Presented at "Short Course VI on Utilization of Low- and Medium-Enthalpy Geothermal Resources and Financial Aspects of Utilization", organized by UNU-GTP and LaGeo, in Santa Tecla, El Salvador, March 23-29, 2014.

UNITED NATIONS UNIVERSITY
GEOTHERMAL TRAINING PROGRAMME

LaGeo S.A. de C.V.

PROBLEMS IN GEOTHERMAL OPERATION – SCALING AND CORROSION

Einar Gunnlaugsson[1], Halldór Ármannsson[2], Sverrir Thorhallsson[2] and Benedikt Steingrímsson[2]
[1]Orkuveita Reykjavíkur
ICELAND
einar.gunnlaugsson@or.is
[2]ISOR-Iceland GeoSurvey
ICELAND
h@isor.is, s@isor.is, bs@isor.is

ABSTRACT

Geothermal systems are found around the world in various geological settings. The high temperature fields are found in the volcanic regions, but medium and low temperature fields are found in most parts of the world. The largest of those are found in sedimentary basins where water heats up to useful temperatures (50-150°C) due to the continuous heat flux through the crust to the surface and in fracture systems in seismically active areas where surface water penetrates into the crust through active fractures and mines the heat out of the formations at few kilometre depth forming a water convection system within the crust.

Geothermal energy resources have been utilized by mankind through the centuries for bathing and domestic uses i.e. for washing, cooking and baking. The utilization spectrum changed drastically at the beginning of last century when technology to produce electricity from geothermal steam became available and various direct uses of geothermal were developed i.e. for space heating and greenhouse heating, in aquaculture and industry and in snow and ice melting in addition to the balneology uses. The utilization of geothermal increased steadily during the last century and the most rapid development during the last decades has been the dramatic increase in use of geothermal heat pumps for space heating and cooling.

The utilization of geothermal has not been without technical, environmental and political/cultural problems. On the technical side, the most common problems have been related to the chemistry of the geothermal fluids which sometimes contain quite considerable concentrations of minerals and gases, which can cause scaling and corrosion in wells and surface installations which the geothermal fluids flow through. Many of these technical problems have been solved, or minimized at least, by improved well design and well operation, proper material selection and chemical treatment of the geothermal fluids, including use of chemical inhibitors.

This paper gives a short overview of the chemistry of geothermal fluids, their corrosive nature and the most common scales and depositions formed in geothermal wells and installations with case histories from Iceland.

1. INTRODUCTION

Geothermal resources are found throughout the world but exploited geothermal systems are mainly found in regions of high geothermal gradients. Even though the greatest concentration of geothermal energy is associated with the Earth´s plate boundaries, geothermal energy resources are found in most countries and the exploitation of geothermal systems in normal and low geothermal gradient areas has been gaining momentum during the last decades.

Geothermal systems and reservoirs are classified on the basis of different aspects, such as reservoir temperature, enthalpy, physical state or their nature and geological settings. Table 1 summarizes classifications based on the first three aspects.

TABLE 1: Classifications of geothermal systems on the basis of temperature, enthalpy and physical state (Bodvarsson, 1964; Axelsson and Gunnlaugsson, 2000).

<table>
<tr><td>Low-temperature (LT) systems with reservoir temperature at 1 km depth below 150°C. Often characterized by hot or boiling springs.</td><td rowspan="2">Low-enthalpy geothermal systems with reservoir fluid enthalpies less than 800 kJ/kg, corresponding to temperatures less than about 190ºC.</td><td rowspan="2">Liquid-dominated geothermal reservoirs with the water temperature much below, the boiling point at the prevailing pressure and the water phase controls the pressure in the reservoir.</td></tr>
<tr><td>Medium-temperature (MT) systems with reservoir temperature at 1 km depth between 150-200°C.</td></tr>
<tr><td rowspan="2">High-temperature (HT) systems with reservoir temperature at 1 km depth above 200°C. Characterized by fumaroles, steam vents, mud pools and highly altered ground.</td><td rowspan="2">High-enthalpy geothermal systems with reservoir fluid enthalpies greater than 800 kJ/kg.</td><td>Liquid-dominated geothermal high temperature reservoir with the water temperature at, or below, the boiling point at the prevailing pressure and the water phase controls the pressure in the reservoir. Steam may be present, especially in the hotter systems where the temperature and pressure follow the boiling point curve through the reservoir</td></tr>
<tr><td>Vapour-dominated reservoirs where temperature is at, or above, boiling at the prevailing pressure and the steam phase controls the pressure in the reservoir. Some liquid water may be present.</td></tr>
</table>

Geothermal hot springs have been used by mankind through the centuries for bathing and for washing, cooking and baking. The hot springs for these uses were mostly outflows from underlying low temperature (LT) reservoir. At the beginning of last century the technology developed to utilize geothermal steam from geothermal high temperature (HT) wells to generate electricity and to use geothermal waters from hot springs and wells for space heating on a large scale. The steam for power generation was obtained from high temperature (HT) reservoirs, first from vapour dominated fields but later from two-phase liquid dominated systems. For conventional geothermal turbines using the steam directly the inlet pressure is in the range of 2-20 bar (Eliasson et al., 2014) On a much smaller scale electricity is also generated from medium temperature resource and low temperature resource for

reservoir temperature, or as a "bottoming cycle" using waste water from conventional generation, at temperatures as low as 120°C with the use of binary turbines. The geothermal direct uses also developed during the last century and soon included greenhouse heating, industrial drying and agricultural drying, fish farming and cooling and snow melting and more. Country reviews presented at the World Geothermal Congress in 2010 confirmed that geothermal energy resources have been identified in over 90 countries and 78 of them utilize geothermal resources. Installed geothermal electric power was 10.7 GW in 2009, producing 67 TWh/y of electricity (Bertani, 2010) and direct uses were estimated to be 122 TWh/y (Lund et al., 2010).

Large scale geothermal utilization has been ongoing for more than a century. The development has not been without problems, of course. The operational problems are of different type and include political, cultural and environmental issues on top of technical problems in harnessing the geothermal resources. The most common technical problems in geothermal utilization have been related to the chemistry of the geothermal fluids which sometimes contain considerable concentrations of minerals and gases which can cause scaling and corrosion in wells and surface installations which the geothermal fluids flow through.

This paper gives a short overview on the chemistry of geothermal fluids with respect to the corrosive nature of these fluids and the most common scales found in geothermal installations. Examples of corrosion and geothermal scales experienced in geothermal exploitation in Iceland are discussed and how they have been handled. Iceland is at a plate margin characterized by high heat flow. Due to the high heat flow hot springs are abundant in the country. About 1000 geothermal localities have been recognized in Iceland. Geothermal water is generally of meteoric origin, i.e. it is rainwater which has fallen to earth and sinks deep beneath the earth's surface where it is heated up by hot substrata and magma intrusions.

The high-temperature geothermal fields are all located within the volcanic zone (Figure 1) and there the temperature is higher than 200°C at 1000 m depth. The thermal manifestations are boiling water, mud pools, fumaroles and steam vents. The low-temperature fields are located at the flank of the volcanic zone, and there the temperature is lower than 150°C at 1000 m depth. The thermal manifestations are warm water to boiling hot springs.

The most significant use of geothermal energy in Iceland is for space heating and the low-temperature geothermal fields are the main source for this utilization.

The chemistry of the geothermal fields differs in composition mainly according to temperature. In the low-temperature fields the water is usually dilute. In the district heating utilities the water is usually used directly in flow through system. Most of the high-temperature geothermal fields are also of the dilute type except the fields on the Reykjanes peninsula. The water flows through basaltic lavas resulting in high pH of the low-temperature waters, usually pH between 9 and 10.

