Proceedings World Geothermal Congress 2020+1
Reykjavik, Iceland, April - October 2021

The Metal Scavenging by Calcite Scaling Formed During Utilization of the Low Temperature Geothermal Waters. a Case Study in Selfoss Geothermal Area, Sw Iceland

Iwona Galeczka[1], Vigdís Harðardóttir[1], Sigurður Þór Haraldsson[2]

[1]ISOR, Iceland GeoSurvey, Grensasvegur 9, 108 Reykjavik, Iceland

[2]Selfossveitur bs, Austurvegi 2, 800 Selfoss, Iceland

Iwona.M.Galeczka@isor.is

Keywords: geothermal, district heating, calcite scaling, partitioning coefficient, mixing modelling, Selfoss

ABSTRACT

To increase the hot water production and meet the district heating demands caused by the growing population in Selfoss, SW Iceland, the Selfossveitur heating district utilizes two chemically distinct waters that are mixed at the surface before reaching the distribution system. When fluids are used separately they do not cause substantial calcium carbonate ($CaCO_3$) scaling, however, when they are mixed – calcite scales form, sometimes to a degree of complete blockage of a piping system. Results of this study show that although the metal content in the scales is rather low, the Cr, Cu, Fe, Hg, Mn, Ni, P, Pb, and Zn are substantially scavenged by the precipitating calcite, decreasing the dissolved metal to Ca ratio as shown by a calculated partitioning coefficient (p_{Me}). This is agreement with previous studies where carbonate minerals were proven to scavenge various dissolved trace metals including rare earth elements (REE) and the toxic metals As and Pb from the fluids. The metals are immobilized mainly through formation of sulfide minerals within calcite matrix.

1. INTRODUCTION

Geothermal fluids are capable of transporting and depositing metals even to a degree that are considered as modern analogues of ore deposits in hydrothermal environments (Brown, 1986; Hardardóttir et al., 2009, 2010; Kaasalainen et al., 2012; Rea et al., 2017; Simmons and Brown, 2006, 2007). The metals transported by the utilized fluids can be immobilized by their coprecipitation during the scales formation. Amorphous silica and calcium carbonate scaling are the most common geochemical problems during geothermal utilization, and often considerable efforts are taken to prevent scaling formation for longer lifetime of the production and reinjection wells (Arnórsson, 1981; 1989; Brown and Dunstall, 2000; Gunnarsson and Arnórsson, 2005; Sigfússon and Gunnarsson, 2011; van den Heuvel et al., 2018). This, however, generates additional costs of energy production. In the nature, secondary mineral alteration immobilizes not only the main metals indicated by chemical formula of the phase but also trace metals that fit into their crystallographic structure. Previous studies showed that carbonate minerals have a potential to scavenge trace metals from fluid such as Cd, Co, Cu, Mg, Mn, Sr, rare earth elements (REE) and the toxic metals such as As and Pb (Olsson et al., 2014) meaning that their co-precipitation decrease their concentration in the water. As shown by Hardardóttir et al. (2010) utilization of saline geothermal waters, might result in formation of the sulfides scales within production wells including sphalerite/wurtzite (Zn,Fe)S, pyrite (FeS_2), chalcopyrite, magnetite (Fe_3O_4), and chalcopyrite, ($CuFeS_2$). These sulfide scales contained also trace metals such Se, Cd, Au, Ag, Ni, Cd, and Mn. (Hardardóttir, 2011).

Low-temperature geothermal fields (up to 150 °C) are widely exploited in Iceland for space heating (Gunnlaugsson et al., 2000). To meet the district heating needs and increase the hot water discharge, the Selfossveitur geothermal plant (Selfoss, SW Iceland; e.g. Guðjónsdóttir, 2017) utilizes two chemically distinct fluids originating from two aquifers located within the same basaltic geological formation. The first fluid from Ósabotnar (wells ÓS in Figure 1) area is rather dilute, whereas the second one from Þorleifskot reservoir (wells ÞK in Figure 1) has higher dissolved mineral content as it contains seawater component. These fluids are mixed at the surface before reaching the power plant distribution system. Both endmembers used separately do not cause major $CaCO_3$ scaling in the surface pipes, however, when mixed in certain ratios – chemical characteristics of the mixture changes resulting in calcite formation sometimes to a degree of complete blockage of the pipes (Ólafsson et al., 2005).

The purpose of this study was to investigate the collected scales for their scavenging potential of the dissolved metals which otherwise would be mobile in the geothermal water for their possible extraction. Number of studies have been focused on developing new methods for metal extraction that are of economic interest such as La, Li, Pt from geothermal waters (e.g. Maimoni et al., 1982; Mroczek et al. 2015; Paranthaman et al., 2017). One of the aim of the CHPM-2030 (Combined Heat, Power and Metal Extraction) EU funded project was to test a gas-diffusion electrocrystallization (GDEx; Dominiquez Benetton, 2017) for removal and recovery of a few metals (e.g., Ce, Fe, Mn, Zn, Cu, La, Pt, Pd, etc.) from geothermal fluids. As a part of this project, we focused here on the mineralogical identification of the scales, characterization of their chemical content and its relation to the chemical composition of hot water. In addition, we discuss the calcite saturation index of the utilized Ósabotnar and Þorleifskot mixture.

