A review of mineral scaling and its mechanisms in Hveragerði geothermal district heating system

Almar Barja

Thesis of 60 ECTS credits
Master of Science in Energy Engineering - Iceland School of Energy

January 2014

A review of mineral scaling and its mechanisms in Hveragerði geothermal district heating system

Almar Barja

Thesis of 60 ECTS credits submitted to the School of Science and Engineering
at Reykjavík University in partial fulfillment of
the requirements for the degree of
Master of Science in **Energy Engineering - Iceland School of Energy**

January 2014

Supervisors:

Dr. Einar Jón Ásbjörnsson, Supervisor
Assistant Professor, Reykjavik University

Dr. Vigdís Harðardóttir, Co-Supervisor
Geochemist, ÍSOR

Examiner:

Halldór Ármannsson, Examiner
Geochemist, ÍSOR

A review of mineral scaling and its mechanisms in Hveragerði geothermal district heating system

Almar Barja

60 ECTS thesis submitted to the School of Science and Engineering
at Reykjavík University in partial fulfillment
of the requirements for the degree of
Master of Science in Energy Engineering - Iceland School of Energy.

January 2014

Student:

_____

Almar Barja

Supervisors:

_____

Dr. Einar Jón Ásbjörnsson

_____

Dr. Vigdís Harðardóttir

Examiner:

_____

Halldór Ármannsson

A review of mineral scaling and its mechanisms in Hveragerði geothermal district heating system

Almar Barja

January 2014

Abstract

Precipitation from geothermal fluid cause serious problems during operation. Clogging of wells, surface equipment and corrosion of pipes are examples of problems arising during production. Many of the problems can be averted or reduced if sufficient research and experience exists beforehand on the reservoir and chemical composition of the geothermal fluid. During production, temperature of the fluid decreases and it boils, leading to super saturation and precipitation of certain minerals. The most common minerals, such as calcite and amorphous silica are well known and extensive research exists on solubility and precipitation rates. Other minerals are often a product of interaction between mixing of geothermal fluid with groundwater and corrosion of surface equipment. Hveragerði district system was established in the 1950s and has since than experienced many different operational problems due to the high dissolved content of the geothermal fluid available. Recently a new scaling mineral was observed in a heat exchanger in Hveragerði. The scale was analyzed by geochemists at Ísor and their findings published in a report for the municipality of Hveragerði. Their findings revealed that the majority of the scaling was made of the iron-carbonate, siderite. Chemical analysis was done on the fluid from the well in 1980 which showed no iron present in the fluid. The iron was assumed to be present due to corrosion within the pipes leading from the well and precipitating in the heat exchanger as iron-carbonate. This paper reviews the results presented in the report and analyses the possibility of sulfide scaling within the pipes due to a reaction between H2S present in the fluid and the dissolved iron. The reason for the precipitation of siderite is also examined since siderite has a retrograde solubility and should not precipitate due to decreasing temperature.

Yfirlit yfir útfellingar í hitaveitum

Almar Barja

Janúar 2014

Útdráttur

Útfellingar úr hitaveitum og jarðvarmavirkjunum er viðvarandi vandamál sem taka þarf tillit til þegar slík kerfi eru hönnuð. Stíflaðar borholur og búnaður ásamt tæringu eru nokkuð algeng vandamál tengd jarðvarmavirkjunum og hitaveitum. Sé til þekking á efnainnihaldi jarðvarmavökvans er hægt að hanna virkjanir og haga vali í pípum þannig að sniðgengið er framhjá mestu vandamálunum. Þegar vökvinn síður eykst styrkun uppleystra efna í vökvanum. Sé styrkurinn nægilega hár fara útfellingar að myndast sem geta stíflað og eyðilagt búnað. Algengustu útfellingarnar eru kalsít og myndlaus kísill. Kalsít fellur aðallega út í borholunum sjálfum á ákveðnu dýptarbili. Algengast er að kísillinn falli út við hitastigslækkun vökvans. Bæði þessara útfellinga hafa skapað vandamál við íslenskar hitaveitur á háhitasvæðum. Hitaveita Hveragerðis er ein af fyrstu hitaveitunum á Íslandi til að nota háhitavökva við upphitun. Mikil vandamál sköpuðust varðandi útfellingar og stífluðust borholur ítrekað vegna kalsít útfellinga. Allar borholur í Hveragerði fella út kalsít og til að afköst haldist, þarf að bora út útfellingarnar árlega. Árið 2012 var nýtt uppblásið íþróttahús byggt í Hveragerði og var jarðvarmavökvi úr holu HV-04 fenginn til að knýja alla upphitun og uppblásun í íþróttahúsinu. Stuttu eftir að íþróttahúsið var tengt holunni fóru að myndast útfellingar í varmaskipti íþróttahússins. Jarðefnafræðingar Ísor voru fengnir til að greina útfellingarnar og skrifa skýrslu fyrir sveitarfélagið. Niðurstaða skýrslunnar var sú að meginuppistaða útfellingarinnar var járnkarbónatið siderít. Vökvinn úr HV-04 var greindur árið 1980 og leiddu þær niðurstöður í ljós að ekkert járn er í vökvanum. Járnið, sem myndar uppistöðuna í útfellingunni, hlýtur því að koma annarsstaðar frá. Niðurstöður Ísor voru þær að járnið tærist úr pípunum á leið í íþróttahúsið.

Acknowledgements

Contents

List of Figures

x

List of Tables

Chapter 1

Introduction

Natural waters are usually undersaturated with regard to all common minerals in the Icelandic bedrock[1]. As the water filtrates through the crust it heats up and dissolves minerals and precipitates others until it reaches equilibrium[2]. If the thermal energy of the geothermal fluid is to be extracted it has to be brought to the surface. During production the fluid will boil and its temperature will decrease, both of which can lead to precipitation of minerals and clog surface equipment. It is therefore extremely important to grasp a good understanding on the complex affects pH levels, saturation levels and temperature have on saturation levels of different minerals. Much has been written on solubility of the most common scaling minerals. In Iceland all geothermal waters are in equilibrium with quartz and chalcedony at a reservoir level[3]. Amorphous silica scaling in surface equipment is very well known in Iceland and prevention methods, such as dilution, are well known. In the first district heating systems the geothermal fluid was diluted with cold groundwater, which was found to cause silicate scaling. Kristmannsdóttir et al.[4] established the reason for this scaling to be the retrograde solubility of silicate and degassing of the fluid mixture. Hveragerði district heating system was established in 1940 and has ever since suffered calcite, amorphous silica and silicate scaling[5]. Recently an inflated sport-center was connected to a borehole in Hveragerði. Transferring the heat from the geothermal fluid to the inflating equipment is a heat exchanger located outside the sports-center. In the heat exchanger a new type of scaling was found. The scaling was analysed and results revealed it to be siderite, an iron-carbonate[6].

Hveragerði was chosen as an area of interest due to its long history with geothermal energy and numerous boreholes. Hveragerði has also provided many problems for the district heating system operators. Most of the common scaling minerals have been there and dealt with. The appearance of siderite in a heat exchanger provides many questions

regarding the complex interactions between the surface equipment and the geothermal fluid. The heat exchanger is fed through borehole HV-04, where fluid chemical analysis exists. The fluid was analysed in 1980 but the data is available in the National Energy Authority's database. The scaling was analysed by geochemists at ÍSOR and samples sent to Canada for further analysis. This paper will review the results published by ÍSOR regarding scaling from well HV-04 and an attempt will be made to further analyse the system with regards to the available chemical analysis of the geothermal fluid.

In this paper a review of scaling mechanisms and the most common scaling minerals found in Iceland will be presented. The area of interest, Hveragerði, will be introduced and a brief overview of the history of the district heating system and the problems it has faced discussed.

Chapter 2

Background

2.1 Geology of Iceland

Iceland is an extremely active volcanic island in the middle of the North-Atlantic ocean. It's origins date back over 55 m.y ago with the opening of the Atlantic Ocean [7] through the divergent plate boundary separating the Eurasian and North-American plates. The continuous volcanic activity in Iceland and the relatively thin and hot crust leads to an abnormally high geothermal gradient within the Icelandic volcanic zones[8]. The geothermal gradient contributes to the numerous low-temperature geothermal reservoirs found all over Iceland. The majority of volcanic eruptions in Iceland are basaltic with rhyolitic eruptions only occurring in evolved volcanic systems.

There are currently nine active volcanic zones with individual volcanic systems, usually recognized by a fissure swarm and a central volcano near the center of the fissure swarm (see Figure 1)[7]. The thermal energy from volcanic eruptions or intrusions and the added permeability brought by fissures is a major contributor towards the formation of high-temperature geothermal reservoirs.

2.1.1 Icelandic basalts

Iceland's basalts are divided into three igneous rock series. The alkalic, transitional alkalic and tholeiitic series. The tholeiitic basalts are of the closest resemblance to the relatively homogeneous Mid Atlantic Ridge (MAR) and other Mid Ocean Ridge Basalts (MORB)[10].
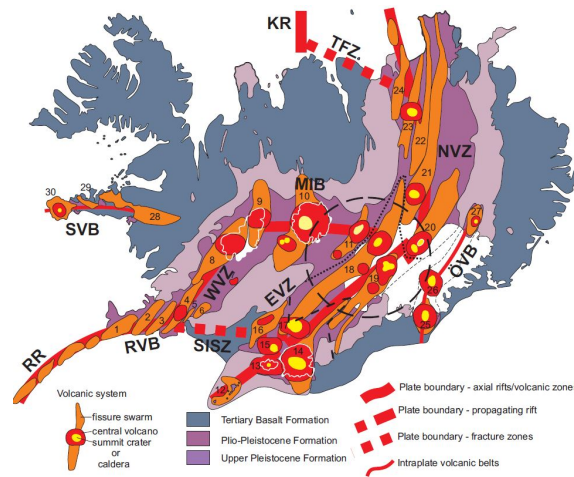
Figure 1: The 24 active volcanic zones in Iceland[9]

Major and Minor Elements

When discussing elements in rocks, a simple guide is used when a definition is needed between Major, Minor and trace elements[10].

$$Major\ elements > 1.0\ wt.\%$$
$$Minor\ elements\ 0.1\text{-}1.0\ wt.\%$$
$$Trace\ elements < 0.1\ wt.\%$$

Since rock dissolution and deposition of secondary mineral is the biggest contributor of TDS in geothermal fluids, the composition of the rocks is very important.

2.1.2   Major minerals

By viewing Table 1 it is clear that there is a great variation in chemical composition of rocks depending on their origin and type, which translates into a great difference between geothermal fluids (see Table 2).

Table 1 lists concentration of elements as oxides and from that it is clear that the two most abundant elements in the crust are oxygen and silica. That is also evident when analysing scales from geothermal fluids as amorphous silica is usually the biggest contributor to scaling on the surface. A much more complex process happens at reservoir level where the fluid dissolutes primary minerals and precipitates secondary minerals. The secondary minerals form when the fluid becomes sufficiently supersaturated with regards to specific components under correct conditions. Given time, the geothermal fluid will come

Table 1: Average Analysis of MORBs and Selected Samples, Major and Minor elements

Oxide (wt%)	Avg MORBs[1]	Granite[2]	Tholeiite[3]	Olivine-tholeiite[4]
SiO_2	50.5	71.6	50.7	47.07
TiO_2	1.56	0.2	0.8	1.66
Al_2O_3	15.3	11.7	17.7	14.86
FeO_x	10.5	4.0	10.5	11.28
MgO	7.47	0.2	6.4	8.52
CaO	11.5	0.5	11.3	11.47
Na_2O	2.62	5.5	2.0	2.24
k_2O	0.16	4.7	0.3	0.2
P_2O_5	0.13	0.0	0.1	0.18
Total	99.74	99.5	99.8	97.48

[1] Average of samples from MORBs[10]
[2] Samples of Granitic rocks from Ascension, South-Atlantic ocean[11]
[3] Avg of samples from tholeiitic basalts[12]
[4] Samples from Olivine-Tholeiit rocks in Kistufell, East Iceland [13]

close to reaching equilibrium between dissolution of primary minerals and precipitation of secondary minerals[14].

These are the main contributors towards altered chemical composition of geothermal waters. Alteration rates of minerals are well studied and the order in which the primary minerals alter at a laboratory level are quite well known. Volcanic glass is the first to be altered, then Olivine, Pyroxene and Plagioclase[15].

Secondary Minerals

At a reservoir level in Iceland geothermal fluids are close to equilibrium with most all major aqueous species. Cl equilibrium in geothermal fluids is very interesting as it's very soluble. It dissolves from rocks, even though Cl bearing minerals are poor in Icelandic lavas. As Cl reaches supersaturation it precipitates easily soluble salts. The type of secondary minerals formed is very much affected by the temperature at which the minerals precipitate. Each mineral is stable over a limited temperature range. As temperature increases or decreases these minerals become unstable, dissolve and different minerals form if the fluid is supersaturated with regard to specific elements [16]. Figure 2 shows the most common secondary minerals and their range of temperature stability.

Different minerals can form from the same components. The product is affected by more than chemical composition as pressure and temperature also affect crystallization[10]. A
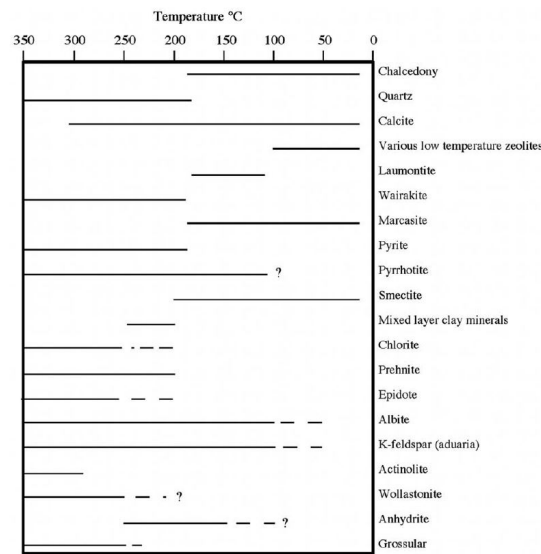
Figure 2: Mineral Stability of secondary minerals[17]

good example of the different minerals formed based on temperature is silica, the most abundant dissolved solid in geothermal fluids. It precipitates as amorphous silica at the surface, as chalcedony at temperatures <200°C and as quartz at higher temperatures. Quartz and chalcedony precipitate at much slower rates than amorphous silica making them very uncommon scales in surface equipment, even though high levels of supersaturation have been reached. The most common secondary minerals are listed in Figure 2 and the ones relevant to geothermal utilization are listed in section 2.6.1.