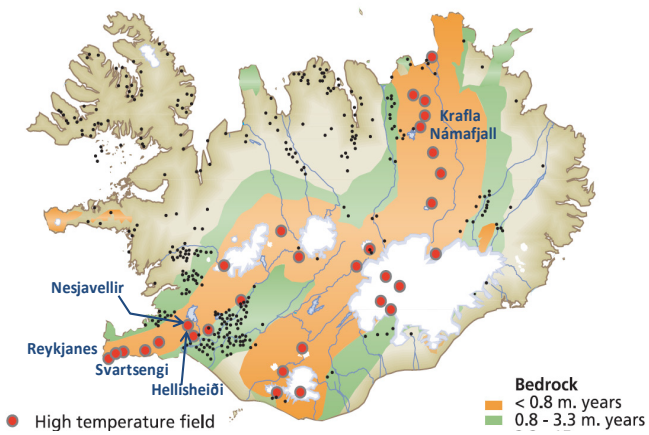

FIGURE 1: Location of geothermal fields in Iceland. The developed high temperature geothermal fields are shown with blue text.

2. GEOTHEMAL RESERVOIR FLUIDS AND THEIR CLASSIFICATION

Geothermal fluids refer to the fluids (steam, water, gas) in geothermal reservoir. These are liquid waters with dissolved solids and gas for the low- to medium temperature reservoirs but in boiling high temperature system geothermal liquid, steam and gas are found separately or together. Whatever state the fluid is in, depends on the reservoir temperature and pressure. When the fluid travels as a mixture of liquid and vapour (water and steam), it is referred to as two-phase. The dissolved minerals, silica and salts, are practically only found in the liquid phase. Another component of the geothermal fluids is the gas, mainly carbon dioxide, which is dissolved in the liquid phase inside the reservoir but is transferred to the steam phase upon boiling of the water. Other common geothermal gases are hydrogen sulphide, hydrogen, methane, nitrogen and argon. Oxygen, however, is usually of very low concentration in geothermal fluids for three reasons (1) the solubility of oxygen in water decreases rapidly with temperature from atmospheric and is practically zero at temperatures above 100°C and (2) geothermal fluids usually contain hydrogen sulphide which reacts with the oxygen and eliminates it from the fluid solution and (3) down to a temperature of about 80°C oxygen is taken up by rock in water-rock reactions. Oxygen is therefore only found in low temperature (<80°C) non-sulphide fluids in geothermal systems at relatively shallow depths in the crust.

Geothermal waters in-land areas are mainly of meteoric origin but oceanic waters are found in geothermal systems in coastal areas and in systems under the oceanic floor. Magmatic waters have been detected in geothermal waters in volcanic systems. Ellis and Mahon (1978) classified geothermal water into four categories based on major ions:

- Alkali-chloride water: pH 4-11, least common in young rocks, e.g. Iceland. These are mostly sodium and potassium chloride waters although in brines Ca concentration is often significant. Alkali-chloride water is however found in some mature geothermal waters in Iceland, e.g in the Theistareykir system.
- Acid sulphate water: These waters arise from the oxidation $H_2S \rightarrow SO_4$ near the surface and most of its constituents are dissolved from surface rock. Thus such water is generally not useful for prediction of subsurface properties.
- Acid sulphate-chloride water: such water may be a mixture of alkali chloride water and acid sulphate water, or it can arise from the oxidation $H_2S \rightarrow SO_4$ in alkali-chloride water or dissolution of S from rock followed by oxidation. Sulphate-chloride waters need not be very acid and may then reflect subsurface equilibria and be used for prediction of subsurface properties.
- Bicarbonate water: Bicarbonate water may derive from CO_2 rich steam condensing or mixing with water, it is quite common in old geothermal waters or on the peripheries of geothermal areas in outflows. They are commonly at equilibrium and may be used to predict subsurface properties. This is probably the most common group in equilibrated waters in Iceland.

A good way of distinguishing between the different types of geothermal water is the use of the chloride-sulphate-bicarbonate ternary diagram described by Giggenbach (1991). An example from Uganda is shown in Figure 2, where the geothermal water from one area, Kibiro, is a typical alkali-chloride water, the water from another, Buranga is a relatively alkaline chloride-sulphate-bicarbonate water, but the geothermal water from the third one, Katwe, is a sulphate water. The cold groundwater in the areas is scattered.

The dissolved constituents of geothermal water may originate in the original meteoric or oceanic water, but more likely they are the result of water-rock interaction and possibly modification by magmatic gas. They are divided into rock forming constituents, e.g. Si, Al, Na, K, Ca, Mg, Fe, Mn and incompatible constituents, e.g. Cl, B, Br.

Products of geothermal alteration are of rocks is controlled by temperature, pressure, chemical composition of water (e.g. CO_2, H_2S), original composition of rock, reaction time, rate of water and

steam flow, permeability and type of permeability and these products in turn control the chemical composition of the fluid. Some of the effects are that the silica concentration of the reservoir water depends on the solubility of quartz/chalcedony which is temperature dependent Al-silicate ion-exchange equilibria control Na/K, Na/Rb ratios, pH is controlled by salinity and Al-silicate equilibria involving hydrogen and alkali ions, Ca^{+2} and HCO_3^- concentrations depend on pH and CO_2 concentration because of equilibrium between the fluid and calcite, F^- and SO_4^{-2} concentrations are related to that of Ca^{+2}, limited by solubility of fluorite and anhydrite and temperature and salinity dependent silicate equilibria control a very low Mg^{+2} concentration. The results of alteration studies show that the chemical composition of geothermal fluids originates in controlled reactions dependent on temperature, pressure and rock composition. Therefore it is possible to deduce the properties of subsurface water, e.g. the reservoir temperature, from the chemical composition of water which has been collected at the earth's surface.