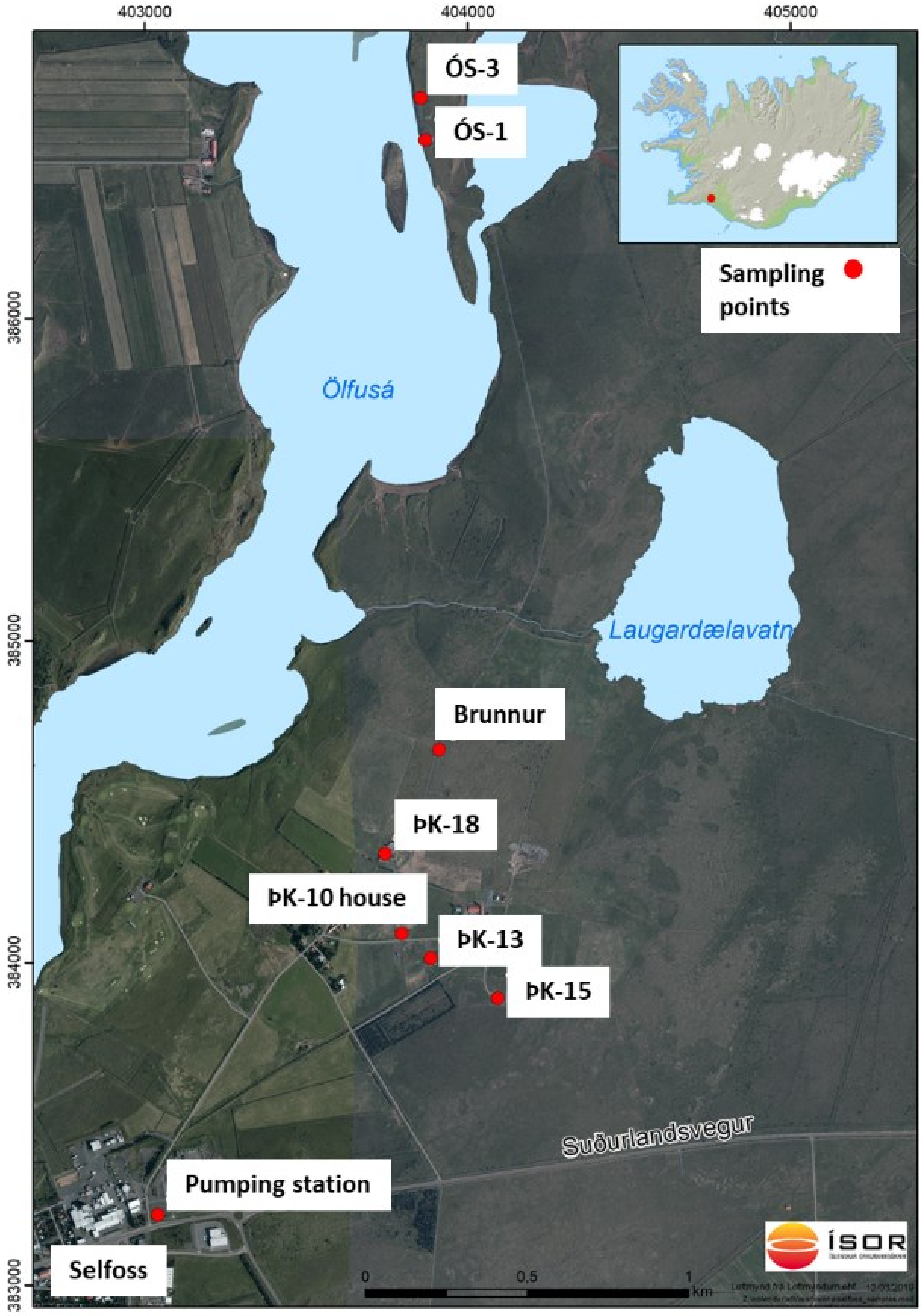

Figure 1: The location of the water sampling points. Waters sourced from Ósabotnar and Þorleifskot geothermal areas are mixed and pumped from the pumping station into the Selfoss district heating system.

2. METHODS

2.1 Sampling and analysis

The sampling area is located within Selfoss district heating (Figure 1). The producing boreholes are sourced from chemically distinct feeding aquifers. The Ósabotnar area is represented by boreholes ÓS-01 and ÓS-03, whereas the Þorleifskot aquifer is represented by ÞK wells. The sample collected at Brunnur is an H_2SO_4 acidified mixture of ÓS-01 and ÓS-03. The water from Brunnur flows and cools down on a way to ÞK-10 house (Figure 1, Table 1), therefore the concentrations of conservative constituents in both samples are identical. The amount of acidification varies with time and at the time of sampling it was equal to 0.046 L of H_2SO_4 acid per hour based on SO_4 concentration and pH difference between initial mixture of ÓS-01 and ÓS-03 and the Brunnur fluid. During sampling, only ÞK-13 and ÞK-15 in Þorleifskot were connected to the pumping station.

The hot waters samples were collected from the operating boreholes using a stainless steel (SS) tubing connected to the well heads and a cooling spiral. The *in situ* water temperature was measured directly by attaching the temperature probe to the sampling outlet at the well head, whereas other parameters such as conductivity, dissolved O_2 and pH were measured after cooling of the water to <25 °C. Cooled and unfiltered water aliquots were collected in brown amber glass bottles with air-tight caps for NH_3, pH and total dissolved carbon (DIC) measurements. Samples for SiO_2, major cations and anions were filtered through 0.2 µm Millipore cellulose acetate membranes and collected into 200 ml polypropylene bottles. In addition, water aliquots for trace metals were collected into acid washed high density polypropylene bottles and together with samples for cations were acidified using Suprapur® 1 % (v/v) HNO_3.

The *in situ* pH was determined using a ColePalmer combined glass electrode together with an Orion pH meter whereas both pH and DIC were measured in the laboratory using Metrohm DMS Titrino titrator and Metrohm pH and temperature electrodes. The H_2S was determined *in situ* by precipitation titration using Hg-acetate titrant and dithizone as colour indicator. The oxygen content was measured using CHEMetrics ampules. The NH_3 was determined using spectrophotometry. The anions were measured using an IC-2100 ThermoScientific anion chromatograph (ThermoScientific, 2012). Major cations and few trace elements were then analysed using ICAP-7400 ThermoScienfic inductive coupled plasma, optical emission spectrometer (ICP-OES; ThermoScienific, 2013) at ÍSOR, calibrated with a Sigma-Aldrich certified ICP Standards. The trace elements which concentrations were below the detection limit were analysed using inductive coupled plasma sector field mass spectrometry (ICP-SFMS) at ALS Laboratory in Luleå, Sweden. The analytical error of the analyses was within 5%.

Two scale samples were collected from a hot water pipe located several km from the pumping station towards the Selfoss town centre (Figure 1, Figure 2). Owners of the property where the sample was collected had been observing a decline in a water pressure for several years until there was decided to investigate the possible causes of the flow restriction and open a hot water piping system in the area. Two scale samples collected from the pipe were characterised by X ray diffractometry (XRD) at ÍSOR laboratory. Samples were powdered with an agate mortar and pestle, and then analysed using a Bruker AXS D8 Focus diffractometer equipped with Bragg–Brentano goniometer and a Cu anode lamp with NaI crystal type scintillation counter. Scale samples were also analyzed using a LEO Supra 25 and a JEOL 6360 LV Scanning Electron Microscope. The solids were coated with gold prior to the analysis that used an acceleration voltage of 15 kV. The Energy Dispersive X-ray Spectroscopy (EDX) was used together with the SEM to assess the distribution of the main and trace constituents within the scale samples. Chemical composition of the scales was determined by Perkin Elmer Sciex ELAN 6000, 6100 or 9000 ICP/MS at Activation Laboratories, Ontario, Canada.