The geothermal fluid can alter the surrounding rock by substituting certain ions from the minerals' crystal structure and dissolving them in the fluid. The substituted ions are usually of a similar size or charge as the original ion but due to the alteration, the crystal structure becomes less stable. As long as temperature or pressure of the rock does not change drastically or no new undersaturated fluids mix with the original fluid, the alteration minerals will remain intact[1].

2.2   Geothermal energy in Iceland

The geothermal resource is classified into many different categories based on its properties. The simplest classification is based on water temperatures at 1000 m depth, dividing them into low- and high-temperature reservoirs. This classification was first proposed by Gunnar Böðvarsson [18] and then improved by Ingvar Friðleifsson[19]. Low-temperature fields are defined as having temperatures <150°C and high-temperature >150°C. This classification is very practical when it comes to categorizing geothermal reservoirs for

potential development as water temperature is the most important factor for electricity production. Different classifications have been proposed such as liquid-dominated and vapour-dominated geothermal reservoirs[20], but are more relevant to high-temperature reservoirs since steam is rarely present in low-temperature reservoir. All reservoirs in Iceland are naturally liquid-dominated but localised steam pockets have, for example, been found in Nesjavellir[21]. Production in Svartsengi has caused a minor drawdown in water table levels forming a steam cap[21].

Most geothermal fluids are of meteoric origin but alternatives, such as sea-water dominated reservoirs exist. An example of a seawater dominated reservoirs is the Reykjanes geothermal field. Some fields, such as Svartsengi geothermal field, show signs of a mixture between meteoric and seawater origin [22]. Recharge sites of geothermal fields are important to gain a better understanding of groundwater flow and potential extraction from geothermal wells. Deuterium analysis on geothermal fluids has been used to identify recharge sites and the origin of the groundwater feeding the reservoirs[2].

High-temperature

Iceland's high temperature fields are situated within the active volcanic zone or near its margins on very young active volcanic areas that offer good permeability. Fissure swarms and faults offer extra permeability and are common in and around high-temperature fields. Iceland's high-temperature fields are mostly due to magma intrusions or magma chambers which provide the geothermal field with thermal energy. High-temperature fields are defined as areas where the temperature is >150°C at 1 km. depth. Surface manifestations of high-temperature geothermal energy varies depending on depth to water levels. In high altitude areas, such as mountains, a stem cap can be formed. The high pH levels of the steam alter and dissolve the surface rock, leading to fumaroles, steam vents and mud pools. In other lower lying regions or regions with a high groundwater table, the surface manifestations can be more modest, hot pools or hot rivers.

The water seeps down the bedrock through cracks. As it nears the heat source it heats up and rises to the surface due to buoyancy and thermal expansion. If magma is present it can release gases which combine with the water and lower its pH. The low pH in the water increases the waters ability to dissolve silica and other minerals from the surrounding rocks creating fluid with higher dissolved solids. The chemistry of geothermal waters will be further explained in section 2.4.1.

Iceland's high-temperature geothermal fields have been used for electricity production since 1969 when a small back pressure power plant was built in Bjarnarflag. Today

geothermal resources generate 27% of Iceland's electricity and supplies about 90% of space heating energy demand[23]. Over 20 active high-temperature fields are found in Iceland and all of them are in or close to the active volcanic belts and most of them are surrounded by active fissure swarms that create sufficient permeability.

Low-temperature

The low-temperature geothermal fields are found outside the active volcanic zones where the geothermal gradient is still high. The geothermal gradient near the active volcanic zones is abnormally high, can vary from 50°C/km up to 150°C/km[24], and heat up circulating groundwater. The water in low-temperature areas is either driven by a hydraulic head or a local density driven convection systems, transporting the hot fluid to the surface[25].

The most potent low-temperature systems lie just outside the active volcanic zone where the bedrock is still affected by the tectonic mechanics. Surface manifestations within low-temperature fields are much more modest than high-temperature fields with warm or boiling springs being the most common manifestations. The most potent low-temperature field in Iceland is in Reykholt where the main spring is the Deildartunguhver, one of the most largest hot spring in the world with about 180 l/s of 100°C water[26]. It is now used for heating up nearby towns and farms. Low-temperature fields do not always have surface manifestations, but have been known to create a fertile environment for vegetation. Recent advances within the field of geothermal exploration have revealed many new geothermal fields that were previously unknown due to the lack of surface manifestations.

2.2.1   Geothermal utilization in Iceland

Geothermal energy is extremely widespread in Iceland and is the nation's most important energy source with 69% of its primary energy coming from geothermal energy in 2013. Most of that energy goes into space heating and 90% of households use geothermal energy for heating. The remaining 10% live in areas without access to geothermal energy and have to resolve to electric heating[23]. Five high-temperature fields have been developed for electricity generation, the Námafjall field in 1969, the Krafla field in 1977 and expansion in 1996, the Svartsengi field has been in continuous development since 1979, the Hengill/Nesjavellir fields has been in development since 1990 with expansions in 1998 and the Hellisheiði power plant in 2006 and the Reykjanes field also in 2006. De-

velopment of the Þeistareykir geothermal field is currently under way with an estimated potential of 270 MW of installed capacity. The first phase, 45 MW, is currently under construction with further research boreholes scheduled in the next years[27].
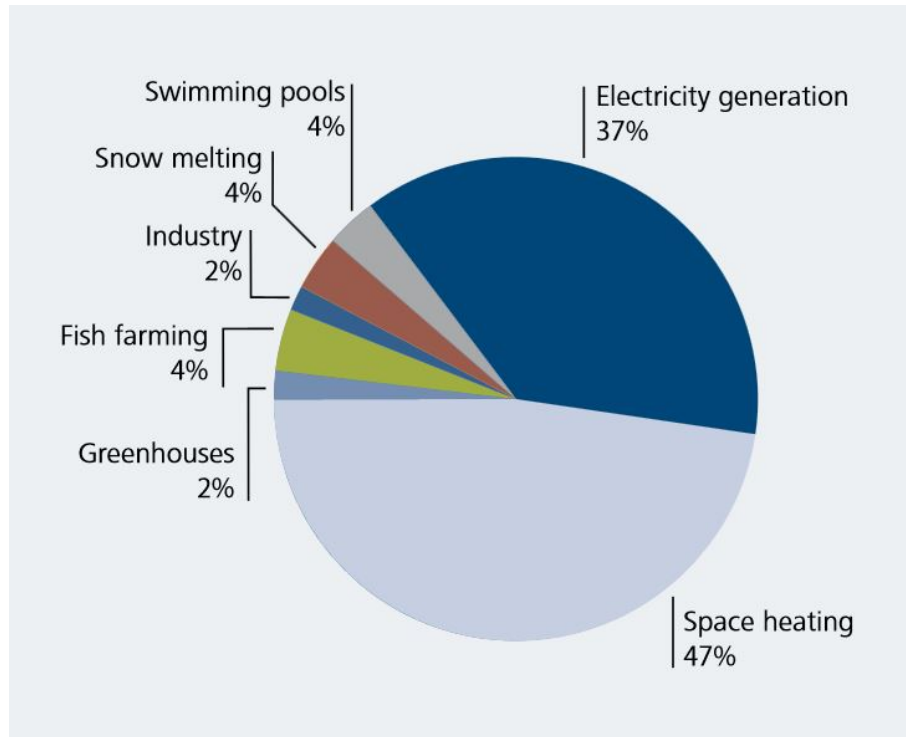
Figure 3: Overview of geothermal energy use[28]

Geothermal energy has been utilized since settlement when farmhouses were conveniently built near hot springs. The warm water was then used for bathing and washing[29]. Population increase and the migration from farms to towns led to centralised district heating systems. At first they were coal and oil powered but the increasing demand for cleaner energy and the sharp price spikes during the 20th century paved the way for geothermal powered district heating systems.

In 1950 about 25% of households in Iceland were heated by geothermal energy. The Oil Crisis in the 1970s created further incentives for investments in geothermal energy and in the following decades municipality or state owned district heating systems where installed in all major towns[30]. Today geothermal energy reaches 90% of Iceland's population, while the rest use electric or oil heating[28]. A recent study assessed the economical benefits from using geothermal over fossil fuels to be more than ISK 1,3 trillion for the years between 1970 and 2009 and roughly ISK 70 billion/year for 2008 and 2009[31].

2.2.2   District heating systems in Iceland

Geothermal utilization for district heating started in 1928 when 14 boreholes where drilled in Laugarnes in Reykjavík[32]. The water available through these boreholes was not sufficiently hot for electricity production but suited fine for a district heating system. The first buildings connected to the new district heating system was an elementary school and a swimming pool in Reykjavík. The Laugarnes field was not able to supply but a part of Reykjavík's inhabitants and it was therefore decided to start exploration in Mosfellsdalur, the same field where district heating experiments started in Iceland. The project was completed in 1943 when the first houses where connected to the new district heating system. This improvement brought hot water to 2850 houses in the Reykjavík area and the system reached about 50% of the inhabitants. Development continued with more boreholes in Mosfellsdalur and the installations of deep well pumps increased the capacity even further[32].

During these times many municipalities all over Iceland started investing in geothermal district heating systems. The first one outside Reykjavík was built in Ólafsfjörður and in 1944 connections had been made to all inhabitants of the town, the first town in Iceland entirely heated by geothermal energy. The same system has been running ever since, apart from regular maintenance[30]. This development continued in Iceland the next years and in 1955 geothermal district heating systems had been established in the majority of places where the resource was known to be available. Many public boarding schools where also built in areas that had easy access to hot springs. Many of these buildings are still in use and are still heated up by a local hot spring. In 1973 the oil crisis hit the world with the sharp increase in oil prices that followed. This created a huge incentive for further investments in geothermal energy and in the following decade 16 new district heating systems were established and power plants using geothermal energy for electricity generation where built. The first one was built in Bjarnarflag in 1969 and produced 3.5 MW, followed by Krafla in 1977, Svartsengi in 1979, further expansions of Svartsengi power plant and then Nesjavellir power plant in 1990. Both Svartsengi and Nesjavellir were built primarily for providing hot water for district heating systems where the hot steam and separated fluid would heat up cold groundwater and use that for the district heating systems. They were later expanded, more wells drilled and turbines installed for electricity generation. Later power plants such as Hellisheiði power plant and Reykjanes power plant on the other hand were built with electricity production in mind and hot water as a by-product. The Nesjavellir power plant currently has a installed capacity of 120 MW_{el} and 300 MW_{th}. Hellisheiði power plant on the other hand has capacity of 303 MW_{el} and only 133 MW_{th}[33].

A very interesting experiment was conducted in Westman islands following the 1973 volcanic eruption. The cooling lava was used as a heat source for the town's district heating system. Cold water was pumped on top of the lava where it trickled down the exterior layers, heated up, evaporated and the steam collected. Holes where drilled in the lava and it covered with plastic to help with the steam gathering. The steam was then used to heat up a closed loop system connecting the entire town of Vestmannaeyjar. This system worked for nearly 15 years until the top layers of the lava had cooled too much[32]. Similar ideas surfaced on creating similar systems where lava eruptions occurred and even producing electricity but technical aspects and difficulties along with a very high potential levelized cost made these ideas unlikely[34].

2.3 Hveragerði

The municipality of Hveragerði was established in 1946. At that time the population consisted mostly of farmers using the available geothermal energy within the town[30]. The people living in the area adapted their lives to the high activity by installing primitive district heating systems from the nearest hot pool. These systems where built from pipes or wooden ducts and the heat used used to heat up radiators. The town is built on land that bears witness to much alteration as can be seen by the numerous hot pools and mud pools in the geothermal area in the middle of the town. The surface manifestations of the Hveragerði geothermal area change constantly and geysers that used to erupt regularly have stopped their activity. Following the 2008 earthquakes there have been major changes in the activity just north of Hveragerði as a new area is increasing in surface activity and many hot pools and mud pools have opened that previous to the 2008 earthquakes where non-existent[35].

2.3.1 History of Hveragarði district heating system

The first space heating equipment in Hveragerði was very primitive, usually only a pipeline, often made of wood, from a nearby hot pool into a single house central heating system powering radiators. It wasn't until the Hveragerði district heating system was established that an effective space heating mechanism was installed for the majority of houses in Hveragerði[30].

During its first years the district heating system operated on two different systems. For bigger customers, greenhouses and other industry, the district heating system supplied

them with liquid and steam directly from a borehole. This system was open ended and the customers charged based on the size of the property. From each property the water would be injected down the drain or into the river that crosses Hveragerði. Residential customers were connected to a different set-up as each house had a small heat exchanger powering an individual closed-loop heating system connected to indoor radiators[5].

As the village grew the need for heating increased and in 1955 two central heat exchangers were installed near the wells creating a double system. These heat exchangers eliminated the problem of scaling at a residential level as the residential areas were getting cold groundwater heated up through the heat exchangers. Newer greenhouses built in that period were also connected to the double system. Finally, after continuous growth the double system could no longer supply the village with enough water and in 1972 construction started on building a steam separator and a storage tank near well HV-04, which was originally built to supply a planned geothermal power station with steam. The well is outside the village and to maintain pressure on the system the storage tank was built. The separated water was stored in the tank before flowing into the district heating system in Hveragerði[5]. Due to the high concentration of dissolved solids, problems with scaling within the system started. A year later experiments started by adding cold water from a nearby river to the geothermal liquid before it entered the town. These experiments gave mixed results and in 1978 construction started on improving the system by using the separated steam to heat up cold groundwater and using that mixture for the district heating system. This proved to be a successful change and in the following years another separator was added that allowed the addition of the separated liquid for colder days and days of cold water drought[5][36]. This change meant that the biggest proportion of the chemically rich separated liquid was not used in the district heating system leading to a drastic decrease in Al-silicates and silica. However, the use of the cold groundwater led to Mg-silicate scaling in pipelines in Hveragerði. The problem of Mg-silicate scaling had never been a problem in Icelandic district heating systems before Hveragerði which started much research on the topic to explain the existence of the Mg-silicate under these conditions. The district heating system of Námafjall also experienced problems with mg-silicate scales due to similar reasons[37][38].

The current system relies on a heat exchanger station at Bláskógar in Hveragerði to supply most parts of town with hot water. Currently only two wells are used, HS-08 and HS-09. Only one is in operation at a time but their use is alternated between summer and winter to allow for maintenance. The liquid is reinjected from the heat exchanger station into wells HS-07 and HS-03 as well as any excess liquid flowing from the production wells.

From the heat exchanger station comes the double district heating system, which is a closed loop system powering a smaller cycle at each residential building through individual heat exchangers. This system has been experiencing losses of water only explainable by a leak somewhere within the system[39].

The steam system at Hveragerði has been in operation since the establishment of the district heating system and supplies customers with two-phase liquid. It has been relatively free of corrosion and scaling. Today the steam system supplies the oldest greenhouses and residential areas in Hveragerði. It feeds the system directly from the well before the geothermal liquid enters the heat exchanger station. Due to the high pressure maintained on the steam system it is able to supply up to 160°C water which under atmospheric pressure is in steam form. A big flaw to the system is that it is only one-way meaning the water is thrown down the drain once it has been used, leading to huge waste[39].