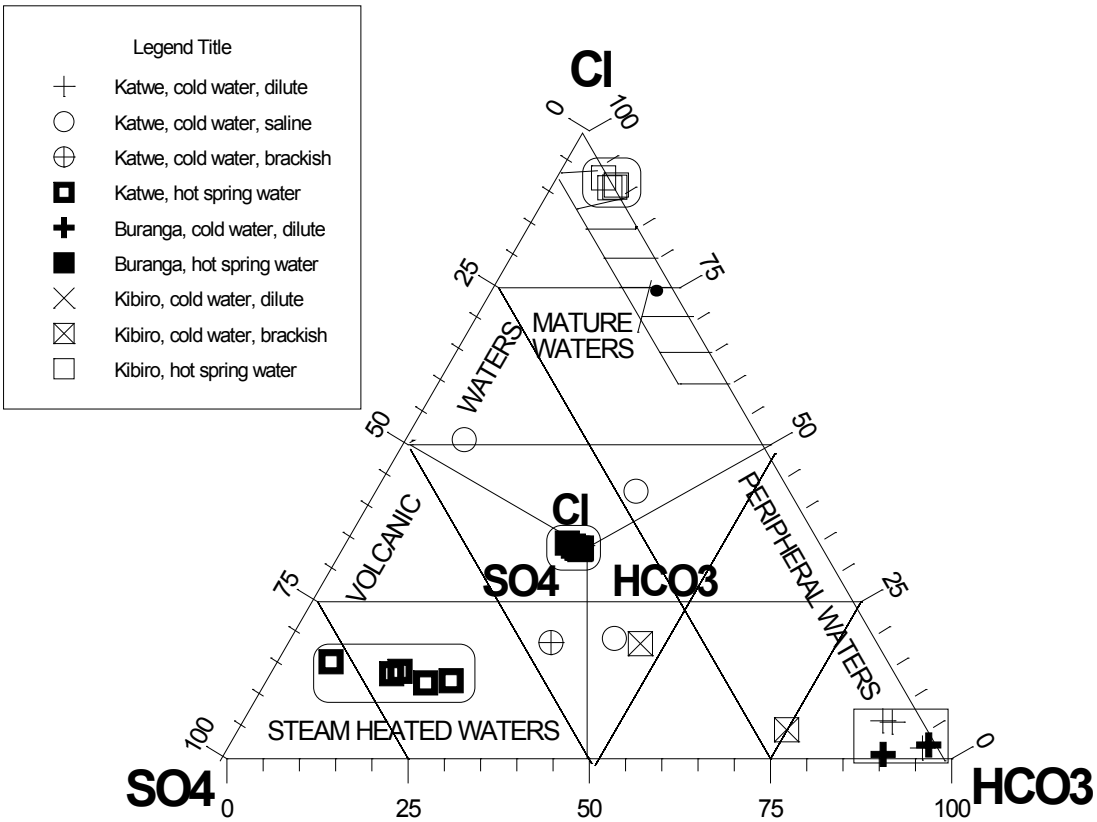

FIGURE 2: A ternary Cl-SO_4-HCO_3 diagram showing the characteristics of waters from different Ugandan geothermal systems

3 CORROSION FROM GEOTHERMAL FLUIDS

The corrosive potential of geothermal fluids is very variable. Miller (1980) identifies the main species in geothermal that are of interest regarding corrosion. These are:

- Hydrogen Ion: The corrosions rates of most materials increases as the pH of the fluid decrease. Geothermal low temperature waters are usually of high pH (pH 8-10) and high temperature fluids near neutral (pH 6-8) but extreme waters exist with pH as low as 2 and as high as 12. Low pH waters corrode carbon steel and cause corrosion cracking in in stainless steels. Thus the most common material selected for casings, pipes and vessels in contact with geothermal fluids is simply mild steel.

- Chloride: The chloride ion accelerates corrosion of metallic surfaces. The corrosion often happens in localized areas so-called "pitting" as well as uniform corrosion. Many grades of stainless steel are susceptible to stress corrosion cracking when exposed to waters high in chloride mild temperatures and oxygen.
- Hydrogen Sulphide. Copper and its alloys are attacked by hydrogen sulphide. Sulphide stress cracking in high strength steels is a potential problem in geothermal and use of these steels should be minimized and mild steels used instead. Hydrogen Sulphide reacts with mild steel and forms a productive coating and perhaps a thin crust of scaling and are thus protective on the inside of pipes and vessels.
- Carbon Dioxide: Carbon dioxide is a mild oxidizing agent that causes increased corrosion of plain carbon steels.
- Ammonia: Ammonia causes increased corrosion of copper-based alloys, and is especially important in relation to plain stress corrosion cracking. Mild steels are adversely affected by ammonia.
- Sulphate: Sulphate is the primary aggressive ion in some geothermal fluids.
- Oxygen is usually not present in geothermal fluids except in fluids at low temperature. Oxygen corrosion is therefore uncommon in geothermal wells but intrusion or diffusion of traces of oxygen into the geothermal fluid as it flows through the geothermal installations can make the water highly corrosive. Hydrogen sulphide in the geothermal water will on the other hand react with the oxygen and prevent corrosion as long as it is found in the solution.

The selection of materials for the construction of geothermal wells and fluids (liquid, steam or both) installation is one of the factors of importance in the original design of geothermal utilization schemes which are expected for long service life. Most geothermal fluids are, however, not corrosive and the main casing and pipe material selection is simply to use mild steel. There are localized problems of corrosions found in most geothermal installations, but most of them are manageable with proper material selection, operation and maintenance. The condensate is, however, corrosive and then stainless steel pipes or fibreglass are required. Copper cannot be used in presence of H_2S in the fluid and H_2S found in the ambient air around geothermal power plants, requires the air in control rooms and electrical switchgear to be filtered to remove any H_2S from the atmosphere to protect the copper wiring.

Acid fluids from geothermal wells. Truesdell et al., (1989) and D'Amore et al., (1990) came to the conclusion after the study of several areas (e.g. Tatun, Taiwan, Larderello, Italy, The Geysers, USA and Krafla, Iceland) that the origin of acid fluids in geothermal systems was magmatic.

Acid fluids in the Krafla geothermal system, North-Iceland. Since the beginning of the development of the Krafla field in 1974, the output and the chemical properties of steam and water from wells has been closely monitored.

Initially the wells were drilled in fields north of the power plant (Leirbotnar and Vítismór). It turned out that in these areas the reservoir is of dual character. The shallow part down to 1000 to 1400 m depth contains hot water (210 to 220 °C). The water in this upper zone contains little gas and has alkaline character. Silica and other dissolved ions are in close equilibrium with the rock minerals at measured temperature.

In these shallow wells the CO_2 gas concentration increases towards the fissure Hveragil (Figure 3) that is considered the main upflow path for steam from the deep reservoir to the surface. In the shallow wells close to the Hveragil fissure, calcite precipitation causes well blocking while in wells, just few hundred meters to the west, this problem is absent (Ármannsson et al., 1982).

Initially deep wells were cased down to 600 m depth and the inflow was both from the shallow hot water aquifer and also from aquifers at around 1800 to 2200 m depth. The temperature of the deep aquifers was 300 to 340 °C and the inflow water and steam and in some cases superheated dry steam. Few months after the construction of the plant started there was an eruption in the Leirhnjúkur volcano to the

northwest of the power plant. At that time only three wells had been flow tested. Well KG-3 was a good producer with a low steam gas concentration. Shortly after the eruption there was a sudden increase of steam gas concentration in this well. The output of the well decreased rapidly and the well was unusable after few months (Gíslason and Arnórsson 1976).