Table 1: The chemical composition of the fluids collected during this study. The *in situ* pH and charge imbalance were calculated using PHREEQC. The discharge was measured by the power plant operator and it referrers to the time of sampling. The ÞK-10 house and Brunnur fluids originate from acidified ÓS-01 and ÓS-03 mixture.

Sample Nr		20180271	20180272	20180273	20180274	20180275	20180276	20180277	20180278
Location		ÓS-1	ÓS-3	Brunnur	ÞK-18	ÞK-10 house	ÞK-13	ÞK-15	Pumping st.
Temp.	(°C)	69.1	85.1	79.8	117.4	22.9	71.2	80.1	75.5
pH		9.96	9.87	9.18	9.18	9.34	8.53	8.79	8.85
Temp./pH	(°C)	25.3	27.9	21.8	33.6	22.9	26	22.5	25.4
Discharge	L/s	29	54	n.m.	n.m.	n.m.	62	10	n.m.
Cond. at 25°C		356	545	n.a.	1313	n.a.	859	1006	741
in situ pH		9.10	8.89	8.36	7.98	9.21	7.98	7.76	8.18
Charge imb.	%	2.69	0.51	2.11	1.21	1.75	1.88	1.12	2.21
CO_2	mg/L	11.5	5.85	3.91	5.68	7.08	30.6	18.9	17.9
H_2S		0.09	0.37	n.a.	0.01	n.a.	0.09	0.11	0.18
O_2		<0.001	<0.001	n.a.	<0.001	n.a.	<0.001	<0.001	<0.001
B		0.178	0.214	0.198	0.272	0.199	0.116	0.153	0.159
SiO_2		60.1	74.8	69.0	102	69.2	67.1	72.6	69.8
Na		73.3	103	93.6	246	94.8	157	183	139
K		1.20	1.91	1.72	9.23	1.71	4.72	5.78	3.93
Mg		0.006	0.005	0.004	0.010	0.003	0.130	0.080	0.007
Ca		7.20	13.3	11.4	32.2	11.5	28.4	32.7	22.9
F		0.618	0.756	0.712	0.177	0.714	0.166	0.177	0.369
Cl		70.0	112	99.0	327	99.0	217	274	182
Br		0.166	0.260	0.229	0.839	0.230	0.543	0.721	0.458
SO_4		23.2	50.4	64.5	123	63.9	55.7	62.3	60.8
TDS		238	384	n.a.	861	n.a.	552	662	512
Al	µg/L	99.7	82.9	99.6	129	101	12.7	32.9	47.6
Fe		2.98	2.76	<0.4	12.8	<0.4	15.2	13.2	11.5
Mn		0.100	0.082	0.018	0.638	0.071	2.42	1.35	1.35
Sr		22.3	84.7	54.1	290	54.0	101	142	96.1
As		1.55	2.09	1.40	4.05	0.972	2.57	3.76	4.09
Ba		0.132	0.472	0.376	2.310	0.328	0.638	1.08	0.585
Cd		0.008	0.012	n.a.	0.017	n.a.	0.003	0.004	0.052
Co		0.014	0.006	n.a.	0.006	n.a.	0.009	0.007	0.006
Cr		0.039	0.043	n.a.	0.077	n.a.	<0.01	0.016	0.021
Cu		<0.1	<0.1	n.a.	1.28	n.a.	0.305	0.255	<0.1
Hg		<0.002	0.004	n.a.	0.002	n.a.	<0.002	<0.002	<0.002
Li		4.11	6.10	2.72	16.2	3.98	26.1	32.1	19.8
Ni		<0.05	<0.05	n.a.	0.058	n.a.	0.213	0.158	0.067
P		<1.0	<1.0	n.a.	<1.0	n.a.	<1.0	<1.0	<1.0
Pb		0.038	0.014	n.a.	0.827	n.a.	0.023	0.059	<0.05
V		0.490	0.509	n.a.	1.12	n.a.	0.031	0.091	0.254
Zn		0.607	0.548	n.a.	59.8	n.a.	1.48	1.95	1.64
Ti		1.47	2.44	2.17	5.61	2.05	4.75	5.23	4.29

n.a.-not analyzed; n.m. – not measured

2.2 Geochemical modelling

The aqueous speciation, charge imbalance and mineral saturation states of Selfoss water samples collected during this study were performed using the PHREEQC 3.3.12 geochemical code (Parkhurst and Apello, 1999) together with a *carbfix.dat* thermodynamic database (Voigt et al., 2018) which is a modification of the *core10.dat* database (Neveu, et al., 2017). These calculations were performed using measured samples compositions, pH, and water temperature at a time of sampling (Table 1). A mixing modelling simulating inflow into the pumping station and final fluid composition within the district heating system was performed using compositions of waters sourced from production boreholes and discharge data given by the power company operator.

2.3 Partitioning coefficient

The partition coefficient (p_{Me}) represents the ability of a particular phase to scavenge a foreign element. The phase in this study is calcite and the foreign element is any metal, non-metal, or metalloid ion (Me). The partition coefficient is defined as:

$$p_{Me} = \frac{X_{Me,s}}{X_{Ca,s}} / \frac{C_{Me,l}}{C_{Ca,l}}$$

where $X_{Me,s}$ and $X_{Ca,s}$ represent the mole fraction of the scavenged constituent and Ca in the solid phase and $C_{Me,l}$ and $C_{Ca,l}$ represent the molar concentration of the component and Ca in the water samples. The partition coefficient is determined empirically and should not be confused with the thermodynamically defined distribution coefficient, (K_D or D; Morse and Bender, 1990; Stumm, 1992). When p_{Me} is above unity, the corresponding metal is scavenged by the precipitating calcite, decreasing the dissolved Me/Ca ratio. For p_{Me} below unity, the metal ion is incorporated into calcite to a lower extent than Ca, so the solute Me/Ca ratio increases. In this study the molar concentration of the metals and Ca in water samples are taken from the pump station sample (20180278; Table 1) which represents the fluid that is pumped to the district heating system in Selfoss. The analytical detection limits (DL) were used for calculating the p_{Me} in case the measured concentrations were lower than DL. Therefore, they will represent a maximum or a minimum partitioning of the dissolved constituent into the solid phase, depending whether the DL was applied to water or solid phase in the equation, respectively.