2.3.2   Boreholes in Hveragerði

The National Energy Authority maintains a database on all boreholes drilled in Iceland. A perfect record exists of all wells drilled for public authority and private boreholes in recent years. In Hveragerði during the first half of the 20th century many wells were drilled and funded by local farmers, industry or other private entities. Some of these wells have been entered into the database. Most of these wells have been documented in news articles and other reports. A detailed report was made by Þorgils Jónasson in 2008[5] listing many of the privately and publicly owned boreholes in Hveragerði.

Due to constant clogging the wells needed to be cleaned regularly of calcite scales. Most of the wells build up such quantities of calcite that they need annual cleaning. Some of the boreholes were dry after drilling and have either been decommissioned or used for re-injection. All the wells that are suitable for the district heating system are free flowing so there is no pumping system connected to the boreholes[5].

All free flowing wells in Hveragerði suffer the same problem, if the flow from the well decreases suddenly, the backpressure will cause a bubble of condensed steam to form within the well. The bubble acts as a plug which will stop all flow from the well. To start the flow the water needs to be extracted from the well by blowing it out. This can cause minor steam explosions. Solutions to those problems have been to install a valve that redirects all excess water down a reinjection well. This maintains stable pressure within the wells, preventing the condensing of the steam within the well[39].

HS-boreholes

The HS-boreholes are the boreholes drilled for the municipality of Hveragerði and used for the town's district heating system. They were funded by the Hveragerði district heating system and the municipality.

Most of the wells were drilled outside any residential area but with rapid expansion of Hveragarði in recent years, many wells are now inside the town's limit. Due to extraction of the fluid from the geothermal reservoir many surface hot pools went extinct and residential areas were commissioned in zones where previously, surface activity had been present.

The first borehole in the HS-series (HS-00) was drilled over a period of one month in 1946. The well was shallow, only 49 m and used when the district heating system was established a few years later. Well HS-01 was drilled in 1957 to replace the shallower HS-00 as the source for the district heating system. HS-02 was drilled a few years later, in 1959, and was used in the district heating system along with HS-01 for the first decades. Both wells have been cleaned over 40 times and were used until HS-08 was drilled in 1989. Boreholes HS-03, HS-04 and HS-05 were drilled in the period between 1963-1968. HS-03 and HS-05 have been used as either re-injection wells or production wells since but HS-04 was unusable from the beginning. HS-06 and HS-07 were drilled in 1979 and HS-07 deepened in 1999 but has never been used. HS-06 was used for a short time but was destroyed when cold groundwater entered the well and cooled it down. The well has been used for re-injection since then[5].

Wells HS-08 and HS-09 are more recent, drilled in 1989 and 1999, and are more powerful than previous wells. They are the only two boreholes still in operation and they take turns in supplying the district heating system with power. Well HS-08 gives approximately 150°C mixture of liquid and steam and free flowing gives about 80 l/s or an estimated 20 MW_{th}[5][39].

HV-boreholes

The HV boreholes are a series of 8 wells drilled between 1958-1961 intended for a small geothermal power plant outside Hveragerði. The power plant was supposed to produce 35 MW_e but the plans were abandoned a few years later[5]. Plans for building a small geothermal power plant in the valley north of Hveragerði surface occasionally either in the form of a 35 MW_e or a 15-17 MW_e binary power plant[40].

These boreholes were relatively deep compared to other wells drilled in that period and were funded by governmental energy funds. Two of the boreholes reach almost 1000 m depth but first plans were to drill a total of 10 wells with some reaching 2000 m[41]. The wells have not gone to waste as they have either been used for farmhouses, a sports-center and the agricultural university in Hveragerði.

2.4   Chemistry of geothermal fluids in Iceland

The general definition of a geothermal fluid is a fluid that consists of a mixture of aqueous and gaseous that have been heated up by hot rocks or magma degassing. They act as the transport media for subsurface thermal energy and can vary greatly in chemical composition, pH, and phases all depending on the fluids origin, temperature, rock dissolution and formation of secondary minerals[3].

To further categorize geothermal fluid, a distinction is made between primary and secondary fluids[25].

- **Primary fluid** is the mixture of the original water (meteoric or seawater), dissolved minerals and magmatic volatiles that reach the deepest level of penetration in the reservoir and highest temperature and dissolved solid content.

- **Secondary geothermal** fluids is used for all geothermal fluids, after they reach their deepest level of penetration and highest solid content. The factors that can affect the composition of the fluid are: mixing with colder groundwater, boiling due to pressure decrease and the formation of secondary minerals due to changes in the fluid's system. These processes will be discussed in greater detail in section 2.4.1

The study of the origin of geothermal fluids and composition of the primary fluids can give valuable information on reservoir temperature, inflow to the reservoir and fluid mixing. By analysing ratios between elements a geothermometer can be used for temperature prediction at reservoir levels[42]. All geothermometers are based on the principle that the fluid is in equilibrium with secondary minerals at its highest temperature and as they cool down the elements are used to form secondary minerals in known ratios. Extensive work has been done on geothermometers, most notable is the work done by Fournier and Truesdell[43], Fournier[44] and Arnórsson et al.[42]. Mixing and upflow models are available to correct for changes in chemical composition due to boiling and mixing with shallower groundwater. By compiling these models as well as known solubility equations into specific software an assessment of reservoir conditions can be made[42].

2.4.1   Factors Affecting Chemical Composition

The chemical composition of a geothermal fluid is affected by many external factors. Most geothermal fluids start out as meteoric water and therefore have very low concentration of dissolved solids. The original fluid is undersaturated with regard to the most common minerals in the bedrock. The major element composition of geothermal fluids is largely controlled by dissolution of primary minerals and equilibrium with secondary minerals. Other factors such as temperature, pH, access to magmatic volatiles and inflow or mixing with other fluids can also have a big impact on the final chemical composition.

Origin of water

is usually meteoric water which has a very low concentration of dissolved when it trickles through the surface to the geothermal reservoir. As can be seen in Table 2 the total dissolved solids (TDS) of meteoric water is in the range 100-250 ppm compared to >36000 ppm in seawater[45]. The origin of the fluid can therefore have a significant impact of TDS of geothermal fluids. Geothermal fluid originating in seawater can only be seen in coastal reservoirs where the bedrock allows for easy penetration of the seawater to deeper levels. Reykjanes (Table 2 and Figure 1), with its heavily fractured bedrock, is a perfect example of a seawater dominated reservoir. It is interesting to compare the composition of the geothermal fluid from Reykjanes and Svartsengi. The fluid in Svartsengi is a mixture of seawater and meteoric water as can bee seen by comparing the chloride concentrations in Table 2[25]. Icelandic basalts generally have very low Cl concentrations[25] which increase the benefits of using Cl to deduce seawater portions[46].

Isotopes in geothermal fluids

within the geothermal fluids are used assessing water age and origin. The two isotopes that are used are deuterium ^{2}H and Oxygen ^{18}O. Deuterium levels in geothermal fluids are compared to those of local precipitation where anomalies can give further evidence of the fluids' origin. In Iceland lower deuterium levels have been explained as originating from higher altitudes within Iceland and distance from shore. Árnason[47] did extensive work on mapping hydrothermal systems in Iceland based on deuterium levels and mapped out the ratios of present day precipitation (Figure 4). Elevated levels of deuterium have been linked to mixing with magmatic waters from andesitic volcanism[48] or from direct contact with hot rock[49]. Anomalies from local ^{18}O precipitation levels have been

linked with rock interactions but results vary between fields[1]. Other isotope ratios such as $^3He/^4He$ and $^{34}S/^{32}S$ have also been used for determining the origin of groundwater. Helium isotope ratios give evidence of depth of heat source and Sulphur isotopes have been used for distinguishing between marine and rock leaching sources[1].
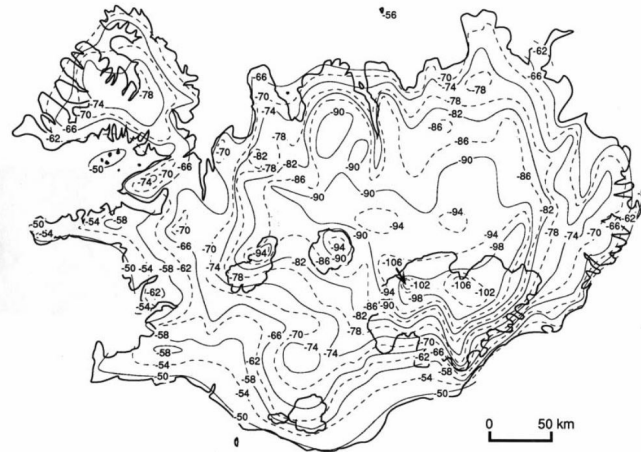
Figure 4: Measured deuterium levels in Iceland[50]

The most common variables and processes that affect the chemical composition of geothermal fluids are:

- **Rock dissolution and precipitation of secondary minerals** is by far the most important process contributing to geothermal fluid chemistry. When meteoric water starts seeping down towards the reservoir it is undersaturated with most, if not all, common minerals. As the fluid reaches deeper penetration it heats up and reaches equilibrium with the surrounding rocks by dissolving primary minerals until it becomes saturated with a secondary mineral. Perfect equilibrium is only obtained if the fluid acts as it is in a closed system, that is if no circulation or inflow takes place. This is rarely the case so how close the fluid comes to reaching a perfect equilibrium is affected by reaction time, formation rate of secondary minerals and the rate of recharge. Rock dissolution will be discussed in further detail later (Section 2.6.1[1]).

- **Boiling** also has much impact on geothermal fluid chemistry. As the fluid rises, the pressure decreases which leads to boiling. The fluid is separated into two phases, liquid and vapour. If the fluid was saturated with the most common minerals before boiling it will become supersaturated once the gaseous phase has been separated. This can lead to precipitations of secondary minerals(see section 2.1.2)[25].

- **Mixing with shallower water** can alter the chemical composition of the geothermal fluid drastically. Depending on composition of the shallower water it can dilute the

fluid leading to less scaling. By mixing cold groundwater with hotter water Mg-silicate scaling can take place (see section 2.6.1)[14].

- **Mixing of gases with shallow waters** can create acidic geothermal fluids. This is especially the case where a shallow magmatic intrusion affects groundwater in-directly. As the intrusion degasses it expels acidic gases which when coming into contact with shallow groundwater can significantly lower the water's pH. The water heats up and starts dissolving the surrounding rocks. This can lead to the formation of mud pools and highly altered rocks. Gases originating from the degassing of magma can enter geothermal fluid[14].

- **pH levels** are very influential on precipitation of different minerals. This process is very closely linked with boiling, since it separates acid gases (CO_2 and H_2S) from the liquid phase and dissolution and precipitation of minerals. Components affecting the pH can precipitate or dissolve from the fluid. Most mineral equilibria are affected by changes in pH which complicates all estimates of precipitation. Computer models are therefore required to calculate these complex interactions[51].

2.5   Geothermal Fluids in Iceland

Table 2: Comparison of various analyses from different geothermal fields. Salton Sea samples are chosen to express the drastic variation in chemical composition of geothermal fluids.

ppm	Sea water[1]	Meteoric Water[3]	Reykjanes RN-12[2]	Svartsengi SV-07	Salton Sea[1]	Hellisheiði HE-52[1]	Krísuvík SHM-5[1]	Hveragerði Average from wells[1]	Groundwater Nesjavellir[4]
Reservoir Temperature (°C)			295	238	316	266	96	181	
pH at 25°C	7.9	5.9	5.3	5.35		7.04	3.24	6.997	7.9
SiO2	6.4		702	455	400	510	151	271	16.9
B	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.6	<0.1
Na	10,770	5.8	9,650	6,396	50,400	134	28.5	147	11.8
K	390	0.5	1,410	937	17,500	21.4	2.52	12.9	0.9
Ca	410	0.5	1,660	1,028	28,000	0.96	56.4	1.67	6.5
Mg	1,350	0.6	0.78	0.36	54	0.001	23.5	0.002	4.7
Fe	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.008	<0.1
Al	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	3.92	0.134	<0.1
Cl	19,350	10.2	19,220	12,610	19,200	58.3	14.9	106	7.8
CO2	99		1,700	463	1,700	785.4	<0.1	154	30.4
SO4	2,712	0.7	14,7	28	14.7	22.9	361	42.1	7.2
H2S	0		45,5	9.8	45.5	42.8	<0.1	23.2	<0.1

[1] [52]   [2] Reykjanes well RN-4   [3] Average data from Írafoss[53]   [4] [37]

Major components in Icelandic geothermal fluids

Table 2 gives an overview of the chemical composition of different geothermal fluids in Iceland and Salton Sea in California. From the table it can be seen that the concentration of some elements varies more than others. The chemical composition can in many cases give good information on the development, origin and reservoir temperature.

Here some of the other elements will be discussed, their origin and role in the analysis of the fluid explained.

- **Silica** exists in many different forms but quartz is the predominant form of silica in nature. Its origin in geothermal fluids is almost exclusively in dissolution from the surrounding rock. It can be noted that no silica is found in meteoric water and only very low levels in seawater (see Table 2) due to its nutritional values for phytoplankton. The solubility of silica increases with reservoir temperature and its levels can therefore be evidence towards the highest temperature. At reservoir level the geothermal fluid is in equilibrium with quartz, chalcedony or amorphous silica at surface level[51].

- **Magnesium** usually does not occur at concentrations higher than 0.1 ppm in geothermal reservoirs in Iceland. Exceptions are the reservoirs at the Reykjanes peninsula where the origin of the geothermal fluid is from seawater which slightly increases Mg concentrations. Under normal circumstances the Mg that may be present in the original water (seawater in Reykjanes) precipitates as the fluid heats up[4]. This is evident by looking at table 2, the Mg concentration in Reykjanes is twice as high as Svartsengi concentrations and a order of magnitude higher than in reservoirs where the fluid is of meteoric origin (Hellisheiði and Nesjavellir). They are however orders of magnitudes lower than the original seawater.

- **Sodium and Potassium** are reactive constituents in geothermal systems and are therefore very important when reservoir temperature is assessed through geothermometry. The concentration of both these components decreases with increased temperature[1].

2.5.1   Dissolution and Precipitation

When precipitation and dissolution are discussed with a quantitative approach the Saturation Index (SI) is often referred to and is defined as:

$$SI = log(\frac{Q}{K_{sp}})$$

Where Q is the reaction quotient and K_{SP} is the equilibrium constant[54].

The Saturation Index is a very convenient way to describe the saturation state of elements and predict potential scaling.