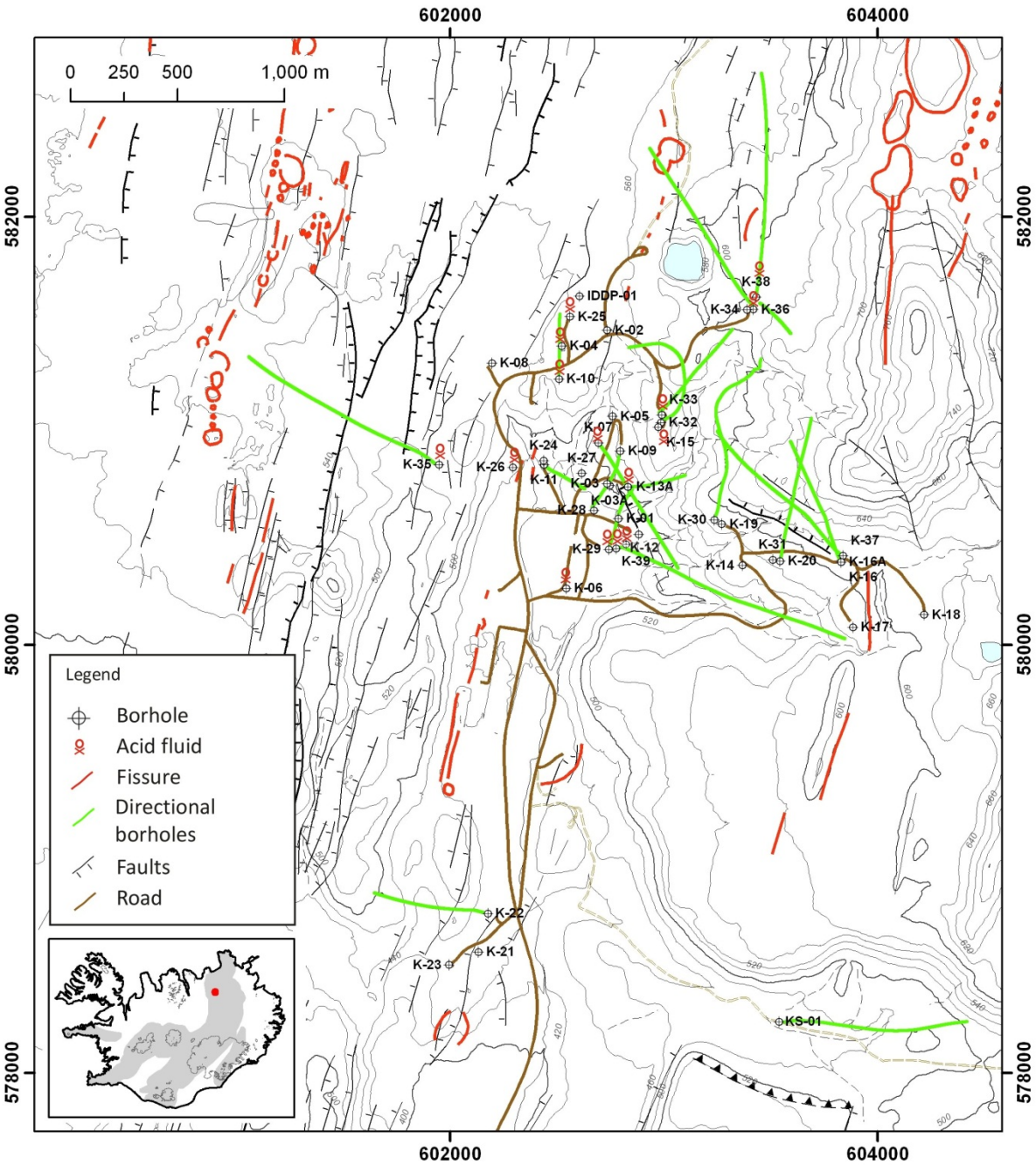

FIGURE 3: Krafla - wellfields and wells

Well KG-4 was being drilled when the eruption started. Before well completion, high-pressure steam, from deep aquifers, flowed up the well and into the shallower aquifers of the upper zone. The well was completed in a hurry but the wellhead was not designed for the high pressure and started to leak. The steam contained acid and the wellhead corroded rapidly and in the end the situation was uncontrollable and the well went out of control and formed a crater. The water, which flowed from the crater, had a pH of 1.86 (Gíslason and Arnórsson 1976).

Further drilling was postponed and the well design revised. The casing depth was increased to 800 m and the wellhead pressure-class increased.

Some of the wells drilled subsequently in Leirbotnar and Vítismór (KJ-6, KJ-7 and KG-10) turned out to be high in enthalpy and high in gas concentration. The effluent water had a black colour caused by precipitation of iron sulfides and silicates that formed in the well when acid fluids, containing iron from the corroding liner, mixed with alkaline water from the upper aquifers. The output of these wells decreased rapidly, produced mostly from the upper zone and were unusable. They were reamed and found to be clogged with iron sulfide and silicate scales (Swanteson and Kristmannsdóttir 1978). When flow tested, after reaming they were rapidly clogged again.

The well design was again revised and the casing depth increased to block the inflow from the upper zone and avoid precipitation of iron compounds in the wells. Well KG-12 was drilled to 2222 m depth and cased to 985 m. Its flow was superheated dry steam containing hydrogen chloride (HCl) which was converted to hydrochloric acid upon condensation. Examination of the wellhead showed great damage by acid corrosion and the turbine blades suffered erosion by iron chloride dust formed during the corrosion. The corrosion was most rapid at sites with conductive cooling (vents and flanges) and where the flow speed was high (orifices and bends). To make the steam usable for the plant the wellhead was insulated to prevent condensation and the steam mixed with alkaline water from the nearby well KJ-9 (Hauksson 1979).

Well KG-12 produced for a few years but the enthalpy dropped gradually and water started to flow from the well. The steam flow decreased rapidly for the first two months but was after that relatively stable until 2004 when the wellhead pressure was too low for the well to be usable (Hauksson and Benjamínsson 2005).

The CO_2 gas concentration in steam from the wells in Leirbotnar field decreased steadily after reaching a maximum soon after the eruptions started. A few wells have been drilled over the years to check whether the acid character of the deep zone was also decreasing (KG-25, KG-26 and KJ-29). The flow from the deep aquifers turned out to be acid as before, despite the decrease in CO_2 gas concentration of the steam.

It became evident that the drilling field would have to be relocated in order to supply the plant with sufficient good quality steam. Wells were drilled in the south slopes of the Krafla mountain (Suðurhlídar) and in an area south of the power plant (Hvíthólaklif) where chemical analysis of steam from fumaroles had indicated less magmatic influence than in the Leirbotnar and Vítismór (Ármannsson et al., 1982).

The steam quality was better but the productivity of the wells was insufficient. The plant was thus operated at half power for several years. The gas changes due to the magmatic activity were described in detail by Ármannsson et al., (1982, 1989).

Later (1997 to 2000) a new drill field in the west slopes of the Krafla mountain was explored (Vesturhlíðar). This field was productive and since 1999 the power plant has been operated at full power (Guðmundsson 2001). The concentration of CO_2 and H_2S gas in well steam is relatively high, but acid steam was not observed.

Recently seven new wells have been drilled to obtain steam for further expansion of the Krafla power plant.

Well KJ-35 was located northwest of the plant and directionally drilled towards the Leirhnúkur volcano. It was a good producer but the output declined steadily during flow test. The chemical analysis of the fluid collected at wellhead did not show clear evidence of acid or iron precipitation in the well (Giroud

et al., 2008). Logging of the well showed blocking at 1960 m depth and a plug consisting of iron sulfide and silicate similar to the scale that had blocked other acid wells in Krafla.

Well KJ-36 was located southeast of the Víti crater and directionally drilled to northwest under the crater. When flow tested the well was very powerful. The steam collected at the wellhead was acid and corrosive. The flow test was stopped after 6 days when a hole had formed in the wellhead pipe. The well was tested again for 32 days after fortification of the wellhead. The steam was still acid but turned from dry steam into saturated steam after a while. The corrosion rate was very rapid so the well was shut in and the acid aquifer blocked off by cementing (Hauksson and Gudmundsson 2008). Now the well produces from aquifers at 1600 to 1700 depth and the steam is used for the plant.

Well KJ-38 is located on the same platform as well KJ-36 and drilled to the north. It has also hit acid aquifers.

The location of the wells in Krafla is shown in Figure 3 and those wells, that have hit acid aquifers, are shown with a red symbol. Generally wells, which are deeper than 2000 m and west of the Hveragil fissure, have hit acid aquifers. Wells east of this fissure have not been contaminated.

Collection of representative samples from the deep acid aquifers has been difficult. The first wells were of dual character and alkaline water from the upper zone obscured the character of the deep zone steam. By mass balance calculations it was possible though to show that the inflow was of acid character (Hauksson 1980).

Well KG-12 was drilled with a 985 m deep casing and a sample of the deep steam could be obtained (Hauksson 1979). The casing in well KG-25 was drilled was 1145 m deep but the upper alkaline zone reached deeper there and alkaline water flowed into the well at a depth of 1455 m (Ármannsson and Gíslason 1992).