3. RESULTS

3.1 Water and scale chemical composition

Chemical compositions of water samples collected during this study are presented in Table 1. The charge imbalance of waters calculated with PHREEQC was <5%. The O_2 content in all the samples was below detection limit of the analytical method. The chemical composition, temperature, pH, and conductivity of the samples collected during this study are within the range of measured before. Comparing to chemical composition of samples collected previously the Mg and CO_2 concentration increases with time since 2005 in Þorleikskot wells and therefore in pumping station. At the same time there is small decrease in pH. The mass balance calculations based on the S content in Ósabotnar wells and in Brunnur indicates that the amount of acid added to the Ósabontar outflow is 0.046 L/hour.

The XRD spectrum of scales correspond to crystalline calcite. Other minor phases which content is below the analytical detection limit of 5% are not excluded. A presence of other phases is indicated by the chemical composition of the scales (**Error! Reference source not found.**). The concentration of the major elements such as Ca, Fe, and Si equals to $391*10^3$, 2332, and 1683 ppm, respectively. The most abundant trace metals are Mg, Mn, and Al in concentrations of hundreds of ppm; Na, P, Ti, Cr, Ni, Cu, and Zn in concentrations of tens of ppm.

Table 2: The chemical composition of the scale samples used for calculating the pMe.

Analyte	Unit	1	2
SiO_2	%	0.34	0.38
Al_2O_3		0.08	0.08
Fe_2O_3(tot)		0.26	0.34
MnO		0.045	0.047
MgO		0.080	0.100
CaO		54.11	55.42
Na_2O		0.02	0.02
K_2O		0.01	<0.01
TiO_2		0.005	0.007
P_2O_5		0.03	0.01
LOI		43.74	43.68
Total		98.71	100.1
C-Tot		n.a.	12.3
S-tot		n.a.	0.030
Ag	ppm	<0.5	<0.5
As		<5	<5
B		n.a.	5.8
Ba		6	3
Br		n.a.	19
Cd		n.a.	<0.5
Cr		<20	<20
Cu		70	140
Hg		n.a.	72
Li		n.a.	<1
Mo		<2	<2
Ni		<20	<20
Pb		< 5	8
Sr		97	98
Zn		7	4

The p_{Me} calculated for the constituents present in the pumping station water samples (20180278; Table 1) and in the scales (Table 2) can be seen in Figure 3. The p_{Me} calculated for Cr, Cu, Fe, Hg, Pb, Mn, Ni, P, and Zn exceeded 1. Note, that due to analytical detection limits the p_{Me} calculated for As, Cd, Cr, Li, and Mo is the maximum, whereas p_{Me} assessed for Hg, P, and Pb represent the minimum scavenging ability of calcite towards these elements. The trace metals were incorporated within secondary alteration that precipitated within calcite matrix. These phases identified using SEM/EDX (Figure 4) possibly Cu-Fe-sulfides with minor amounts of other metals such as Zn, Sn, As, Sb, Ni, and Pb. There were also Fe-silicate phases, and Fe-oxides.

Figure 2. The calcite scales collected from the surface pipes within Selfoss district heating system several kilometers from the pumping station.

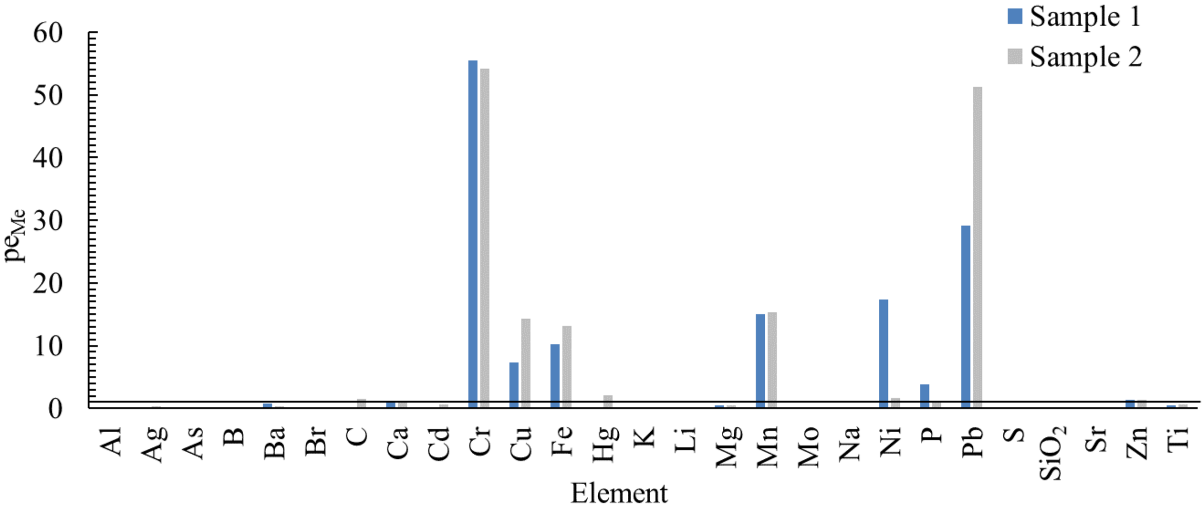

Figure 3: The p_{Me} calculated for elements present in two scales samples and the pumping station water. The horizontal line indicates p_{Me} of 1.