If:

$$SI > 1 \text{ the solution is supersaturated}$$
$$SI = 0 \text{ the fluid is in equilibrium with mineral}$$
$$SI < 0 \text{ the solution is undersaturated}$$

The SI is an easy way to present saturation levels and potential scaling. In theory minerals only require a SI>1 to precipitate but due to difference in precipitation rates, a certain level of supersaturation needs to be reached for certain minerals to precipitate.

Temperature is the biggest factor determining saturation for most minerals. For most minerals the solubility increases with temperature but some minerals have retrograde solubility leading to solubility decreasing with increased temperature. Other factors such as pH are also important but affect some minerals more than others (see section 2.6.1)[55].

Calculations of mineral solubility will become very complex once all thermodynamic variables have been accounted for. Computer software has therefore been created aiding in these calculations. The software Watch[56] has been used extensively in Iceland when calculating aqueous speciation and solubility. The solubility constants used in the program are gathered from published thermodynamic data on the common minerals in geothermal systems.

Many factors affect the rate of precipitation and can be the determining factor in many cases. Quartz is only visible in extremely rare cases in geothermal power production. The geothermal fluids are almost without exception supersaturated with regard to quartz. The reason being that the precipitation time needed for quartz does not allow for quartz formation[57]. The biggest factor when determining deposition kinetics are the level of supersaturation, pH, flowrate of the fluid, temperature, aeration and the interactions between different ions in the fluid.

2.6   Scaling Mechanisms

Even though the geothermal fluid is supersaturated with regard to a specific compound it does not mean that scaling will happen instantaneously as the supersaturation is reached. The level of supersaturation depends on the kinetics of the mineral reaction. While minerals like calcite precipitate rather quickly, minerals like albite, quartz and some silicates do not precipitate fast enough to even create a problem in the utilization of geothermal systems[1].

Colloids

When small particles are suspended in a medium they are called colloids. They can stay suspended in the medium for a long period of time due to the random motion of the particles in the medium, also called Brownian motion. The colloids can be in all sorts of media but solids in a fluid is the most relevant for geothermal fluids. As long as the particles stay suspended in the medium they are referred to as being colloidally stable. While the particles are in that state, no precipitations will form. Brown described the formation of colloids in three stages[58]:

1. **Nucleation** is when two molecules dispensed in a supersaturated solution come together.

   When silica colloids form the formula for the reaction is:

   $$\text{H}_4\text{SiO}_4 + \text{H}_4\text{SiO}_4 \longrightarrow \text{H}_6\text{Si}_2\text{O}_7 + \text{H}_2\text{O}$$
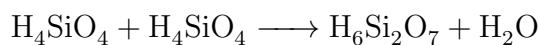
   The product has no crystal structure and is therefore amorphous. The driving force and what controls the formation speed of the process is the supersaturation of the silicic acid in the fluid.

2. **Ripening** of the nuclei involves bonding more particles from the supersaturated solution with the nuclei. It grows until monomeric silica particles become to few for further growth. Smaller colloids then start to dissolve to keep up the growth of the bigger colloids. The colloids grow until an equilibrium is reached under the current conditions. This step controls how many particles form. The reaction above can continue and grow even longer polymers. The longer the polymers, the easier the next steps of precipitation will be.

3. **The growth** stage takes over if there are any external changes that affect the level of supersaturation. The changes could include further cooling or boiling. It is rare that new particles form during this stage, instead the particles formed during the **ripening** stage continue to grow until a new equilibrium is reached.

The level of supersaturation strongly affects this process. If the supersaturation levels increase slowly, fewer nuclei will be formed and the growth will be concentrated onto them, resulting in fewer particles but larger.
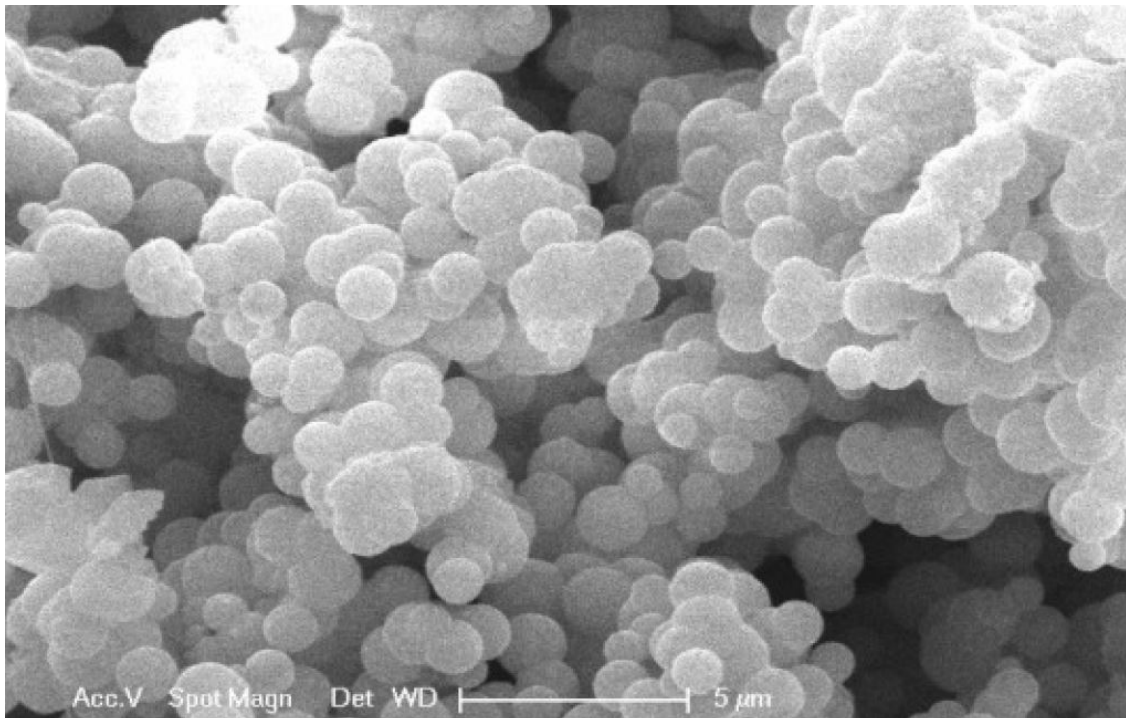
Figure 5: Typical silica colloids[58]

Colloid deposition

Once the colloids have been formed in the supersaturated fluid they need a solid surface to form scales. The precipitation continues until it reaches equilibrium. Many factors influence the precipitation rate of the reaction once it has begun. The colloids have a negative surface charge and the concentration of positively charged ions affect the precipitation rate as they can react with the colloids and lower the negative charge. This increases the chance of colloids combining and precipitate from the solution since due to their weight and size they cannot be suspended in the fluid. The higher the concentration of positive ions like Na^+ the faster precipitation will occur. Highly positively charged ions also affect the precipitation rate by attracting cations in the solution which then act as a bridge be-

tween colloids and binds them together, forming an agglomerate which precipitates. Fe^{+3} and Al^{+3} are found in geothermal systems and can greatly affect the precipitation rate. Al^{+3} is especially efficient in precipitating silica since the ion is of a similar size as Si^{+4} which makes it easy to substitute in the colloids[58].

The particle size of colloids can have much impact on the amount of precipitation that will occur. Experiments with silica particles have shown that very small particles (<15 nm) show almost no scaling while bigger particles (120 nm) showed much more precipitations[57].

Flow rate of the fluid also affects the precipitation rate as the colloids need to have time to form and precipitate. The affect of flow rate on precipitation is very much mineral dependent as some minerals need the solution to be still to precipitate while others such as calcite and amorphous silica precipitate even in high flow rates[58].

2.6.1   Fluid-Rock Interactions

Silicates

At reservoir level the silica concentration of the geothermal fluid is controlled by the solubility of quartz, which increases with temperature[59]. Due to its importance in geothermal power production it has been extensively researched and detailed solubility equations established[60][44][56]. Amorphous silica is often contaminated with different cations available in the geothermal fluid during precipitation. This leads to the possibility of many different silica minerals as can be seen in Table 3. Silica scaling is only common in high-temperature geothermal systems but Mg-silicates occur in low-temperature systems where colder groundwater is mixed with the hotter geothermal fluid[45]. This has also been witnessed in many high-temperature systems where the mixing of hotter geothermal fluid with colder groundwater has occurred. Examples of Mg-silica scaling in high-temperature systems include Hveragerði district heating system [15], Reykjahlíð and Nesjavellir[15][38].

The equilibrium between quartz and H_4SiO_4, the dominant aqueous silica species can be expressed as[58]:

$$SiO_2(s) + H_2O \rightleftharpoons H_4SiO_4(aq)$$
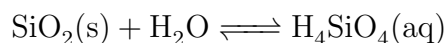
Table 3: Different silicate scaling occurring in Icelandic geothermal systems

Type of scales	High-temperature systems[1]	Low-temperature systems[1]
Amorphous silica	x	
Magnesium-silicate		x
Iron-silicate	x	
Iron-magnesium-silicate	x	
Zinc-silicate		x
Aluminium-silicate	x	

Data from Kristmannsdóttir[45]

The equation is valid for amorphous silica as well as quartz as the amount of water present does not affect the solubility.
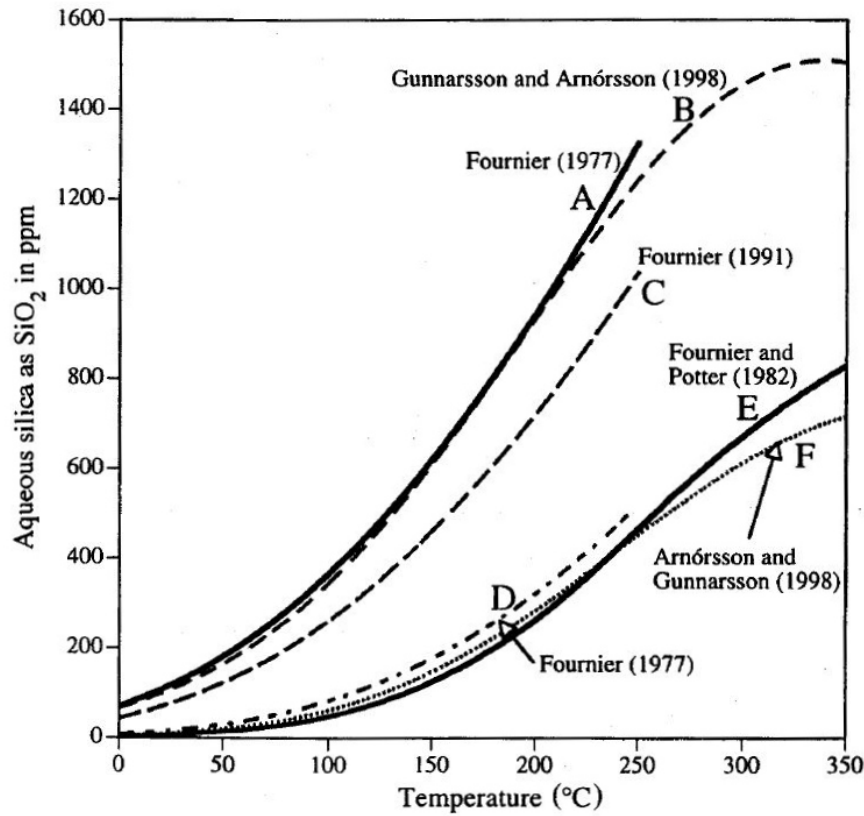
Figure 6: Solubility of Silica with temperature[1]. The lower lines represent the solubility of quartz while the top ones the solubility of amorphous silica.

The affect of temperature on solubility can be expressed by:

$$logC = -1309/T + 5.19$$

C = Silica concentrations in mg/kg, T = temperature (K).

Figure 6 shows the solubility curves of amorphous silica and quartz as functions. From the figure it is clear that there is a difference in solubility between the two minerals. As the geothermal fluid cools down there is a period where no silica precipitates. This window makes it possible to extract energy from the geothermal fluid without precipitating the dissolved silica[58].

Silica solubility is not only temperature dependent but also dependent on the pH of the geothermal fluid. In high pH fluids the H_4SiO_4 reacts with hydrogen atoms to form silicic acid:

$$H_4SiO_4 \longrightarrow H^+ + H_3SiO_4^-$$
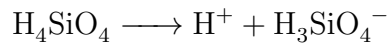
The solubility of amorphous silica as a function of pH can be derived as[60]:

Solubility of silica depending on pH can be seen in Figure 7. Since solubility increases with higher pH it can be used for inhibiting silica scales in various geothermal processes. It is particularly efficient when reinjecting separated geothermal fluid as scaling tend to form in the rocks near the bottom of the reinjection well and thus reducing permeability.
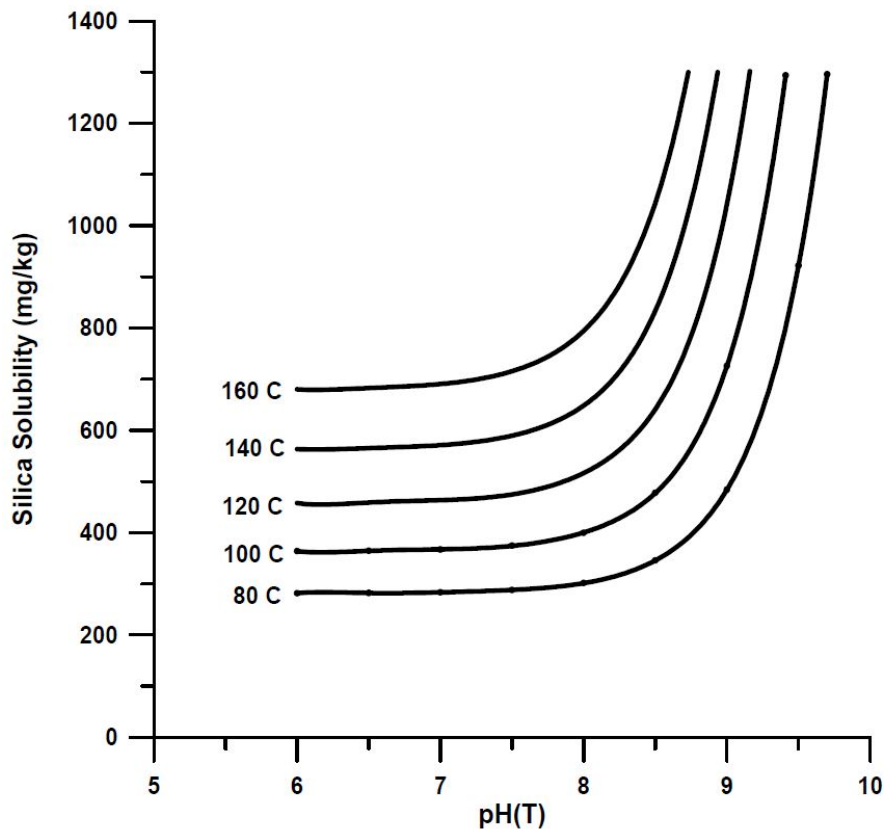
Figure 7: Solubility of Silica depending on pH[58]

Carbonates

Calcite scaling is the most common form of carbonates in geothermal fluids. It usually forms subsurface in production wells or in the reservoir. It is very common in most geothermal systems, particularly in upflow zones. Most systems are generally calcite saturated until they reach very high temperatures >300°C[61]. Low-temperature zones in Iceland have been found to be saturated with calcite if the fluids exceed 100∘C and if the fluid flashes it will precipitate calcite[45]. Solubility of calcite increases with partial pressure of CO_2. As the CO_2 content in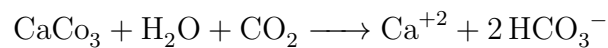 the fluid increases it can dissolve the calcite in the surrounding rock and converts it into aqueous Ca^{2+} and HCO_3^- according to this equation:

$$CaCo_3 + H_2O + CO_2 \longrightarrow Ca^{+2} + 2\,HCO_3{}^-$$

The dissolved CO_2 in the fluid continues to dissolve the surrounding calcite until no more CO_2 is available and an equilibrium is reached. If the geothermal fluid flashes it separates into two phases and the CO_2 separates from the mixture. This reverses the earlier reaction leading to rapid precipitation of calcite[58].

$$CaCo_3 + H_2O + CO_2 \longleftarrow Ca^{+2} + 2\,HCO_3{}^-$$
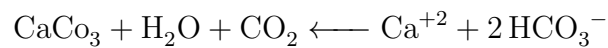
Due to calcite's retrograde solubility, scaling usually only occurs during boiling due to increased pH. Calcite scales are therefore primarily found over 200-300 m long section in the well. The flashing point can be controlled and therefore the calcite scaling managed[14].