In well KJ-36 the deep acid aquifer was very powerful and initially the flow from shallower aquifers did not obscure the character significantly (Hauksson and Gudmundsson 2008).

The first Iceland Deep Drilling project well was drilled in Krafla in the first half of 2009 (IDDP-01, Figure 3). The drill rig hit magma at about 2100 m depth and drilling was stopped. The well was designed to be drilled into a high temperature hydrothermal system with the goal of finding a 400 – 600 °C hot superheated or supercritical fluid. The composition of the superheated steam shows acidity similar to that of wells K-12 and K-36 but appears relatively benign. The chloride concentration was considerably higher in both wells KG-12 (112 mg/kg) and KJ-36 (400 mg/kg) fluid. The pH is certainly not lower and there seems no chance of condensation during the steam‘s passage to the surface so no acid fluid should be formed until the steam has reached the surface and condensed and can be dealt with adequately. The acid gas could effectively be scrubbed from the steam with water. The steam contained a gaseous sulphur compound (80–100 mg/kg S), which could only be scrubbed from the steam with alkaline water. The steam contained both silica dust and dissolved silica which was effectively washed from the steam with wet scrubbing. Experiments on corrosion and erosion resistance of metals and alloys were problematic to run because of equipment clogging by silica dust.

4. GEOTHERMAL SCALES

Several types of scales are observed in geothermal wells and installations. These include carbonate minerals (calcite and aragonite), amorphous silicates, and metal oxides and sulphides. The most common geothermal scales are silica (SiO_2) and calcite ($CaCO_3$). Both these scales are white coloured and visually not easy to tell apart. The silica scales often appear grey or black due to small amounts of iron sulphide, a corrosion product found inside all geothermal pipelines. A quick method to distinguish these two is to put a drop of hydrochloric acid on a scale sample and if bubbles are formed it is calcite.

Scale analysis is otherwise a tedious process where X-ray diffraction (XRD) for identification of crystalline substances and electron microscopy (SEM) for distributive and qualitative analysis, are used together with wet chemistry analytical methods (Figure 4).

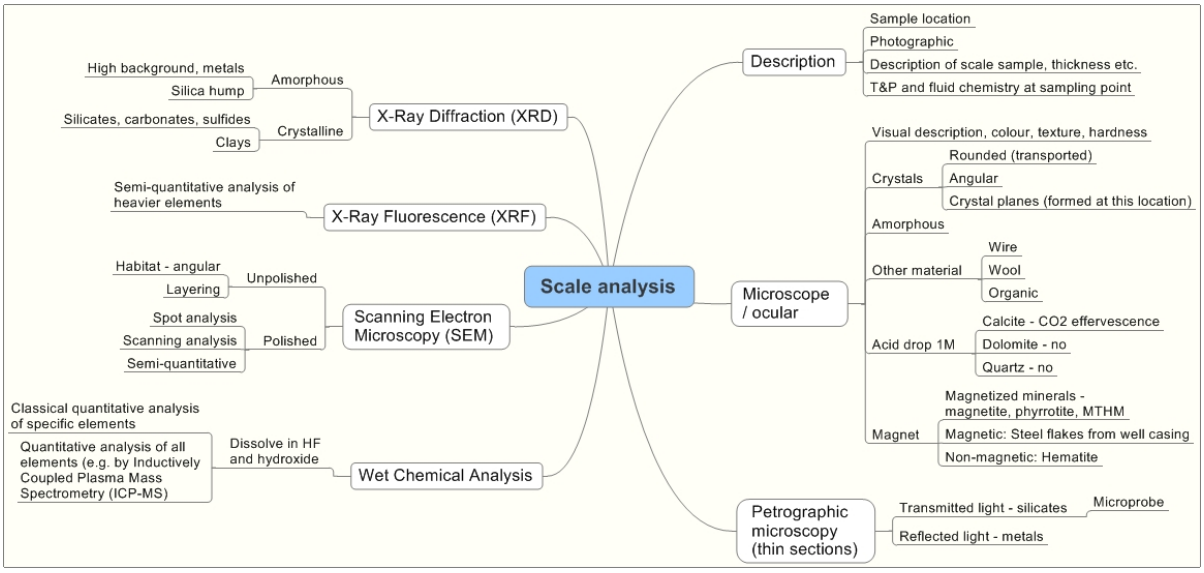

FIGURE 4: Methods used for geothermal scale analysis in Iceland (Thórhallson, 2012)

Silica scales. Silica scales are found to some extent in all high temperature geothermal installations but by maintaining the temperature above the solubility level for amorphous silica (the non-crystalline form of silica), the scaling should not occur and thus this is one of the design criteria for most geothermal plants. In this way the high-pressure separator will not scale, nor the reinjection pipeline, assuming that the so called "hot-injection" method is used. In the high temperature reservoir before the fluid is extracted, the silica concentration is usually in equilibrium with quartz, the crystalline form of silica. Once the water starts to boil and cool down, the silica concentration in the water increases due to the steam loss. The water immediately becomes quartz supersaturated but quartz precipitates are not formed because of the slow growth of quartz crystals. Silica scales are first formed when the amorphous silica solubility curve is passed (Figure 5). Looking at these two curves it is clear that the "window of opportunity" for operating the geothermal plants free of silica scaling lies between the quartz and amorphous curves. This means in practice that only some 25% of the water can be converted by "flashing" into steam from liquid dominated reservoirs without the danger of silica scales, almost independently of the temperature of the resource (flashing= rapid conversion of water into steam). A silica "rule of thumb" may say that it is only possible to cool the water by some 100°C without the risk of scaling. Reservoir water of 240°C has thus to be

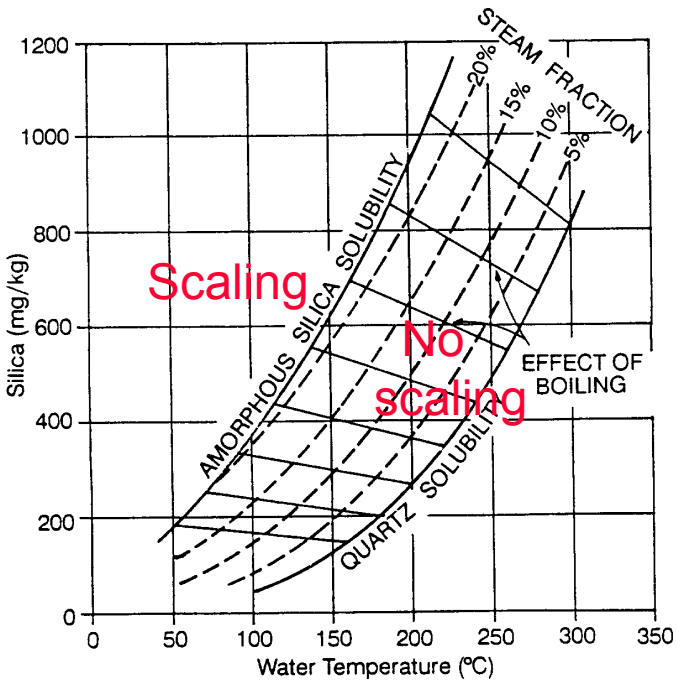

FIGURE 5: Solubility of silica in water. Scaling occurs above the amorphous silica solubility curve.

separated above 140°C to avoid scaling. For this reason it is not of as great importance as one might think that the reservoir temperature be as high as possible, because the higher the reservoir temperature, the higher the temperature of re-injected water needs to be that puts a lid on the thermal efficiency.