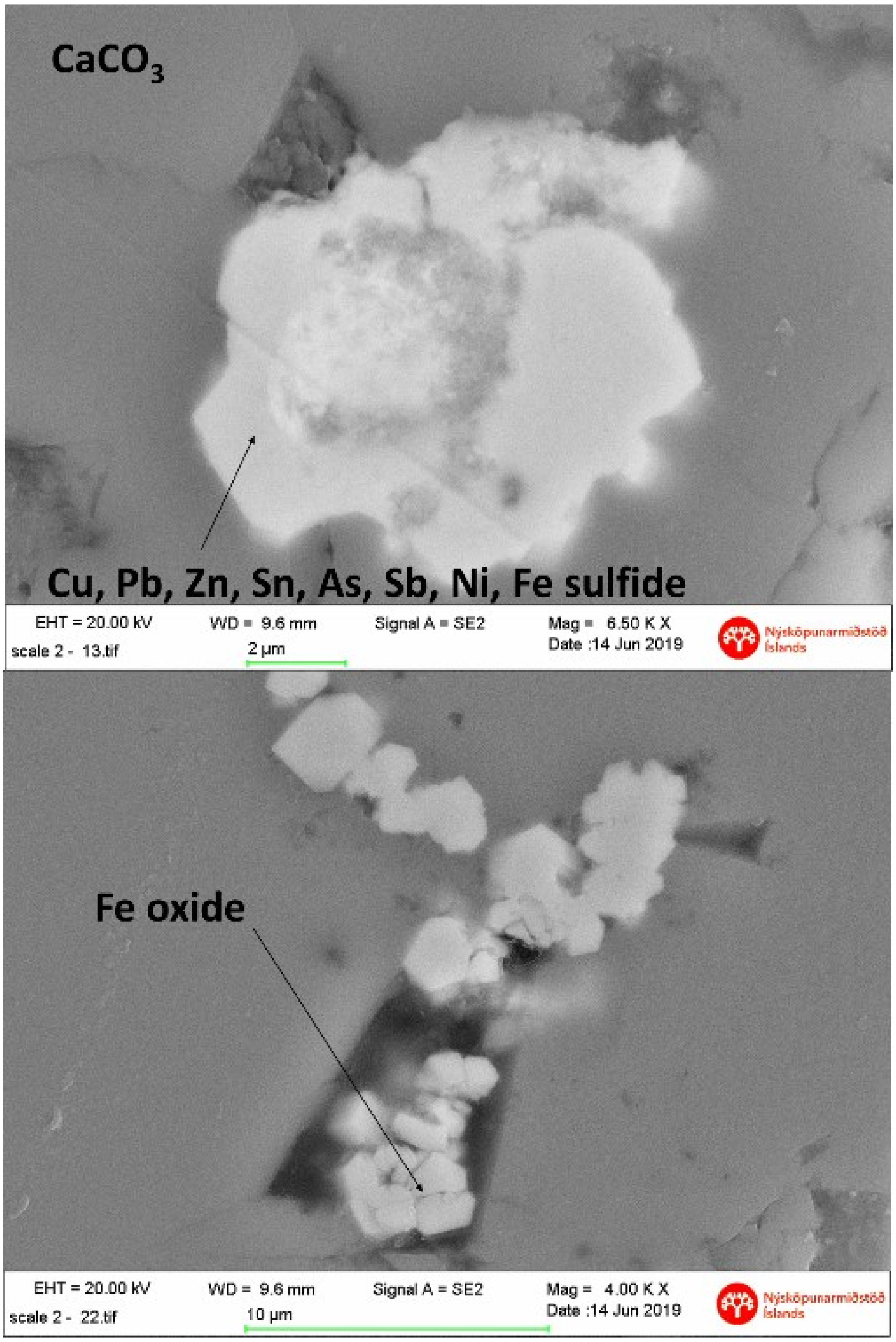

Figure 4. The secondary phases that immobilized the trace metals within the calcite matrix as measured by the SEM/EDX .

3.2 Geochemical modelling

The evolution of the calcite saturation index depending on the mixing ratio of the ÓS-01/ÓS-03 with ÞK-13 and ÞK-15 waters (a) and the acidified ÓS-01/ÓS-03 mixture with ÞK wells is shown in Figure 5. Unacidified mixture of ÓS-1 and ÓS-3 with ÞK-13 and ÞK-15 water is supersaturated with respect to calcite at almost all stages of mixing (Figure 5a), whereas acidified ÓS (Brunnur) and ÞK-13 mixture is undersaturated only if the majority of the mixture volume is sourced from Brunnur (Figure 5b). When mixing Brunnur with ÞK-15 waters – the calcite SI is negative since both waters are initially undersaturated with respect to calcite (Figure 5b). As can be seen in Figure 6 the water in pumping station is most of the time supersaturated with respect to calcite.