Mg-Silicate

The solubility of magnesium is mostly controlled by the concentration of magnesium, silica and the pH of the liquid[38]. As discussed in section 2.1.1 magnesium does not occur naturally in high-temperature geothermal fluids in concentrations high enough to form scales on the surface. It's presence is therefore only explained by the mixing of the geothermal fluid with colder groundwater or heating up colder groundwater. Mg-silicate scaling was a problem in the earlier days of district heating systems in Iceland. The geothermal fluid had very high TDS which led to silica scaling and clogging of pipelines. In some district heating systems the silica problem was solved by diluting the geothermal fluid with groundwater to decrease the concentration. This only created problems with

Mg-silicate scaling where only amorphous silica and Al-amorphous silica scaling had been present[4].

Two Mg-silicate minerals are most common in Icelandic geothermal system. Their formation is influenced by the Si/Mg ratio in the geothermal fluid. In fluids where the ratio is high the mineral serpentine is more likely to form while in fluids rich with silica a talc like mineral forms.

Serpentine:

$$\mathrm{Mg_3Si_2O_5(OH)_4 + 6\,H^+ \rightleftharpoons 3\,Mg^{+2} + 2\,H_4SiO_4 + H_2O}$$

And Talc:

$$Mg3Si4O10(OH)2 + 6H^+ + 4H2O <=> 3Mg^{+2} + 4H4SiO4$$
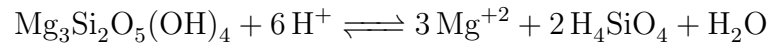
Enstatite ($\mathrm{MgSiO_3}$) is the magnesium endmember of the pyroxene silicate series and is therefore often used to show the theoretical reaction between the geothermal fluid and pyroxene. The reaction is expressed as:

$$\mathrm{MgSiO_3 \cdot H_2O + H_2O \rightleftharpoons Mg^{+2} + H_3SiO_4{}^- + OH^-}$$
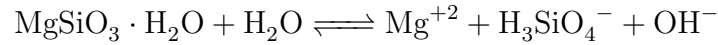
The solubility constant (K_{sp}) for the dissolution is given by:

$$K_{sp} = \frac{\left[\mathrm{Mg^{+2}}\right]^3 \left[\mathrm{H_4SiO_4{}^0}\right]^2}{\left[\mathrm{H^+}\right]^6}$$

As can be seen from the reaction formulas the formation of Mg-silicates is very dependent on access to $\mathrm{OH^-}$ and subsequently to the pH of the geothermal fluid. Since the solubility is also dependent on pH the scaling can be managed if pH can be regulated. This has been proven to work in Hveragerði. By mixing cold groundwater only with separated steam the operators where able to increase the pH of the mixed fluids sufficiently to decrease Mg-silicate scaling drastically[15].

2.6.2   Scale mitigation

Many different solutions exist when trying to mitigate scaling in geothermal power plants. Due to the different solubility of minerals and the effect of temperature and pH changes

on scaling mechanisms, most of the mitigation strategies focus on a single mineral group. Different strategies are often characterised as chemical or mechanical. Chemical strategies often include adding scaling inhibitors that stabilise the colloids, neutralising the attractive powers between the colloids. Other chemical strategies include changing the pH of the fluid to increase the solubility of a certain component[58].

The most successful scaling mitigation strategy when it comes to silica formation in Iceland is to design the power plants with regard to the solubility curve of silica. Figure 6 shows the difference in solubility between amorphous silica and quartz. There is a temperature range where quartz does not precipitate and the amorphous silica scaling starts. By knowing the chemical composition of the geothermal fluid the outflow temperature of the fluid can be decided to minimize silica scaling. In smaller district heating systems in Iceland diluting the geothermal fluid has been tried but that can cause Mg-silicate formation[45].

Calcite scaling takes place when the fluid boils so the scale formation zone can be controlled. If the scaling takes place within the well the most common practice is simply to clean the well by drilling with a smaller drill and clean out the calcite. If the scaling takes place in surface equipment it usually most effective to jet-wash the equipment[51].

For most minerals there exists a chemical antiscalant which interferes with this formation. These antiscalants usually need to be inserted into the fluid in the well, before scaling takes place. This can introduce a big cost increase to the production and if sufficient chemical analysis is not carried out in the beginning it can lead to a project being less profitable than assessed[58].

Chapter 3

Methods of sampling and analysis

3.1 Sampling

When handling and analysing samples a clear guideline must be followed to preserve the integrity of the research and in order to keep the sample clean and uncontaminated. The steps taken during this research were all in order to provide the most accurate data available.

The sampling location has to be well documented, GPS coordinates written down and well photographed. Common practice states that a written description of the sampling location should be made. When collecting the sample it must be noted what kind of samples are planned. If the sample is in liquid and gaseous form a wide array of bottles and equipment must be used in order to get the best samples (see Table 4). When sampling liquids and gases it is customary to collect many sub-samples as each sample is treated for analysis of a single component. Different sample sites require different treatments and preservations techniques. Hot springs and fumaroles require a different approach than two-phase production geothermal wells[62]. A flow diagram showing how to treat samples is presented.

3.1.1 Mineral samples

When collecting mineral samples it is important to handle the sample with care. Corners and other fragile exteriors can be damaged. Care has to be taken not to contaminate the sample with dirt which can alter sensitive tests. Some samples do not withstand coming in touch with liquids while others can be cleaned with distilled water. A flowchart on

analytical methods most used for mineral samples can be seen on next page. The flowchart also explains best practices regarding handling and storing[52].

Start with sample

Preliminary analysis

- Sample location and conditions at sampling location
- Photograph sample
- Describe sample, thickness, colour, texture etc.
- Weigh sample

Split sample

- Sub-sample 1
- Sub-sample 2 → Weigh and store sample

Describe

- Visual description of sample, colour, texture, hardness
- Crystalstructure, rounded corners, angular, etc.
- Amorphous
- Any other material visible?
- HCl acid test for $CaCO_3$
- Magnetic test for magnetic minerals

Examine in binocular microscope

Prepare for further analysis

Thin section
- Identify individual minerals
- Alteration of minerals
- Mineral origin

XRD
- X-ray diffraction
- Identify molecular structure of crystals
- Amorphpous or crystalline
- Silicates, carbonates, sulfides or amourph

XRF
- X-Ray Fluorescence
- Analysis of heavier elements, metals etc.

SEM
- Scanning Electron Microscopy
- Angularity of crystals
- Spot analysis
- Scanning analyis
- *EDX*

Bulk Analysis

A flowchart explaining how to handle and analyse mineral sample[52]

3.1.2   Liquid and vapour samples from geothermal wells

Much care needs to be taken when collecting fluid or vapour samples in order to not contaminate them. The samples' temperature is most likely >150°C which leads to the use of tools to help condense the vapour which, in turn, increases the chance of contamination. The fluid is usually two-phase so two different methods must be used. The most common practice is to use a Webre separator to separate the vapour phase from the liquid phase. The pressure within the separator should be as close to wellhead pressure as possible in order to maintain the same conditions and steam ratio.

The liquid phase is cooled down and condensed before entering the sampling bottles. Many samples need to be collecting as they often need to be treated specific to extract information on a specific constituent. Table 4 lists all common constituents sampled for and the treatment needed for further analysis.

Very similar principals apply when sampling the vapour phase as the vapour needs to be cooled and condensed before sampling is possible. The samples that do not need condensing are gas samples that enter the evacuated double port bottle, but the bottle must be cooled while sampling. If special treatment, such as filtration is required it must be carried out in a clean environment where filtration pads have been cleaned with distilled water[62].

3.1.3   Sampling from fumaroles and springs

When sampling from fumaroles a strong, direct outflow is the best option. The outflow should be concentrated to a single vent in order for the most representative sample to be collected. If an outflow is diffusive it can mean that the gas mixes with atmosphere in the ground. Once the correct fumarole has been chosen a funnel is placed over the outflow and covered so all of the gas enters the funnel. The funnel is then connected to a tube which helps the gases condense. If the outflow is not strong enough there might be a need for a peristaltic pump. The sub-samples that are most commonly taken are listed in Table 4.

Samples from hot springs need to be collected as close to the outflow as possible. This can be tricky as it is not always clear where the springs originates. Ink can be used to help realise the outflow by backwards trace the flow direction. Usually a pump is used to collect water samples from hot springs[62].

Table 4: An overview of sampling and analytical methods applied to geothermal fluids

	Gaseous phase from well			Liquid phase from well			Hot spring		
Constituent	Container[62]	Treatment[62]	Analytical method[63]	Container[62]	Treatment[62]	Analytical method[63]	Container[62]	Treatment[62]	Analytical method[63]
pH, CO_2 and H_2S	Gas sampling bulb	Condensed vapour	Titration	Amber glass bottle	Measured at 25°C	Titration	Amber glass bottle	Measured at 25°C	Titration
Anions	Gas sampling bulb	Condensed vapour	IC	Plastic bottle	Filtration	ICP-FUS/MS	Plastic bottle	Filtration	ICP-FUS/MS
Cations	Gas sampling bulb	Filtration; 0.8 ml conc. HNO_3 added to 200 ml sample	AES	Enclosed container	Filtration and 0.8 ml conc. HNO_3 added to 200 ml sample	IC	Enclosed container	Filtration and 0.8 ml conc. HNO_3 added to 200 ml sample	ICP-FUS/MS
SiO_2 if > 100ppm	N/A	N/A	N/A	100 ml plastic bottle	Dilute, 10 ml sample:90 ml distilled deionized water	Spectrophotometer	3 x 100 ml plastic bottles	Dilution, 50 ml sample:50 ml distilled deionized water	Spectrophotometer
Mg, SiO_2 if <100ppm	N/A	N/A	N/A	200 ml plastic bottle	No special treatment	Spectrophotometer	200 ml plastic bottles	No special treatment	Spectrophotometer
Residual gases	Evacuated double port bottle	Samples added to 50 ml 40% NaOH evacuated bottle to dissolve CO_2 and H_2S	Titration	N/A	N/A	N/A	N/A	N/A	N/A
SO_4, $\delta^{34}S$ and $\delta^{18}O$ in SO_4	Glass flask[1]	0.5 ml 0.2 M $ZnAc_2$ added to sample to precipitate sulphide[1]	IC[1]	Filtration, 2 ml 0.2 M $ZnAc_2$ added to sample in 100 ml glass flask and >10 ml to 500 ml bottle containing >25 mg SO_4 to precipitate sulphide	Precipitate to prevent further reaction	Selective electrode	Filtration, 2 ml 0.2 M $ZnAc_2$ added to sample in 100 ml glass flask and >10 ml to 500 ml bottle containing >25 mg SO_4 to precipitate sulphide	Precipitate to prevent further reaction	SC
δ^2H, $\delta^{18}O$, ^{13}C and ^3H	Amber glass bottle	No special treatment	MS	1 x 60 ml and 2 x 1 l amber glass bottle	Filtration	Selective electrode	1 x 60 ml and 2 x 1 l amber glass bottle	Filtration	MS

[1] Only for SO_4 in gas samples

3.2   Analytical Methods

Mineral samples are collected by hand and stored and catalogued. Best practices on sampling state that the sample size should be sufficient to split into two halves and store one half if subsequent analysis is required. The used half is then described, weighed and prepared for different tests. The main tests used for scale analysis are described in Table 4 and in a flowchart of the sampling and preparation process.