In the combined heat and power geothermal plants the precipitation of amorphous silica can occur when the separated water flows through heat exchangers. In the heat exchangers the separated water is cooled down and becomes supersaturated with respect to amorphous silica. This commonly causes scaling in the tubes of the heat exchangers which have to be removed regularly. In the dilute high temperature fields where the chloride concentration is low the precipitation of amorphous silica can be postpone by slow flow rate through heat exchangers allowing the aqueous silica to form polymers in the solution. This has been applied at the Nesjavellir power plant reducing silica scaling in the heat exchangers. After heat exchangers the separated water flows through a large retention tank for further polymerisation of the silica before condensate is mixed with the separated water and re-injected into subsurface.

In low temperature geothermal systems the silica content is governed by the solubility of the silica mineral chalcedony at low temperature and quartz at higher temperature. In water from the low-temperature areas, although it is cooled in the district heating systems down to about 20°C, silica saturation does not occur.

Iron silicate scales. If there is a significant concentration of iron in the fluid, deposition of iron silicates will set in at a higher temperature than the silica deposition but at lower temperatures iron tends to be deposited in the form of oxides. They often form with sulphide scales in saline geothermal fluids or in fluids disturbed by the effects of volcanic gas. These scales normally do not form at higher pressures than 16-18 bar and are contained by keeping the wellhead pressure above that.

Sulphide scales. In saline geothermal fluids or in fluids disturbed by the effects of volcanic gas sulphide deposits are prone to form by reaction of metal(s) with H_2S. In saline solutions these tend to comprise PbS (galena), ZnS (wurtzite, sphalerite), CuS (covellite), Cu_2S (chalcocite), $CuFeS_2$ (chalcopyrite) and bornite (Cu_5FeS_4). In Mt Amiata, Italy SbS_2 (stibnite,) is a major deposit. Where volcanic gas affects the system FeS_2 (pyrite) and FeS (pyrrhotite) are the most common sulphides. As recounted above such scales along with iron silicates were observed in several wells in Krafla, North Iceland during the Krafla fires 1975-1984 (Figure 6). In Reykjanes, Iceland wurtzite deposits are observed at high pressures but sphalerite becomes the dominant sulphide scale with pressure lowering. Galena, chalcopyrite, pyrrhotite and traces of bornite have also been observed (Ármannsson and Hardardóttir 2010). No specific measures have been taken there to deal with such deposits but one well was reamed due to loss of power and sulphide deposits removed but this did not help restore the power of the well.

FIGURE 6: Iron sulphide and silicate deposits in flow from a Krafla well

Calcium carbonate scales (in the crystalline forms calcite or aragonite) are common in wells with reservoir temperatures of 140-240°C, and are primarily found at the depth where the water starts to boil in the well. Flashing causes CO_2 stripping and a pH increase, which may lead to calcite deposition according to

$$Ca^{+2} + 2HCO_3^- \leftrightarrow CaCO_3 + CO_2 + H_2O$$

Calcite solubility is retrograde, i.e. it decreases with increasing temperature and as the water and steam travel up the well, the calcite deposition stops rather suddenly. Calcite scales are thus primarily found over a 100-300 m long section in the well. The extent of supersaturation can be calculated and the reaction is very fast so rate experiments need not be carried out. A certain degree of supersaturation needs to be reached for calcite scaling to set off, so there is a small "window of opportunity" in this case. Geothermal water is saturated with respect to calcite at <240°C in the reservoir but at >260°C calcite deposition is usually not a problem.

Prediction of calcite scaling in Krafla wells. During the early stages of production from the Krafla field calcite scaling was observed in some of the shallower wells and reaming with a drill rig was the chosen method for controlling the scaling. It was important to know the extent of formation, its rate and the depth at which it was formed. The first step is to predict whether or not a deposit will form which is carried out by a thermodynamical calculation in which the supersaturation of calcite is found by comparing analysed values with theoretical values. In Figure 7 there is an example of a diagram showing supersaturation for well KJ-9 in Krafla. The diagram shows that at the reservoir temperature at the bottom of the well the sample is saturated but as the sample boils and cools it becomes significantly supersaturated but less so with further cooling. Deposition is expected to start soon after the initial boiling, rise to a maximum and then diminish.

A method of finding the extent of deposition is to collect a downhole fluid sample below the boiling level and compare the calcium concentration with that of a wellhead sample collected at a similar time and assume that the difference in concentration is due to calcite deposition. Information on flow from the well and the time of production can then be used to calculate the total mass of deposit formed in the well. This was done for well KJ-9 and a check could be carried out on this method because it was decided to deepen the well and the liners were removed from it. Thus it was possible to measure the length and thickness of the scale inside the liner and combine with caliper logs from the casing to determine the volume of scale formed. Analysis of the scale was 98.6% calcite and its density 2500 kg/m^3 and thus it was possible to calculate the mass of the deposit. The two results were compared as presented in Table 2.

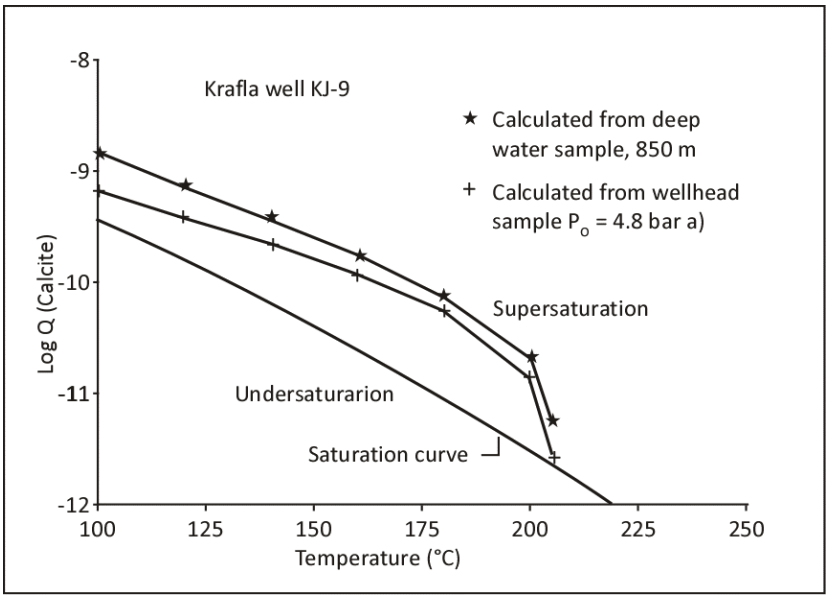

FIGURE 7: Calcite supersaturation in samples from well KJ-9, Krafla, North Iceland

TABLE 2: Quantity of calcite formed in well KJ-9, Krafla in 1977 according to determinations of volume of deposit and by calculation based on differences in calcium concentrations at wellhead and close to the bottom of the well.

Method	**Volume determined (m^3)**	**Mass determined (kg)**
Caliper log and thickness measurements	1.1	2700
Chemical analysis		2400

Thus it was confirmed that the method of determination of calcium in downhole and wellhead samples and assuming the difference to be due to calcite deposition was justified. It was also important to know how fast the deposition was taking place and this was observed by monitoring the flow of the wells and determining when a decrease in flow started. Generally when a decrease started it was very fast and the well soon became a very poor producer. The monitoring results for well KJ-9 (KJ-9, before deepening, KJ-9b after deepening showed that the period of relatively undisturbed flow was similar between reamings and this helped very much in planning the use of the well, the time at which the drill rig should be brought in for reaming. As is to be expected the wellhead pressure affects the scale formation because it will affect the depth at which the scale is formed. The higher the wellhead pressure the shallower is the depth at which deposits form. The clogging of the well occurs when the opening through which the fluid flows has become extremely narrow and therefore it is possible to prolong the period of relatively undisturbed flow by varying the wellhead pressure although this means that a greater quantity of deposit forms. Wangyal (1992) used the program Hola (Björnsson and Bödvarsson 1987) to calculate the flashing depth at different wellhead pressures for several wells in Iceland with the results shown in Figure 8. It is clear that by controlling the wellhead pressure the depth of deposit formation can be varied and if the producer can tolerate the reduced flow due to high pressure a smaller and cheaper drill rig may be deployed for reaming wells with deposits at a shallow depth.