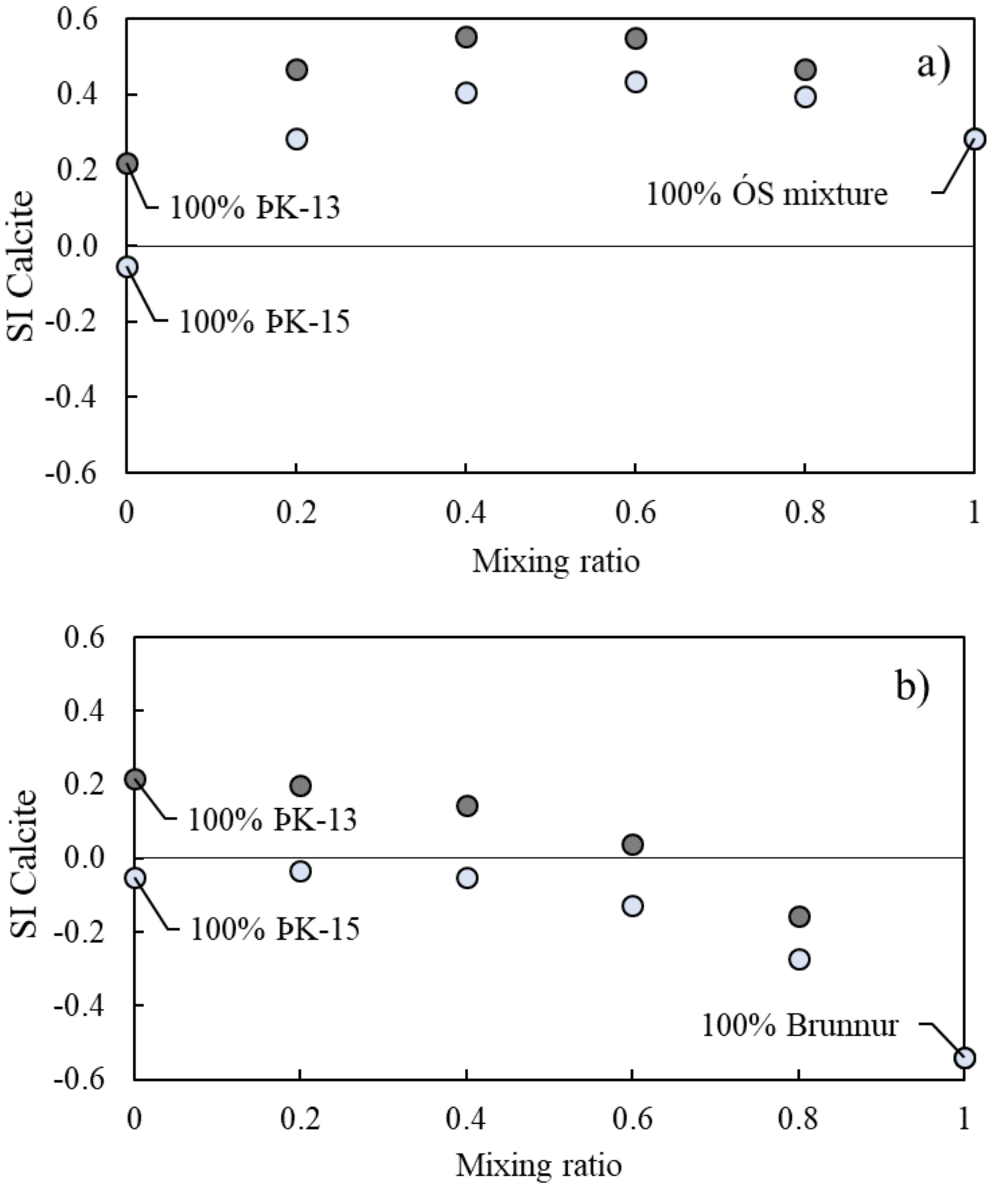

Figure 5: Results of the mixing modelling of waters from ÓS-01 and ÓS-03 with ÞK-13 and ÞK-15 (a) and acidified ÓS-01 and ÓS-03 mixture (Brunnur) with ÞK-13 and ÞK-15 (b) using the PHREEQC geochemical code. The percentage on the primary (lower) x-axis represents the volume percentage of ÓS-01/ÓS-02/Brunnur water.

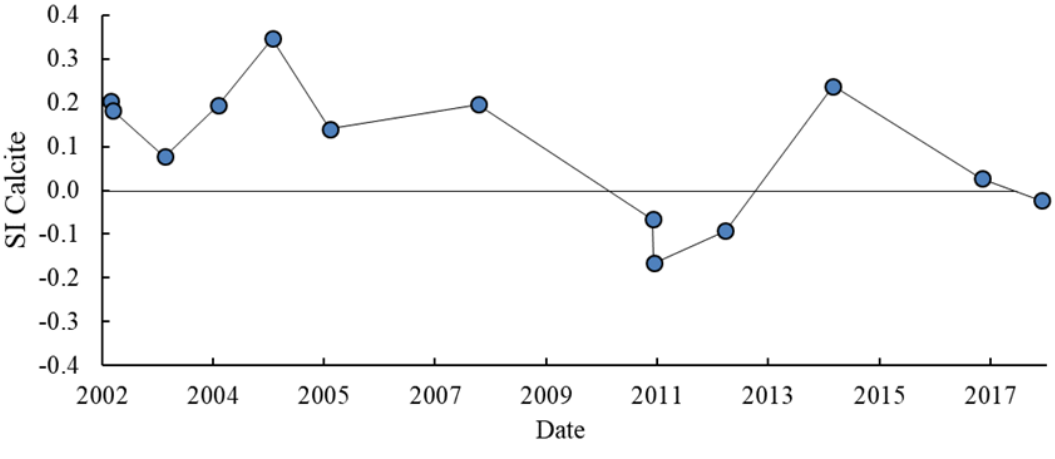

Figure 6: The evolution of the saturation state of water pumped into the district heating system with respect to calcite calculated using the chemical composition of samples collected at the pumping station. The mixing ratio of waters from Ósabotnar and Þorleiskot vary with time, as the specific well discharges vary.

4. DISCUSSION

Calcite scaling was observed in Selfoss immediately after when Ósabotnar and Þorleikskot waters were mixed and pumped into the Selfoss district heating system. Carbonates precipitation is often observed when two fluids with distinct salinities are mixed. Adding a salt to a solution attracts water molecules that would otherwise hydrate other ions (e.g. Stumm, 1992). The more salt there is in solution the less water molecules can solvate other ions which can more easily combine to form solids with lower solubilities than the salt. Mixing decreases salinity of more concentrated waters and increase salinity of more diluted ones. If the latter is already slightly supersaturated (or at equilibrium with respect to calcite), then this increase in salinity enhances the precipitation of calcite, especially at higher temperatures. Zuddas and Mucci (1998) found that the precipitation rate of calcite increases up to four orders of magnitude when ionic strength of the fluid increases from 0.1 to 0.9 mol/kg.

The geothermal experience in Iceland suggests that calcite precipitation is unlikely when the saturation index is below 0.4 (Ólafsson et al., 2005). Therefore, the experiments were performed in 2003 where the ÓS waters were acidified using 18 M H_2SO_4 to lower their pH and therefore decrease the calcite SI below 0.4. Based on results of those experiments, it was advised to inject 0.033 L/hour of H_2SO_4 for each L/s of produced water from ÓS well (Ólafsson et al., 2005). After this procedure started, no scaling had been observed, until November 2018.

Although the acidification had been continuing and as it can be seen in Figure 6 the calcite SI in pumping station did not exceed 0.4, the presence of the calcite scaling in surface pipes suggests that this rule did not apply in this case. Bai (1991) showed that in ÞK-11 – another well in Þorleikskot area – calcite scaling was observed even though calcite SI was close to zero. Experiments studies of calcite precipitation rates suggest that calcite precipitates at SI close to 0 (e.g. Stockman et al., 2014). Similar, calcite SI close to 0 was calculated for ÞK-18 and ÞK-15 based on recent samples. The calcite SI of the water from pumping station based on wells discharges at the time of sampling was 0.06. This can indicate that the system was at equilibrium meaning that calcite formation decreased the SI index to 0. Based on experiments and observations (Ólafsson et al., 2005), the acidification of ÓS waters limited substantially the calcite precipitation, however, it did not prevent it. Further studies should be performed on the structure/texture of calcite scales because it might reveal the mechanism of its formation and therefore a proper method of its inhibition can be applied. Unfortunately, we do not know how long these scales had been forming and therefore it is impossible to connect their formation kinetics with utilized fluid chemical composition based on sampling frequency. In addition, some of the utilized fluids from ÞK wells show changes in salinity affecting also the calcite SI.