3.2.1   XRD analysis

XRD refers to X-ray diffraction and is used to identify the atomic and molecular structure of a crystal. The sample is prepared and inserted into the machine where the crystal is subjected to a beam of incident X-rays. Because the wavelength of X-rays is of a similar magnitude to the lattice points in crystal structures they will diffract the X-rays. This makes it possible to identify the crystal structure based on the diffraction. Figure 8 shows two X-rays diffracting from two parallel planes. They hit the first plane in phase but in order to be in phase again once they exit the extra distance travelled by the second wave will be an integral number of wavelengths[54].
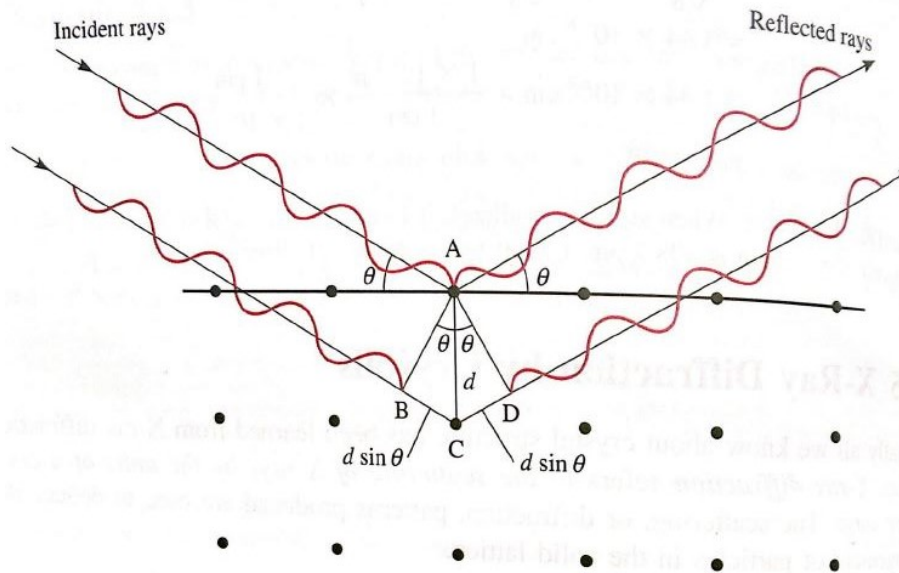

Figure 8: X-ray diffraction from two parallel layers of atoms[54]

This relationship can be explained with Bragg's law[54]:

$$BC + CD = 2d \sin \theta = n\lambda$$

Were θ is the angle between the X-rays and the crystal plane, d is the distance between the planes, λ is the X-ray wavelength and n is an integral multiple of θ

From the data it is possible to assess the level of crystallised material in the sample. If there is crystallised material in the sample it will have a specific diffraction pattern which is then used to determine the crystal structure and the mineral. A major drawback of the XRD analysis is that it is only able to assess the composition of the sample but not the concentrations of each element. The researcher therefore needs to deduct the potential scaling minerals from which elements are present in the sample. This can lead to uncertainty in when assessing the wt% of the mineral scales.

When preparing the samples for XRD analysis the sample needs to be powdered, rendering it unusable for some other analytical methods. It is therefore important that the sample is not used in its entirety but rather a smaller, representative, part of the original sample.

3.2.2 XRF analysis

X-ray fluorescence analysis is different from XRD in that the goal of the study is not to analyse crystal structure but rather to identify specific elements within the sample. XRF analysis is a none-destructive analytical method which has been used for decades. Even though the method is non-destructive it requires some preparation which leaves the sample mostly unusable for other analytical methods. The sample is bombarded with high-energy X-rays which eject the electrons from the innermost shell causing instability. The electrons from the outer shells then fill the vacancy created by the ejection. While transferring to the inner shells the electrons give off X-rays which have the same energy as the difference in binding energy of the shells that the electron transferred through. Since all elements have a specific binding energy and energy levels the X-rays emitted because of the shell transfer can be used to identify the excited element. By bombarding the sample with high-energy X-rays it will create a spectrum of radiation coming from the sample which is then compiled and used to determine the elements present in the sample[64].

3.2.3 Whole rock analysis

Inductively coupled plasma technology is used to prepare the sample for further analysis. The sample is ionized in a inductively coupled plasma and analysed with with mass

spectrometer (MS) or an optical emission spectrometer (OES) to separate and quantify the ions present.

3.2.4   SEM

A Scanning Electron Microscope is an electron microscope able to produce very high resolution images of the sample. A beam with focused electrons is used to scan the surface of the sample. The electrons react with the surface and produce signals that the microscope identifies and translates into an image. Samples used in SEM have to be prepared by creating a thin-section of the sample. The thin-section can be used in a petrographic microscope when analysing the optical mineralogy.

3.2.5   Thin Section Microscopy

When rock or mineral samples are analysed in a petrographic microscope a thin section of the sample is prepared. The sample is usually only 10's of μm thick, thin enough for light to be able to shine through many minerals. The light is polarized which gives minerals a distinctive refraction angle allowing for the identification of some minerals. The method is very common due to its simplicity and relatively little preparation required.

Chapter 4

Description of the problem

The scaling which will be examined further takes place in a sports center in Hveragerði. Hot water and steam is collected from well HV-04 to use in an inflated sports-arena's inflation system. The fluid coming from the well passes through a plate heat exchanger fuelling a closed loop system within the sports center. When the hot water from the well condenses in the heat exchanger it precipitates an unknown mineral which decrease the flowrate through the heat exchanger. The scale (Figure 9) precipitates on the inflow side of the heat exchanger and the amount is so that near annual maintenance is necessary to remove the scales. The mineral scales have been shown to contain a high concentration of iron. Chemical analysis of the geothermal fluid from well HV-04 was carried out in 1980 (Table 5) and zero amounts of iron where found in that sample.

Work has been carried out on the sample by ÍSOR and findings published in a report for the municipality of Hveragerði[6]. The report will be analysed and further research suggested.

4.0.6   Corrosion

The fluid sample available in National Energy Authority database from well HV-04 (table 5) shows a relatively high concentration of H_2S in both the steam and liquid phases of the sample. All oxygen in the sample should therefore have reacted with the H_2S eliminating all potential corrosion related to dissolved oxygen. CO_2 levels in the sample collected in 1980 was relatively high, or 54.10 ppm. The aqueous speciation of the CO_2 was calculated by ÍSOR using the software Watch. The reference temperature used for the calculations was 163°C which is the temperature at wellhead during sampling, calculated from pressure. The temperature was adjusted according to the chalcedony geothermome-
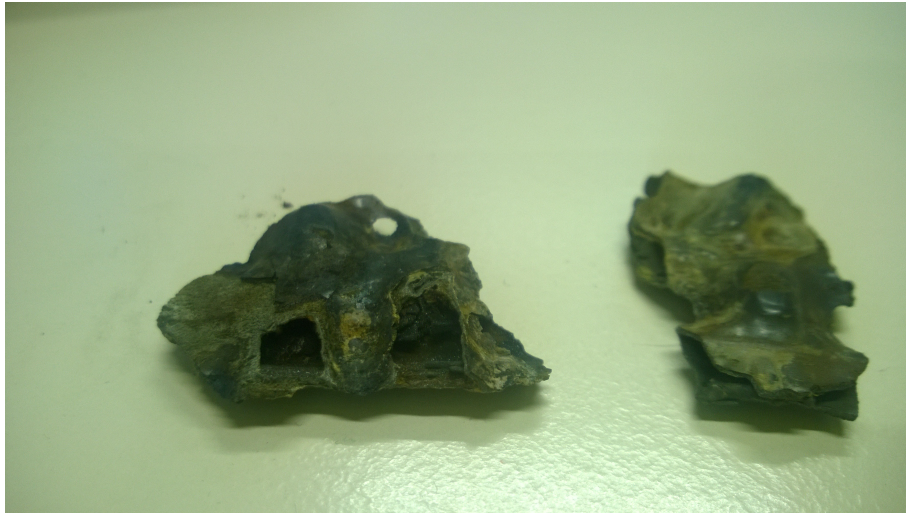
Figure 9: A picture showing the scales in the heat exchanger at the sports-center, sample collected December 2

ter to give a reservoir value of 175.9°C. Watch results show that the CO_2 has two dominant species, HCO_3^- (100 ppm) and H_2CO_3 (61 ppm)[6]. The latter acid is widely known to cause increased corrosion in steel and solutions containing H_2CO_3 are even more corrosive to mild steel than solutions containing HCl or H_2SO_4 at the same pH[65].

4.1 Description of the research location

Well HV-04 is a part of the HV series which was drilled to supply steam to a planned 35 MW_e geothermal power plant, in the 1960s in Hveragerði. Plans to build the power plant where cancelled after the first wells where drilled. Well HV-04 is 692 m deep and the casing reaches 196 m depth. The well has been operated since 1961 for space heating for nearby farmhouses and greenhouses. The fluid is saturated with calcium, like all wells in the Hveragerði area, and precipitates calcite within the production casing of the well. The scales need to be cleaned annually by drilling out the calcite. Silica geothermometers suggest that temperatures reach 197°C but highest recorded temperature is a bit lower or 184°C. The wells thermal power, calculated down to 40°C is 38 MW_{th} and the flow rate at 1 bar-a was 62.0 kg/s[5].

4.1.1 HV-04 wellhead and connections

The well has been in constant operation since it was drilled, both for residential houses as well as space heating and disinfection for greenhouses. The well's production has

Table 5: Chemical composition of the fluid from well HV-04[66]

HV-04		
pH: 9.04/23°C		
Steam fraction: 0.046		
	Fluid sample (mg/kg)	Steam sample (volume%)
H_2S	20.90	1.96
SiO_2	260.0	0.00
CO_2	54.10	82.89
H_2	0.00	2.43
N_2	0.00	11.69
Na	167.20	0.00
K	12.50	0.00
Mg	0.00	0.00
Ca	2.26	0.00
F	1.60	0.00
Cl	130.40	0.00
Fe	0.00	0.00
SO_4	40.90	0.00
TDS	751.00	

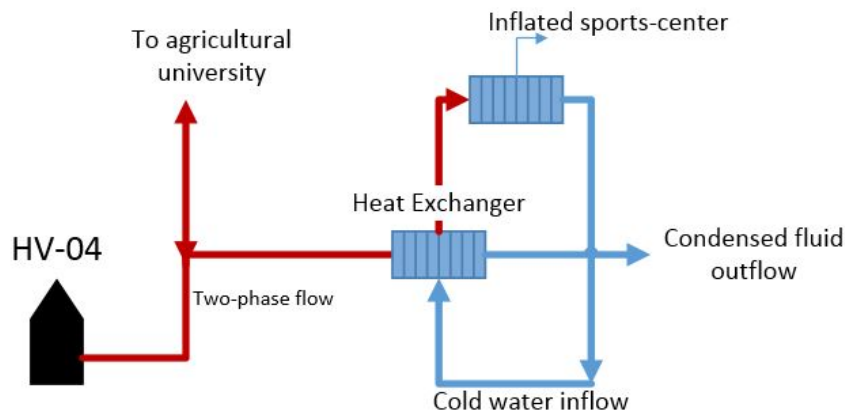
Figure 10: A schematic overview of the system connecting the inflated sports-center with well HV-04

been increased in recent years with the addition of the Agricultural University of Iceland, located close-by, and the inflated sports-center. No flow rate measurements have been carried out after the increased supply was added, nor an estimate of the thermal energy used from these institutions.

Figure 11: Overview of HV boreholes, north of Hveragerði. The location of the inflated sports-center is shown. Figure modified from Jónasson[5]

Shortly after the sports-center was added the flow rate entering the heat exchanger was measured and it was 1.9 l/s[39]. This measurement was carried out in the spring of 2013. No data is available for the temperature at the time of measurement but it must be assumed that flow rate is substantially higher during the winter.

Most of the users connected to HV-04 are connected to the well close to the wellhead with each user connected uniquely to the well. At least six different pipes are connected to the well leading to the users and a pipeline connects HV-04 to HV-02, which is close by in order to maintain minimum heat flow within the pipes. One pipeline supplies the agricultural university, another connects nearby farms and the third one supplies greenhouses. A spillage pipe comes from the well and leads to the river Varmá. The well is free-flowing and the spillage pipe is used to maintain a regular flow from the well in order to avert the creation of backflow pressure. When the well was visited in November the flowrate of the spillage was estimated to be 2 l/s (Figure 12). Near the outflow the fluid had precipitated a light yellow substance. The pipe to the sports-center is connected to

the top of the pipe leading to the agricultural university. The ÍSOR report[6] suggests that this set-up could greatly distort the steam ratio levels entering the pipe leading to the sport-center. By connecting to the upper part of the pipe, the less dense steam is more likely to go through that pipe[6]. By altering the steam ratio, the pH levels will be lower and the chemical composition of the mixture will be different from the data available in NEA's database[66]. This was suggested in the ÍSOR report to distort the mixture of fluid that flows to the sports-center by increasing the proportion of steam and thus lowering the pH of the fluid mixture[6].

Figure 12: Spillage from well HV-04. The flowrate was estimated at 2 l/s

Table 6: Temperature and flow rate measurements in well HV-04

HV-04		
Measurement	Temperature[1]	Flow rate
2007[2]	184	62 kg/s
2013[3]	145[4]	N/A
2014[5]	143[6]	x

[1] Silica temperature 197°C   [2] [5]   [3] [39]
[4] Measurements at wellhead
[5] This study   [6] Calculated from the pressure of the inflowing fluid
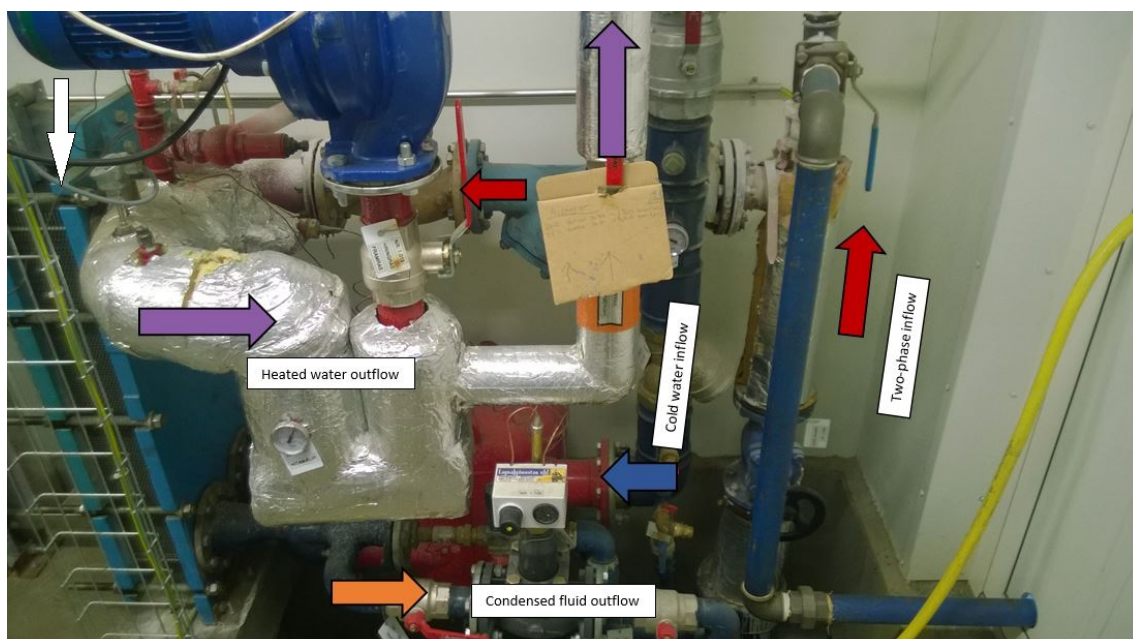
4.1.2   Sports-center piping system

Figure 13: A photo showing the piping system supplying heat to blowers. The heat exchanger is a plate heat exchanger rated at 3.5 MW and can be seen in blue at the left of the picture. Red and orange arrows represent the flow of the geothermal fluid while the purple and blue arrows represent the cold groundwater that carries the heat to the blowers. The white arrow points to the where the mineral scales precipitate.

