-Rich scales in the Reykjanes geothermal system, Iceland. *Economic Geology*, **105**, (2010), 1143–1155.
- Henley, R.W., Truesdell, A.H., and Barton P.B., Jr.: Fluid-mineral equilibria in hydrothermal systems: *Reviews in Economic Geology*, 1, (1984), p. 267.
- Hurtado, R., and Mercado, S.: Scale Control Studies at the Cerro Prieto Geothermal Plant. *Geothermal Resources Council Transaction*, **14**, Part II, (1990).
- Jónsson, J.: Geological map of Reykjanes Peninsula. National Energy Authority Report No. OSJHD7831, (1978), 303 p.
- Jónsson, S.S., Kristjánsson B.R., Gudmundsson, Á., Björnsson G., Gunnarsson G., Danielsen P.E. and Thórhallsson, S.: Reykjanes well RN-12, 3. Stage: Drilling from 854 m to 2506 m depth (in Icelandic). National Energy Authority Report No. OS-2003/010, (2003), 62 p.
- Karpov, I.K., Chudnenko, K.V., Kulik, D.A., Avchenko, O.V., Bychinskii, V.A.: Minimization of Gibbs free energy in geochemical systems by convex programming. *Geochem. Int.* **39**, (2001), 1108–1119.
- Karpov, I.K., Chudnenko, K.V., Kulik, D.A., Bychinskii, V.A.: The convex programming minimization of five thermodynamic potentials other than Gibbs energy in geochemical modeling. *Am. J. Sci.* **302**, (2002), 281–311.
- Kristmannsdóttir, H.: Chemical evidence from Icelandic geothermal systems as compared to submarine geothermal systems, in Rona, P.A., Bostrom, Laubier, L., and Simith, K.L. Jr., eds., Hydrothermal processes at seafloor spreading centers: *Plenum Press, NATO Conference Series, IV Marine Sciences,* 12, (1984), 291-320.
- Kulik, D.A., Wagner, T., Dmytrieva, S.V., Kosakowski, G., Hingerl, F.F., Chudnenko, K.V., and Berner, U.R.: GEM-Selektor geochemical modeling package: Revised algorithm and GEMS3K numerical kernel for coupled simulation codes: *Computational Geosciences*, 17, (2013), 1–24, doi: 10.1007/s1056-012-9310-6.
- McKibben, M.A., and Elders, W.A.: Fe-Zn-Cu-Pb mineralization in the Salton Sea geothermal system, Imperial Valley, California: *Economic Geology*, **80**, (1985), 539-559.
- Mortensen, A.K., Richter, B., Franzson, H., Egilson, Þ., Ásmundsson R., Danielsen, P.E., Sigurðsson, Ó., Ágústsson, F., and Skarphéðinsson, K. Reykjanes Well RN-22. Pre-drilling, drilling sections 1, 2 and 3 (in Icelandic). Iceland GeoSurvey, ÍSOR-2008/005, (2008). 104 p.
- Ocampo-Diaz, JDeD., Valdez-Salaz, B., Shorr, M., Sauceda-M, I., and Gonzlez, N. R.: Review of Corrosion and Scaling Problems in Cerro Prieto Geothermal Field over 31 Years of Commercial Operations. *Proceedings* World Geothermal Congress 2005 Antalya, Turkey, 24-29 April 2005.

Hardardottir and Hurtig

- Richter, B, Franzson, H., Kristjánsson, B.R., Jónsson S.S., Gudmundsson Á., Gunnarsson, G., Sigurdsson, Ó., and Skarphéðinsson, K.: Reykjanes well 12, 1. Stage, drilling from 119 to 300 m depth and 2. Stage, drilling from 300 to 854 m depth. National Energy Authority Report No. OS-2003/008, (2003), 50 p.
- Sæmundsson, K., Jóhannesson, H., Kristinsson S.G., and Sigurgeirsson, M.A.: Geological map of Southwest Iceland, 1:100,000. Iceland GeoSurvey, (2010).
- Simmons, S.F., and Browne, P.R.L.: Hydrothermal minerals and precious metals in the Broadlands-Ohaaki Geothermal system: Implications for understanding low-sulfidation epithermal environments. *Economic Geology*, **95**, (2000), 971–999.
- Seyfried, W., and Bischoff, J.: Hydrothermal transport of heavy metals by seawater: the role of seawater/basalt ratio: *Earth and Planetary Science Letters*, **34**, (1977), 71–77.
- Sigurdsson, Ó.: Reykjanes wells history. HS Orka, short report, (2012). 23 p.
- Skinner, B.J., White, D.E., Rose, H.J., and Mays, R.E.: Sulfide associated with the Salton Sea geothermal brine. *Economic Geology*, **62**, (1967), 316–330.
- Tómasson, J., and Kristmannsdóttir, H.: High temperature alteration minerals and geothermal brine, Reykjanes, Iceland. *Contributions to Mineralogy and Petrology*, **36**, (1972), 123–134, doi: 10.1007/BF00371183.
- Wagner, T., Kulik, D.A., Hingerl, F.F. and Dmytrieva, S.V.: GEM Selektor geochemical modeling package: Tsolmod library and data interface for multicomponent phase models. *Can. Mineral.* **50** (5), (2012), 1173–1195.
- White, J. L., Orr, R. L. and Hultgren, R.: The thermodynamic properties of silver-gold alloys. Acta Metall. 5, (1957), 747-760.