As has been showed earlier metals such as Cd, Co, Cu, Mg, Mn, Sr, rare earth elements (REE) and the toxic metals As and Pb have been intensively incorporated into calcite in natural systems (Olsson et al., 2014). Several physicochemical factors can impact the partition coefficient for some metals. These include pH, temperature, pressure, ionic strength, redox state, precipitation rate and composition of parent solution (Kitano et al., 1980; Morse and Bender, 1990; Stumm, 1992; Rimstidt et al., 1998; Curti, 1999). The p_{Me} calculated for analysed constituents reflect that in general they follow the mobility of the dissolved constituents. For example, the p_{Me} of B, Cl, Na was below 1 indicating that calcite do not scavenge these elements to substantially limit their dissolved concentration. In basaltic groundwaters and thermal water systems they are considered as the mobile elements (e.g. Arnórsson and Andrésdóttir, 1995; Galeczka et al., 2014; Gislason et al., 1996) and often are used to trace the origin of the waters and the extent of the subsurface water-rock interaction. Metals such as Cr, Cu, Fe, Pb, Mn, Ni, Hg, P, and Zn were significantly scavenged by calcite scale. This secondary metal co-precipitation has also been seen in the natural systems. During eruptions, volcanic gases dissolve and dissociate in the rain and surface waters decreasing their pH. Acidic water enhances the dissolution of rocks and mobilization of metals. Upon water-rock interaction, the pH of the water increases and the precipitation of secondary mineral phases such as Fe(hydro)oxides scavenge the metals limiting their availability and therefore their negative impact on biological activity (e.g. Galeczka et al., 2016, 2018). Although the p_{Me} of calcite scale was high for certain metals, their overall concentrations in the production fluids and therefore in scale are insufficient for the metal extraction during the geothermal utilization at current extraction costs and availability of their natural deposits (e.g. Neupane and Wendt, 2017).

5. CONCLUSIONS

Following conclusions can be drown from this study on calcite scales in low temperature geothermal waters in Selfoss.

1) The concentration of trace metals in all production wells in Selfoss is too low for their economical extraction nowadays.
2) The metal scavenging potential of calcite scales formed during low temperature geothermal utilization and naturally occurring travertine deposits is similar based on the calculated p_{Me}. The mechanisms of their formation are probably distinct as observed from their microscopical appearance. Further study including experimental work is recommended for better understanding of this process and therefore development of a long term and sustainable solution to minimize it.
3) Although geothermal experience in Iceland show that calcite scaling is rarely present when the calcite SI is <0.4, mixing of saline and dilute waters might enhance calcite precipitation at lower SI.
4) The metals present in the calcite scales were immobilized mainly by formation of sulfide minerals in calcite matrix instead of their incorporation in calcite crystallographic structure.

ACKNOWLEDGEMENTS

This study is a part the EU funded project CHPM-2030 (Combined Heat, Power and Metal Extraction) Horizon 2020 research and innovation programme under grant agreement nº 654100. The authors would like to thank ÍSOR project managers Árni Ragnarsson and Daði Þorbjörnsson for supporting the idea of this study. Heimir Ingimarsson is acknowledged for delivering the scale samples and Sigurður Sveinn Jónsson for the XRD analysis. We thank Domenik Wolff-Boenish, Gunnar Þorgilsson, Tobias Weisenberger, Magnús Ólafsson, and Grétar Lárus Matthíasson for valuable discussion.

REFERENCES

Arnórsson, S., and Andrésdóttir, A.: Processes controlling the distribution of boron andchlorine in natural waters in Iceland. *Geochimica et Cosmochimica Acta,* **59**, (1999), 4125–4146.

Arnórsson, S.: Deposition of calcium carbonate minerals from geothermal waters-theoretical considerations. *Geothermics,* **18**, (1989), 33-39.

Arnórsson, S.: Mineral deposition from Icelandic geothermal waters, environmental and utilization problems. *Journal of Petroleum Technology,* **33-1**, (1981), 181-187.

Bai, L.P.: Chemical modelling programs for predicting calcite scaling, applied to low- temperature geothermal waters in Iceland. *UNU-GTP, Iceland, report* **3**, (1991), 45 pp.

Brown, K.L., and Dunstall, M.: Silica scaling under controlled hydrodynamic conditions, *Proceedings of the World Geothermal Congress 2000*, Kyushu- Tohoku, Japan, 3039-3044.

Brown, K.L.: Gold deposition from geothermal discharges in New Zealand. *Economic Geology*, **81**, (1986), 979-983.

Curti, E.: Coprecipitation of radionuclides with calcite: estimation of partition coefficients based on a review of laboratory investigations and geochemical data. *Applied Geochemistry*, **14**, (1999), 433–445.

Dominguez Benetton, X.: Flexible and versatile nanoparticle synthesis platform by gas-diffusion electrocrystallization. Proceedings of 19th Nano Congress for Next Generation. Journal of Nanomaterials & Molecular Nanotechnology, **6**, (2017), ISSN: 2324-8777.

Galeczka, I., Oelkers, E., and Gislason S.R.: The effect of 2014-15 Bárðarbunga volcanic eruption on denundation rates and the CO_2 budget. *Energy Procedia*, **146,** 201853-58.

Galeczka, I., Sigurdsson, G., Eiriksdottir, E.S., Oelkers, E. and Gislason, S.R.: The chemical composition of rivers and snow affected by the 2014/2015 Bárðarbunga eruption, Iceland. *Journal of Volcanology and Geothermal Research,* **316**, (2016), 101-119.

Galeczka, I., Wolff-Boenisch, D., Oelkers, E.H., Gislason, S.R.: An experimental study of basaltic glass-H_2O-CO_2 interaction at 22 and 50 °C: Implications for subsurface storage of CO_2. *Geochimica et Cosmochimica Acta,* **126**, (2014), 123-145.