Calcite inhibition. Several inhibitors have been used to prevent calcite deposition in geothermal wells. Examples of much used inhibitors are Dequest 2006 (Aminotri (methylene phosphonic acid) 38-42%), Nalco 95D0666 (Polymaleic acid 30-60% ,maleic acid 1-5%), Nalco 1340 HP (Polyacrylate) and Drewsperse 747A (Polycarboxylic acid 40-55% (Acrylic copolymer)). Tests in Krafla proved Nalco 1340HP most effective Hauksson et al., 1999), but a 5% concentration was too low because of precipitation due to bacterial growth and polymerization of the inhibitor. Increasing the concentration to 10% and using deionized, instead of geothermal water was successful.

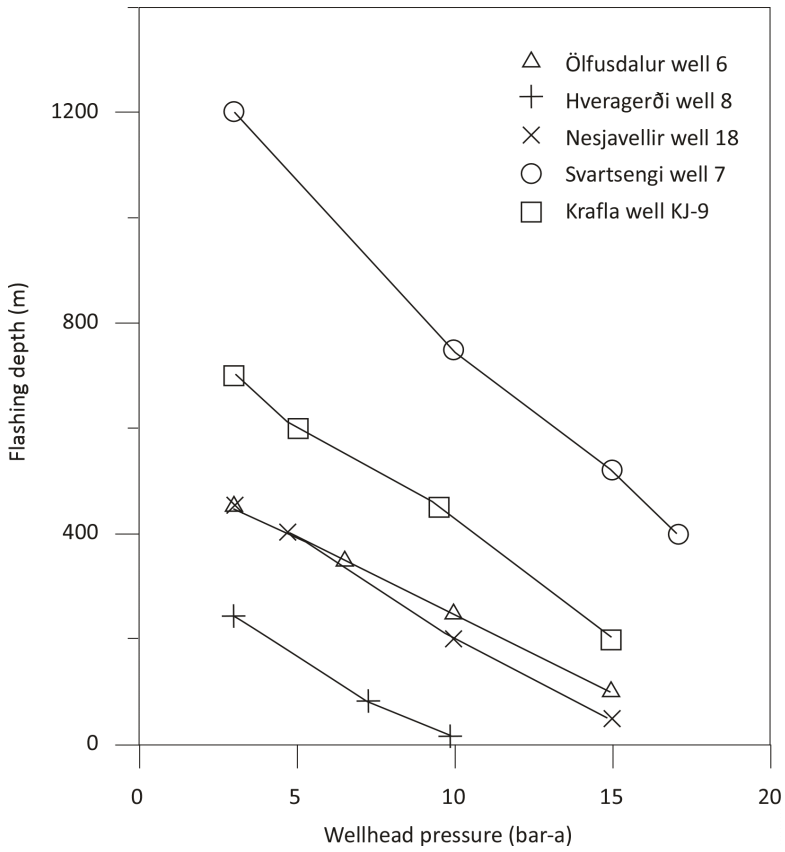

FIGURE 8: Flashing depth versus wellhead pressure in some geothermal wells in Iceland

Calcite scaling in low temperature geothermal fields in Iceland. The most significant use of geothermal energy in Iceland is for space heating and the low-temperature geothermal fields are the main source for this utilization. The geothermal reservoir water is in equilibrium with calcium carbonate and the silica content is governed by the solubility of the silica mineral chalcedony at low temperature and quartz at higher temperature. Saturation with respect to amorphous silica is not reached in water from the low-temperature areas although it is cooled in the district heating systems down to about 20°C. Here two examples will be given of calcite scaling in low-temperature fields in Iceland.

Sudureyri district heating. Sudureyri geothermal field is located in Northwest Iceland. This district heating started operation in 1978 serving the village of Sudureyri with about 350 inhabitants. Two drillholes are productive and both with calcite scales (Ólafsson, 1999). During exploitation chloride concentration increased up to 300 mg/l during 1975-1987 but reduced when a new well was drilled to 70 mg/l leading to supersaturation of calcite as higher calcium concentrations are in the chloride rich water of seawater origin (Figure 9). The scaling has been overcome by injection of a poly-phosphate inhibitor through a capillary tube to a position below the pump.

Laugarnes geothermal field Reykjavík. Exploitation from the Laugarnes geothermal field in Reykjavík was initiated in 1930. In the beginning only artesian flow was used from relatively shallow drillholes. Deep drilling began in 1958 and the first downhole pump was installed a year later. Artesian flow ceased in 1965 due to draw-down and since then downhole pumps have been operated in the wells (Gunnlaugsson and Ívarsson, 2010). The maximum production rate during the coldest part of the year is about 330 l/s. The fluid from the field was low in total dissolved solids, about 350 mg/kg, of which about 35 mg/kg was chloride.

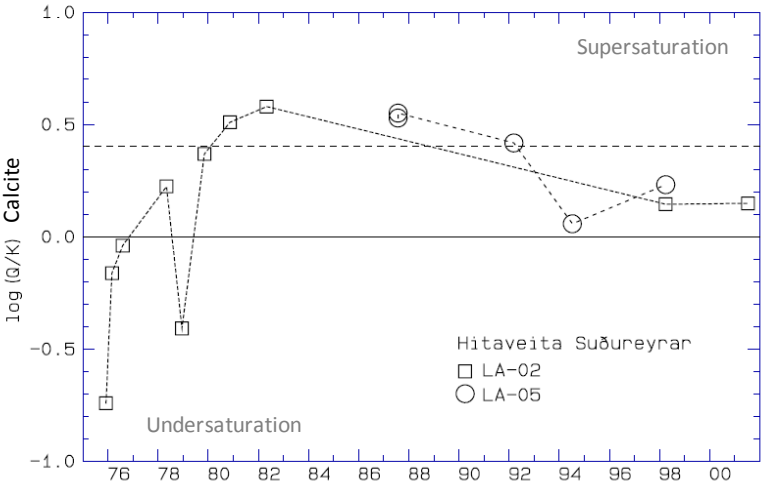

FIGURE 9: Calcite saturation for water from Sudureyri district heating (from Hardardóttir, 2002)

Production from the field has caused pressure drawdown within the production well field. The exploitation of the field has not had any effect on the production temperature, but some gradual changes have been measured in the fluid chemistry after 1980 when production was increased in the western part of the field. The concentration of chloride has doubled in some of the wells while other remains as initially. Two wells produced water in excess of 100 ppm chloride concentration. The changes in chemistry are most likely caused by infiltration of highly saline water into the uppermost part of the reservoir.

The mixing of the reservoir fluid with more saline water has caused calcite deposition in downhole pumps where the chloride concentration is higher than 100 ppm. Figure 10 shows the equilibrium curve for calcite as a function of temperature and comparison of calculated activity product for calcite for water samples from all wells in the Laugarnes field (Gunnlaugsson, 2004). Most samples are close to equilibrium at given temperature but water samples with higher chloride concentration (some of the red dots) show deviation from equilibrium. Figure 11 shows a graph where the solubility product of calcite for samples from one well with increasing chloride concentration is plotted against chloride concentration. The calculations are performed at 120°C and the equilibrium constant for calcite at that temperature is shown on the graph as horizontal line.