The piping system (Figure 13) supplying the blowers with heat is a relatively simple one. The geothermal fluid is approximately 160°C when it enters the system under 4 bar-g. The fluid is therefore two-phase when it enters the heat exchanger. The temperature of the heat exchanger is controlled through a valve on the outflow side of the heat exchanger. The condensed two-phase fluid is then led to a nearby river. No nozzles are present on the outflow pipeline making it impossible to sample the outflow for chemical composition or pH.

The scaling falls on the entrance side of the heat exchanger and the plates were recently replaced due to the scaling. Regular maintenance of the system includes replacing the entire heat exchanger annually due to scaling. The cold water is on a closed loop connecting the heat exchanger to the blowers.

4.1.3   Available data on the sample

Scaling samples were collected and analysed by ÍSOR[6]. As a part of that study a sample of the scale (Figure 9) was collected and analysed in ÍSOR's XRD equipment. XRD

Figure 14: The installed heat exchanger at the sports-center

results showed the sample to contain siderite ($FeCO_3$) and in order to gain further understanding the sample was sent abroad for further analysis. There the sample was analysed with ICP-MS and ICP-FUS(section 3.2.3). The results where analysed and a report created[6]. Hardardottir[6] came to the conclusion that the scale consists of 75% siderite ($FeCO_3$), the rest (25%) being amorphous iron-silicate ($FeSiO_2$). As can be seen in Table 7 iron oxide(Fe_2O_3) makes up more than half of the analysed sample, or 63% of sample weight. Silica (SiO_2) accounts for 10.58% and total carbon is 7.15%. Other elements are in much smaller concentrations. The report assumes the carbon to be the limiting reagent in the precipitation of siderite which leads 75% of the iron to form siderite. The remaining iron is assumed to form amorphous Fe-silica and Fe-silcates.

4.2   Analysis of available data

The well and piping system in the sports-center in Hveragerði was visited in November and December. The inflow of steam to the heat exchanger at the sports-center was 4 barg, after flowing roughly 500 m in regular steel pipes. The well is free-flowing and the pressure at the wellhead is very similar to that at the inlet to the heat exchanger. The well

Table 7: ICP-FUS results from scale sample in heat exchanger[6]

HV-04	
Fe_2O_3	63.12
SiO_2	10.58
C−total	7.15
MnO	0.259
CaO	0.28
MgO	0.05
Al_2O_3	0.07
Na_2O	0.08
S−total	0.05
Other	<0.01

has the same problem as other wells within the Hveragerði area (section 2.3.2), if flow changes suddenly the liquid phase of the discharge will form a plug, inhibiting further usage. To prevent this, all excess fluid goes through the spillage pipe (Figure 12).

Chemical analysis of the geothermal fluid from well HV-04 (Table 5) reveals that high concentrations of H_2S exist in the fluid, inhibiting corrosion due to O_2 in the fluid. Corroding species in the fluid however exist, as was discussed in section 4.0.6, which most likely lead to corrosion of the pipes and thus being the source for the additional dissolved iron in the fluid. The fluid analysis shows that there are high concentrations of sulphur in the fluid when it exits the well. It does however not precipitate in the heat exchanger.

4.2.1   Addition of iron

The presence of iron in the scaling sample suggests that the processes within the system are more complex than anticipated in the beginning. The most likely source of iron is from corrosion from within the pipes the fluid flows through. This is supported by analysis of aqueous species found in the geothermal fluid under the sampling conditions (section 4.0.6). The corrosive species, H_2CO_3, is well known as a very corrosive agent to mild steel[65]. The iron in the pipes is therefore dissolved in the fluid as it flows through the pipes and precipitates in the heat exchanger, as can be seen in Table 7. Iron is a well known scaling element in Icelandic geothermal system and is most commonly found in iron-silicates, iron-sulphides and various iron-oxides. Siderite is however not a common precipitation mineral in geothermal systems.
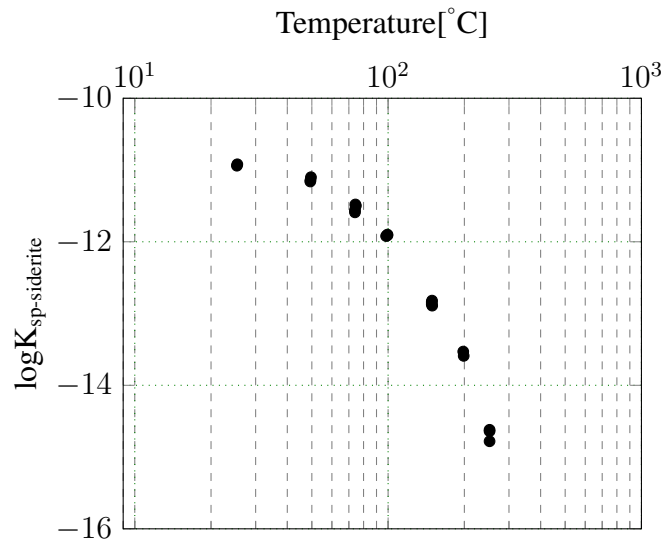
Figure 15: A graph showing the solubility of siderite. [67]

4.2.2   The solubility of siderite

Siderite is the end-member of the magnesite, $(MgCO_3)$ siderite $(FeCO_3)$ series. Its solubility has been established and is shown in Figure 15. The solubility curve is in similar agreement with the solubility of other carbonates and shows a retrograde solubility. The solubility formula used for plotting Figure 15 was established by Bénézeth et al.[67] and showed great correlation with other experimental data.

Implications for HV-04

The retrograde solubility of siderite does not agree well with previous research on the scale sample from the sports-center. The geothermal fluid extracted from well HV-04 flows to the surface due to the expansion that takes place during boiling. The majority of carbonates therefore precipitates within the well and since solubility increases with decreasing temperature it should not precipitate in such great amounts as previous results suggest. XRD analysis shows that the main crystallised material is siderite but does not give adequate information regarding the concentration in relation to the entire sample. Further analysis is therefore required to make better assumptions.

4.2.3   The lack of sulphur

In the chemical analysis of the geothermal fluid a significant concentration of H_2S (20.90 ppm) was recorded, however in the ICP analysis of the scale sample only minimal concen-

trations of sulphur were found. The lack of sulphur in the scale sample is very surprising when the addition of iron to the fluid is considered. The iron-sulphides pyrite (FeS_2) and pyrrhotite (FeS) are very common in geothermal systems due to rapid precipitation rates and low solubility. It is therefore surprising that none were found in the scale sample, suggesting an alternate results to previous studies. It is proposed here that as the iron is corroded from the pipes, it reacts with the dissolved sulphur in the fluid to form iron-sulphides. The point of precipitation must be in the pipes, close to the location of the corrosion. As all the sulphur is used up in the iron-sulphides it allows the remaining dissolved iron to remain in the fluid and then precipitate later, as the temperatures decreases. In order to verify the hypothesis the pipes must be checked for scaling. No attempt at quantifying the amount of iron-sulphide scaling will be made in this study but the scale can accumulate and decrease the production possible through the pipes. In that case, maintenance must be carried out by either cleaning or replacing the pipes.

4.2.4   Analysis of the data available

When considering the lack of sulphur in the scale sample and the retrograde solubility of most carbonates it is clear that earlier studies are not complete. Earlier analysis shows that the geothermal fluid contains a lot of dissolved CO_2 and the setup of the pipes at the wellhead might influence the mixture that goes to the sports-center and thus increases the CO_2 concentrations even further. As discussed earlier it is most likely that the sulphur precipitates with the iron as it corrodes and thus forming iron-sulphide that precipitates in the pipe. No iron-sulphides have been observed as a part of the scales in the heat exchanger and no attempt has been made to investigate possible precipitation within the pipes.

XRD analysis has shown that siderite precipitates in the heat exchanger, despite the retrograde solubility of siderite. This can partly account for the increased CO_2 in the mixture, due to a higher portion of the steam phase going to the sports-center. As the two-phase mixture enters the heat exchanger it undergoes a slight pressure change which can cause the fluid-phase to boil slightly and thus start precipitating the siderite. Carbonates are by far the most common carbon bearing minerals so it is safe to assume that all the carbon in the scale sample should form a carbonate. If the XRD results are analysed with that in mind, the wt% of the carbonate sample can be estimated. The sample consists of just over 7 wt% C which, if assumed is all bound in siderite, is enough to form roughly 75 wt% of siderite. The siderite forming reaction is:

$$Fe^{2+} + CO_3{}^{2-} \longrightarrow FeCO_3$$
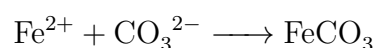
4.2.5 Further studies

It is clear that further studies are needed to gain a better understanding of the processes at work in the system. A new analysis of the geothermal fluid flowing to the heat exchanger would increase the credibility of all analyse since production of the well has increased radically since the last study was carried out. The steam fraction of the fluid entering the pipe leading to the sports-center should also be studied since the effects on pH and chemical composition can be great if increased separation takes place. Since there is no valve on the pipe leaving the heat exchanger, sampling of the outflow fluid is very difficult. Nonetheless it would be very interesting to sample the condensed fluid and analyse the pH and chemical composition. Carbonate precipitation is heavily pH dependent which makes analysis of the condensed fluid very attractive in order to analyse the scaling potential. All these studies would greatly benefit the operators of well HV-04 since it would provide further and more detailed information on the scaling potential of the geothermal fluid from the well.

Chapter 5

Conclusions and discussion

Geothermal reservoirs are classified into high- and low-temperature reservoirs. Low-temperature geothermal reservoirs are heated up by the unnaturally high geothermal gradient outside the active volcanic zone. They are defined as having temperatures <150°C at 1 km depth. High-temperature reservoirs are mostly heated up by intrusions that warm up circulating water and are defined as having temperatures >150°C at 1 km depth.

As the water heats up it dissolves the surrounding rocks and precipitates secondary minerals. The solubility of most minerals is dependent on temperature which leads to higher temperature fluids containing more dissolved solids. If the fluid undergoes any temperature, pressure or pH change it can start precipitating secondary minerals. This can cause problems for geothermal utilization on the surface as the fluid boils on its way to the surface. By boiling it separates into a steam and liquid phase which can cause certain minerals to precipitate. Elements such as silica have very high concentrations in geothermal fluids and their solubility is temperature dependent. In the reservoir the silica concentrations are usually in close equilibrium with quartz but since the precipitation rate is very slow, it is a very rare mineral deposition in surface equipment. On the surface the silica precipitates as amorphous silica as the precipitation rate is almost instantaneous. Its solubility is however lower than that of quartz, making it possible to utilize a temperature range where electricity production is possible without silica scaling.

In order to gain a better understanding of scaling mechanisms and the complex interactions between the geothermal fluid, the surrounding rock and the production equipment, a geothermal reservoir was examined. The area in question is Hveragerði, a high-temperature reservoir on the outskirts of Hengill volcanic system.

The district heating system in Hveragerði is one of Iceland's oldest and one of the first district heating system to use high-temperature fluids for district heating systems. Much

experience and information is available on the Hveragerði district heating systems as it has been operated for more than 60 years. Many privately owned wells have been drilled in Hveragerði and some are still in operation. All of the wells in Hveragerði that are still in operation are free-flowing due to thermal expansion.

Hveragerði has had a continuous scaling problem due to high concentrations of calcium and silica. In most wells the silica scaling has been dealt with by heating up water in a closed loop system for residential areas. The silica scaling is therefore controlled and the scales can be easily cleaned from equipment. All wells also suffer calcite scaling, leading to annual maintenance of the wells by cleaning the calcite from the wells. Most of the wells in the area encounter similar problems and the solutions to dealing with the scaling are the same all around. Well HV-04 is an exception to other wells in the Hveragerði region as a new type of scale has been found in surface equipment connected to the well.

Well HV-04 has been in minor utilisation since it was drilled but recently it has been operating at a much higher rate. Connected to the well are nearby farmhouses and greenhouses that have been using the well since it was drilled. More recent users are the Agricultural University in Hveragerði and an inflated sports-center.

When the sports-center was connected to the well a new type of scale was found to form within a heat exchanger in the sports-center. This type of scaling has not been found by any of the other users. Earliest observations suggest that the scaling was neither calcite nor pure amorphous-silica. The scale had a dark, metallic colour to it and formed on the entrance side of the geothermal fluid in the heat exchanger. The capacity of the heat exchanger began to decrease drastically as the scale accumulated. Samples of the scale has been examined in XRD and ICP-FUS analysis and the results were interpreted as showing the iron-carbonate, siderite.

In order to further examine the scale an overview of the heating system must be carried out. It was found that the different pipes leading to each user are connected to the wellhead. The pipe leading to the sports-center is connected to the top of the pipeline which leads to the Agricultural University. The two-phase fluid flows to a heat exchanger, powering the inflation equipment of the sports-center and then flows to the close by river Varmá. Scale forms within the heat exchanger which causes a decreased flowrate and eventually the breakdown of the equipment.

A scale sample had been analysed by ÍSOR staff and samples analysed by XRD analysis and ICP. The results of this analysis were interpreted and discussed in a report written for the Hveragerði city council. The paper presented here reviewed the report and poten-

tial outcomes are analysed. The results were analysed further and results from previous chemical analysis compared and the potential effect the scaling and corrosion can have on surface equipment presented. The possibility of sulphide in the scaling was assumed to be of particular interest since older fluid analysis showed relatively high concentrations of H_2S.

The only analysis of the fluid from well HV-04 was carried out in 1980 and is listed in ÍSOR's database. That analysis showed relatively high concentrations of H_2S (20.9 ppm) and CO_2 (54 ppm). The results were studied by the aqueous species software Watch. Those results revealed that one of the main CO_2 species in the fluid at the specific temperature was H_2CO_3 which is a very corrosive on mild steel.

The fluid that flows to the heat exchanger is collected from the top part of the pipeline leading to the Agricultural University. This distorts the phase-proportions of the well fluid since the steam phase is more likely to flow through the pipe to the sports-center. This distortion can lead to CO_2 levels in the two-phased fluid to be higher than analysis shows and thus severely increase the corrosion of pipes and precipitation of carbonates.

The pipes going from the well to the sports-center provide the iron as the fluid corrodes the pipes and then precipitates siderite in the heat exchanger. The reason for this being the only equipment experiencing the siderite scaling is most likely that the pipe is connected to the top of a pipe going from the wellhead. This distorts the steam fraction of the fluid flowing to the sports-center, making it much more corrosive than it should otherwise be. The H_2S in the fluid mixture most likely binds to the dissolved iron leaving sulfide scaling within the pipes. ICP-FUS analysis showed only 7 wt% of carbon in the scaling sample. As no other carbonate mineral was found in the sample it can only be assumed that all the carbon was used to form the siderite scales found in the surface equipment in Hveragerðis' inflated sports-center. From those assumptions it can be calculated that 75% of the iron found in the sample is bound in the iron-carbonate while the remaining iron has formed various amorphous iron-silicates.