Gislason, S.R., Arnórsson, S., and Armannsson, H.: Chemical weathering of basalt in Southwest Iceland; effects of runoff, age of rocks and vegetative/glacial cover. *American Journal of Science*, **296**, (1996), 837–907.

Guðjónsdóttir, S.R.: Selfossveitur. Eftirlit með efnainnihaldi jarðhitavatns árið 2017. Report in Icelandic (2018) ÍSOR-2018/012.

Gunnarsson, I., and Arnórsson, S.: Impact of silica scaling efficiency of heat extraction from high temperature geothermal fluids. *Geothermics*, **34**, (2005), 320-329.

Gunnlaugsson, E., Gislason, G., Ivarsson, G., and Kjaran, S.P.: Low temperature geothermal fields utilized for district heating in Reykjavik, Iceland. Proceedings World Geothermal Congress, (2000), Tohoku, Japan, May 28-June 10, 2000.

Hardardóttir V.: Metal-rich scales in the Reykjanes Geothermal system, SW Iceland: sulfide minerals in a Seawater-dominated hydrothermal environment. PhD thesis from the Department of Earth Sciences, Faculty of Science (2011), University of Ottawa.

Harðardóttir, V., Brown, K.L, Fridriksson, T., 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**, (2009), 1106-1106.

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.

Kaasalainen, H., and Stefánsson, A.: The chemistry of trace elements in surface geothermal waters and steam, Iceland. *Chemical Geology*, **330–331** (2012), 60-85.

Kitano, Y., Okumura, M., and Idogaki,M.: Abnormal behaviors of copper(II) and zinc ions in parent solution at the early stage of calcite formation. *Geochemical Journal*, **14**, (1980), 167–175.

Maimoni, A.: Minerals recovery from salton sea geothermal brines: a literature review and proposed cementation process. *Geothermics*, ***11*****(4)**, (1982) 239–258.

Morse, J.W., and Bender, M.L.: Partition coefficients in calcite: examination of factors influencing the validity of experimental results and their application to natural systems. *Chemical Geology*, **82**, (1990) 265–277.

Mroczek, E., Dedual, G., Graham, D., & Bacon, L. (2015). Lithium Extraction from Wairakei Geothermal Fluid using Electrodialysis. *Proceedings World Geothermal Congress*.

Neupane, G., and Wendt, D.S.: Assessment of Mineral Resources in Geothermal Brines in the US. Proceedings, 42nd Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, California, February 13-15, 2017,SGP-TR-212.

Neveu M., Desch, S.J., and Castillo-Rogez J.C.: Aqueous geochemistry in icy world interiors: Equilibrium fluid, rock, and gas compositions, and fate of antifreezes and radionuclides. *Geochimica et Cosmochimica Acta*, **212**, (2017), 324–71.

Ólafsson, M., Hauksdóttir, S., Thórhallsson, S., and Snorrason, Th.: Calcite scaling at Selfossveitur Hitaveita, S-Iceland, when mixing waters of different chemical composition. *Proceedings World Geothermal Congress*, (2005).

Olsson, J., Stipp, S., Makovicky, E., and Gislason, S.R.: Metal scavenging by calcium carbonate at the Eyjafjallajökull volcano: A carbon capture and storage analogue. *Chemical Geology*, **384**, (2014), 135–148.

Paranthaman, M. P., Li, L., Luo, J., Hoke, T., Ucar, H., Moyer, B. A., & Harrison, S.: Recovery of Lithium from Geothermal Brine with Lithium-Aluminum Layered Double Hydroxide Chloride Sorbents. *Environmental Science and Technology*, **51**, (2017), 13481–13486.

Parkhurst, D.L., and Appelo, C.A.J.: User's guide to PHREEQC (Version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations *Report*, (1999), 99−4259, p. 312.

Rae, A. J., Cooke, D. R., & Brown, K. L.: The trace metal chemistry of deep geothermal water, Palinpinon geothermal field, Negros Island, Philippines: Implications for precious metal deposition in epithermal gold deposits. *Economic Geology*, **106**, (2011), 1425–1446.

Rimstidt, J.D., Balog, A., and Webb, J.: Distribution of trace elements between carbonate minerals and aqueous solutions. *Geochimica et Cosmochimica Acta*, **62**, (1998), 1851–1863.

Sigfússon, B., and Gunnarsson, I.: Scaling prevention experiments in the Hellisheidi power plant, Iceland. *Proceedings of the 36th Workshop on Geothermal Reservoir Engineering*, (2011), Stanford University, Stanford, California, 5 pp.

Simmons, S.F., and Brown, K.L.: Gold in magmatic hydrothermal solutions and the rapid formation of a giant ore deposit. *Science* **314**, (2006), 288-291.

Simmons, S.F., and Brown, K.L.: The flux of gold and related metals through a volcanic arc, Taupo Volcanic Zone, New Zealand. *Geology*, **35**, (2007), 1099-1102.

Stockmann, G.J., Wolff-Boenisch, D., Bovet, N., Gislason, S.R., and Oelkers, E.H.: The role of silicates surfaces on calcite precipitation kinetics. *Geochimica et Cosmochimica Acta*, **135**, (2014), 231-250.

Stumm, W.: Chemistry of the Solid–Water Interface: Processes at the Mineral–Water and Particle–Water Interface in *Natural Systems*. Wiley, (1992), New York.

ThermoScientific: Dionex ICS-2100 Ion Chromatography, System Operator's Manual, Document No. 065291, Revision 03, © 2012 by Thermo Fisher Scientific Inc. October 2012

ThermoScientific: Thermo Scientific iCAP 7000 Series ICP-OES: Innovative ICP-OES Optical Design, Technical Note 43153, © 2013 Thermo Fisher Scientific Inc.

van den Heuvel, D., Gunnlaugsson, E., Gunnarsson, I., Stawski, T., Peacock, C., Benning, L.G.: Understanding amorphous silica scaling under well-constrained conditions inside geothermal pipelines. *Geothermics*, **76**, (2018), 231-241.

Voigt, M., Marieni, C., Clark, D.E., Gislason, S.R., and Oelkers, E.H.: Evaluation and refinement of thermodynamic databases for mineral carbonation. *Energy Procedia,* **146**, (2018), 81-91.

Zuddas, P., and Mucci, A.: Kinetics of calcite precipitation from seawater II: The influence of the ionic strength. *Geochimica et Cosmochimica* Acta, **62**, (1998), 757-766.