5.1   Discussion

The only chemical analysis of the geothermal fluid from well HV-04 available was from 1980. This can cause discrepancy from results presented in this study to those of future studies by using more accurate fluid analysis. The main changes that can affect the chemistry of the fluid is the change in the wells usage. The Agricultural University and the sports-center were only recently added on to the well, increasing its outflow drasti-

cally. This increased production can lead to a localised drawdown of reservoir water levels which decreases pressure and can affect the solubility of minerals and therefore decrease the dissolved solid concentration in the fluid.

The fact that no sulphur bearing precipitations are found in the scale sample strongly suggests that sulphide precipitates as the iron is dissolved. The high H_2S levels in the original fluid suggest that sulphur is in concentrations high enough for precipitation and with the addition of iron it will precipitate as various sulphides. The most likely scenario is that the sulphide is precipitating within the pipes as they are corroded and iron dissolved. This can lead to accumulation of sulphide within the pipes eventually leading to decreased flowrate and clogging. The pipes would therefore need replacing or cleaning. Another scenario is that as production continued throughout last decades, the chemical composition of the fluid changed. The H_2S levels could be much lower than when the fluid analysis was done. This would also explain the lack of sulphide scaling.

The data used was acquired by analysing a scale sample collected from the heat exchanger in March and April 2014. Sampling was carried out and prepared for further analysis by ÍSOR. All analytical methods have a certain level of uncertainty. FUS-ICP has approximately 0.01% margin of error on major elements in the sample. That margin of error is negligible compared to accuracy of calculations as most values were rounded to the first decimal place.

Continuous research within the area is essential to gain a better understanding of the chemistry of the fluid from well HV-04. Most information would be gathered by analysing the outflow mixture from the well and the condensed fluid from the heat exchanger. By analysing both fluids' chemical composition, the corrosion and scaling within the heat exchanger and pipes can be assessed.

References

[1] S. Arnórsson, *Isotopic and chemical techniques in geothermal exploration, development and use*, 2000.

[2] S. Arnórsson, "Geothermal systems in iceland: Structure and conceptual models I: High-temperature areas," *Geothermics*, vol. 24, no. 5, pp. 561–602, 1995.

[3] S. Arnórsson, A. Stefánsson, and J. Ö. Bjarnason, "Fluid-fluid interactions in geothermal systems," *Reviews in Mineralogy and Geochemistry*, vol. 65, no. 1, pp. 259–312, 2007.

[4] H. Kristmannsdottir, S. Thorhallsson, and K. Ragnars, "Magnesíumsilikatútfellingar í hitaveitum," Orkustofnun, Tech. Rep. OS-83051/JHD-10, 1983, in Icelandic.

[5] Þorgils Jónasson, "Borholur í Hveragerði," Orkustofnun, Tech. Rep. 2008-21, August 2008.

[6] V. Hardardottir and S. Thorhallsson, "Útfelling úr varmaskipti við Hamarshöllina, íþróttahús fyrir ofan Hveragerði," ÍSOR, Report for the municipality of Hveragerði, May 2014.

[7] I. T. Bjarnason, "An iceland hotspot saga," *Jokull*, vol. 58, pp. 3–16, 2008.

[8] F. K. Lutgens, E. J. Tarbuck, and D. Tasa, *Essentials of geology*. Pearson Prentice Hall, 2009.

[9] T. Thordarson and Á. Höskuldsson, "Postglacial volcanism in iceland," *Jökull*, vol. 58, pp. 197–228, 2008.

[10] J. D. Winter, *Principles of igneous and metamorphic petrology*. Prentice Hall New York, 2010, vol. 2.

[11] J. A. Pearce, N. B. Harris, and A. G. Tindle, "Trace element discrimination diagrams for the tectonic interpretation of granitic rocks," *Journal of petrology*, vol. 25, no. 4, pp. 956–983, 1984.

[12] P. C. Hess, *Origins of igneous rocks*.   Cambridge, Mass: Harvard University Press, 1989.

[13] I. S. E. Carmichael, "The petrology of thingmuli, a tertiary volcano in eastern iceland," *Journal of Petrology*, vol. 5, no. 3, pp. 435–460, 1964.

[14] S. Arnórsson, E. Gunnlaugsson, and H. Svavarsson, "The chemistry of geothermal waters in iceland. ii. mineral equilibria and independent variables controlling water compositions," *Geochimica et Cosmochimica Acta*, vol. 47, no. 3, pp. 547–566, 1983.

[15] H. Kristmannsdottir, "Útfellingar úr upphituðu ferskvatni frá Hitaveitu Hveragerðis," Orkustofnun, Tech. Rep. OS-83011/JHD-02, 1983, in Icelandic.

[16] H. KristmannsdÓttir, "Alteration of basaltic rocks by hydrothermal-activity at 100-300ř c," *Developments in sedimentology*, vol. 27, pp. 359–367, 1979.

[17] B. T. Gudmundsson and S. Arnórsson, "Secondary mineral–fluid equilibria in the krafla and námafjall geothermal systems, iceland," *Applied geochemistry*, vol. 20, no. 9, pp. 1607–1625, 2005.

[18] G. Bodvarsson, "Physical characteristics of natural heat resources in iceland," *Jökull*, vol. 11, pp. 29–38, 1961.

[19] I. B. Fridleifsson, "Geothermal activity in iceland," *Jökull*, vol. 29, pp. 47–56, 1979.

[20] D. White, L. Muffler, and A. Truesdell, "Vapor-dominated hydrothermal systems compared with hot-water systems," *Economic Geology*, vol. 66, no. 1, pp. 75–97, 1971.

[21] S. Arnórsson and E. Gunnlaugsson, "New gas geothermometers for geothermal explorationcalibration and application," *Geochimica et Cosmochimica Acta*, vol. 49, no. 6, pp. 1307–1325, 1985.

[22] K. V. Ragnarsdóttir, J. V. Walther, and S. Arnórsson, "Description and interpretation of the composition of fluid and alteration mineralogy in the geothermal system, at svartsengi, iceland," *Geochimica et Cosmochimica Acta*, vol. 48, no. 7, pp. 1535–1553, 1984.

[23] Ó. Pálsson, Þ. Jónasson, H. Barðadóttir, L. K. Sturludóttir *et al.*, "Orkutölur." 2013.

[24] Ó. G. Flóvenz and K. Saemundsson, "Heat flow and geothermal processes in iceland," *Tectonophysics*, vol. 225, no. 1, pp. 123–138, 1993.

[25] S. Arnórsson, G. Axelsson, and K. Sæmundsson, "Geothermal systems in iceland," *Jökull*, vol. 58, pp. 269–302, 2008.

[26] H. Kristmannsdóttir, A. Björnsson, S. Arnórsson, H. Ármannsson, and Á. Sveinbjörnsdóttir, "The reykholt and husafell geothermal fields in borgarfjördura geochemical study," in *Proceedings World Geothermal Congress, Anatalya, Turkey*, 2005.

[27] Landsvirkjun, "Virkjunarkostir - Þeistareykir," online; accessed 2-January-2015, url:http://www.landsvirkjun.is/Rannsoknirogthroun/Virkjunarkostir/Theistareykir.

[28] S. Björnsson, "Geothermal development and research in iceland," 2010, ISBN: 978-9979-68-273-8.

[29] I. B. Fridleifsson, "Geothermal energy for the benefit of the people," *Renewable and Sustainable Energy Reviews*, vol. 5, no. 3, pp. 299 – 312, 2001. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1364032101000028

[30] S. Þórðarson and o. Jónasson, "Um hitaveitur á Íslandi," in *Norræna sagnfræðiþingið*, 2007.

[31] I. G. Haraldsson, Þ. H. Þórisdóttir, and J. Ketilsson, "Efnahagslegur samanburður húshitunar með jarðhita og olíu árin 1970-2009," Orkustofnun, Tech. Rep. OS-2010/04, 2010.

[32] G. Pálmason, *Jarðhitabók: eðli og nýting auðlindar*. Hið íslenska bókmenntafélag, 2005.

[33] Orkuveita Reykjavíkur, "Jarðvarmavirkjanir Orkuveitu Reykjavíkur," 2013.

[34] H. Bjornsson, S. Bjornsson, and T. Sigurgeirsson, "Geothermal effects of water penetrating into hot rock boundaries of magma bodies," *Trans.-Geotherm. Resour. Counc.;(United States)*, vol. 4, no. CONF-800920-, 1980.

[35] M. Khodayar and S. Björnsson, "Fault ruptures and geothermal effects of the second earthquake, 29 may 2008, south iceland seismic zone," *Geothermics*, vol. 50, pp. 44–65, 2014.

[36] S. Þórðarsson, *Auður úr iðrum jarðar: saga hitaveitna og jarðhitanýtingar á Íslandi*. Hið íslenska bókmenntafélag, 1998.

[37] E. Gunnlaugsson and A. Einarsson, "Magnesium-silicate scaling in mixture of geothermal water and deaerated fresh water in a district heating system," *Geothermics*, vol. 18, no. 1, pp. 113–120, 1989.

[38] T. Hauksson, S. Thorhallsson, E. Gunnlaugsson, and A. Albertsson, "Control of magnesium silicate scaling in district heating systems," in *World Geothermal Congress 1995*, 1995.

[39] G. Ívarsson, "Ástandið í Hveragerði árið 2013," Orkuveita Reykjavíkur, Tech. Rep., 2013.

[40] Morgunblaðið, "Rætt um 15-17 mw jarðvarmavirkjun í gufudal," Newspaper article, July 3 1997.

[41] Morgunbladid, "Orkuver knúið jarðgufu tilbúið í hveragerði 1964," Newspaper article, February 5 1960.

[42] S. Arnorsson, E. Gunnlaugsson, and H. Svavarsson, "The chemistry of geothermal waters in iceland. iii. chemical geothermometry in geothermal investigations," *Geochimica et Cosmochimica Acta*, vol. 47, no. 3, pp. 567–577, 1983.

[43] R. Fournier and A. Truesdell, "An empirical na/k ca geothermometer for natural waters," *Geochimica et Cosmochimica Acta*, vol. 37, no. 5, pp. 1255–1275, 1973.

[44] R. Fournier, "Chemical geothermometers and mixing models for geothermal systems," *Geothermics*, vol. 5, no. 1, pp. 41–50, 1977.

[45] H. Kristmannsdóttir, "Types of scaling occurring by geothermal utilization in iceland," *Geothermics*, vol. 18, no. 1, pp. 183–190, 1989.

[46] S. Arnorsson, "Major element chemistry of the geothermal sea-water at Reykjanes and Svartsengi, Iceland," *Mineralogical Magazine*, vol. 42, no. 322, p. 209, 1978.

[47] B. Arnason, "Hydrothermal systems in iceland traced by deuterium," *Geothermics*, vol. 5, no. 14, pp. 125 – 151, 1977. [Online]. Available: http://www.sciencedirect. com/science/article/pii/0375650577900153

[48] W. Giggenbach, "Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin," *Earth and planetary science letters*, vol. 113, no. 4, pp. 495–510, 1992.

[49] H. Craig, G. Boato, and D. E. White, "Isotopic geochemistry of thermal waters," in *Conf. on Nuclear Processes in Geological Settings, Proceedings. Second National Academy of Sciences, Natl. Res. Council Publ*, vol. 19, 1956, pp. 29–44.

[50] B. Árnason, *Groundwater systems in Iceland traced by deuterium*.   Prentsmidjan Leiftur HF, 1976, vol. 42.

[51] S. Thorhallsson, "Common problems faced in geothermal generation and how to deal with them," in *Proceedings of the Workshop for Decision Makers on Geothermal Projects and Management, Naivasha, Kenya*, 2005.

[52] V. Hardardottir, "Subsurface exploration," University Lecture, 2013.

[53] J. M. Thorlacius and Árni Sigurðsson, "Niðurstöður efnagreininga á daglegum loft- og úrkomu- sýnum frá Írafossi 2004 - 2007," Icelandic met office, Tech. Rep. VÍ-ES-04, August 2008, in Icelandic.

[54] R. Chang, *Chemistry*.   McGraw Hill Higher Education, 2008.

[55] H. Armannsson, "Predicting calcite deposition in Krafla boreholes," *Geothermics*, 1989.

[56] S. Arnorsson, S. Sigurdsson, and H. Svavarsson, "The chemistry of geothermal waters in iceland. i. calculation of aqueous speciation from 0 to 370 c," *Geochimica et Cosmochimica Acta*, vol. 46, no. 9, pp. 1513–1532, 1982.

[57] K. Brown and M. Dunstall, "Silica scaling under controlled hydrodynamic conditions," in *Proceedings World Geothermal Congress*.   Citeseer, 2000, pp. 3039–3044.

[58] K. Brown, "Mineral scaling in geothermal power production," UNU-GTP, Tech. Rep. 2013-39, 2013.

[59] R. Fournier and J. Rowe, "Estimation of underground temperatures from the silica content of water from hot springs and wet-steam wells," *American Journal of Science*, vol. 264, no. 9, pp. 685–697, 1966.

[60] I. Gunnarsson and S. Arnórsson, "Amorphous silica solubility and the thermodynamic properties of h4sioř4 in the range of 0ř to 350řc at psat," *Geochimica et Cosmochimica Acta*, vol. 64, no. 13, pp. 2295 – 2307, 2000. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0016703799004263

[61] S. Arnórsson, "Deposition of calcium carbonate minerals from geothermal waters-theoretical considerations," *Geothermics*, vol. 18, no. 1, pp. 33–39, 1989.

[62] H. Ármannsson and M. Ólafsson, "Collection of geothermal fluids for chemical analysis," ÍSOR, Tech. Rep., 2006, report. ÍSOR-2006/016.

[63] S. Arnórsson, J. Ö. Bjarnason, N. Giroud, I. Gunnarsson, and A. Stefánsson, "Sampling and analysis of geothermal fluids," *Geofluids*, vol. 6, no. 3, pp. 203–216, 2006.

[64] Amptek.Inc., *The X-Ray Fluorescence Process*, online, accessed 2.12.2014, http://www.amptek.com/pdf/xrf.pdf.

[65] K. George and S. Nešic, "Investigation of carbon dioxide corrosion of mild steel in the presence of acetic acid-part 1: basic mechanisms," *Corrosion*, vol. 63, no. 2, pp. 178–186, 2007.

[66] N. E. A. of iceland, "Well database," June 2014.

[67] P. Bénézeth, J. Dandurand, and J. Harrichoury, "Solubility product of siderite (feco3) as a function of temperature (25–250c)," *Chemical Geology*, vol. 265, no. 1, pp. 3–12, 2009.