Some of the saline water enters the reservoir through wells due to shallow casings. To avoid leakage of saline water into the reservoir, the contamination has been stopped by plugging by cement some of the older drillholes in the field which showed inflow of saline water.

Magnesium silicate scaling. Magnesium silicates are formed upon heating of silica containing ground water or mixing of cold ground water and geothermal water. They have been shown to consist mainly of poorly developed antigorite (Gunnarsson et al., 2005) Their solubility decreases (deposition increases) with increased temperature and pH. The rate of deposition has been found to increase linearly with supersaturation but exponentially with temperature.

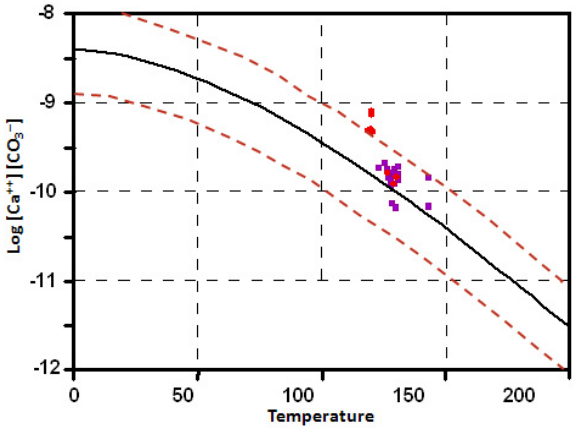

FIGURE 10: Solubility of calcite and degree of saturation of water from the Laugarnes field

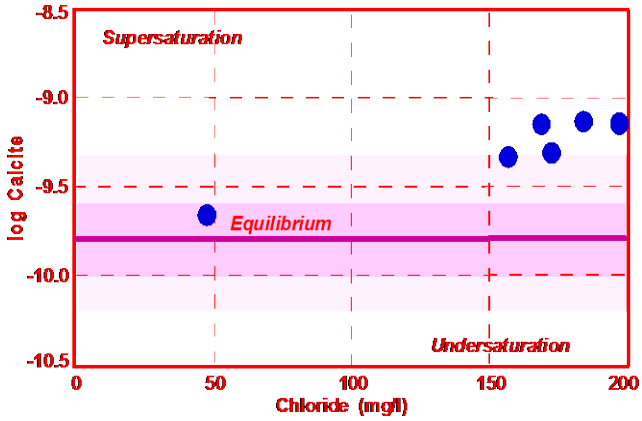

FIGURE 11: Changes of the solubility product of calcite with increasing chloride concentration

Magnesium silicate scaling has been encountered in several geothermal district heating systems in Iceland. The scaling occurs in power plants where heated freshwater after thermal deaeration reaches a high pH and also when geothermal and fresh waters are mixed.

Magnesium-silicate scaling in Icelandic district heating systems was first encountered in Hveragerdi where high temperature geothermal water and fresh water were mixed. In other district heating systems where magnesium rich fresh water is heated, precipitation of magnesium silicate may occur.

In 1990 the Reykjavík District Heating began utilizing heated freshwater from the Nesjavellir power plant. Previously, the company had only used low temperature waters from the geothermal fields in Reykjavik and the surroundings. Pilot plant experiments had indicated that some mixing of the deaerated freshwater and geothermal water could be tolerated if the mixing ratio was carefully controlled (Gunnlaugsson and Einarsson, 1989). After introducing the water from Nesjavellir, the deaerated water and heated freshwater was allowed to mix with the geothermal water, but control of the mixing ratio was insufficient and heavy scaling occurred in the pipeline system. It soon became evident that scaling was more severe than expected and an elaborated study of the problem was initiated. The results of experiments lead to the abandonment of any mixing and the distribution system was modified to keep the waters in two separate distribution networks, each serving different regions of the city (Hauksson et al., 1995).

The presence of magnesium silicate can be explained by studying the chemical composition of the water and compare it to the solubility of magnesium silicate precipitate.

The solubility of magnesium-silicate can be described by:

$$MgSiO_3 \cdot H_2O + H_2O = Mg^{++} + H_3SiO_4^- + OH^-$$

The solubility constant for the reaction depends on what precipitate is formed. The material has showed to be near amorphous magnesium silicate. In experiments in connection with magnesium scaling in Reykjavík the solubility of the precipitate was determined at few temperature values from 60 to 120°C, as shown in Figure 12 (Hauksson et al., 1995). The equilibrium constant can be described by the equitation:

$$\log(K_{sp}) = -12.90 + 0.00262T - 0.00006212 * T^2 \quad (1)$$

where T is in °C.

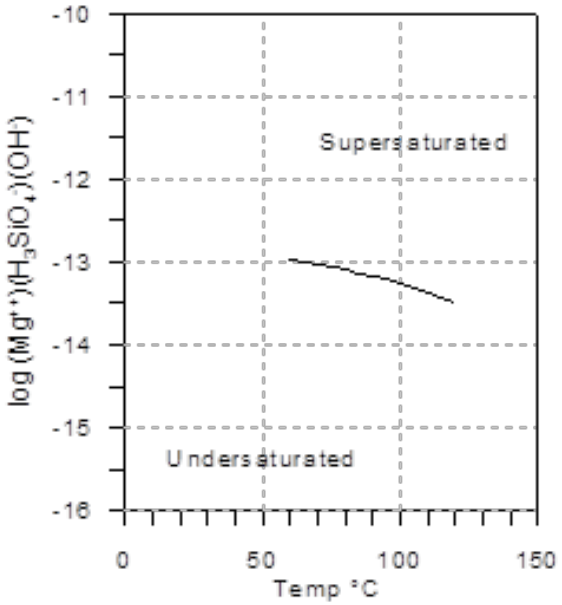

FIGURE 12: Solubility of magnesium silicate in the temperature range 60 to 120°C

REFERENCES

Axelsson, G., and Gunnlaugsson, E. (convenors), 2000: Long-term monitoring of high- and low-enthalpy fields under exploitation. *World Geothermal Congress 2000 Short Course, Kokonoe, Kyushu District, Japan*. International Geothermal Association, 226 p.

Ármannsson, H., and Gíslason, G., 1992: The occurrence of acidic fluids in the Leirbotnar field, Krafla, Iceland. In: Kharaka, Y.K, and Maest, A.S. (editors), *Water-rock interaction.* Balkema, Rotterdam, Holland, 1257-1260.

.

Ármannsson, H., and Hardardóttir, V., 2010: Geochemicqal patterns in saline high temperature geothermal systems. In: Birkle, P., and Torres-Alvarando, I.S. (editors), *Water-rock interaction.* CRC Press, Taylor and Francis Group, London, 133-136.

Ármannsson H., Benjamínsson J., and Jeffrey A., 1989: Gas changes in the Krafla geothermal system, Iceland. *Chem. Geol., 76*, 175-196.

Ármannsson, H., Gíslason, G., and Hauksson, T., 1982: Magmatic gases aid the mapping of the flow pattern in a geothermal system. *Geochim. Cosmochim. Acta*, *46*, 167-177.

Bertani, R., 2010: World geothermal power generation 2005–2010. Update report. *Proceedings World Geothermal Congress 2010, Bali, Indonesia,* 41 pp.

Björnsson, G., and Bödvarsson, G.S., 1987: A multi-feedzone wellbore simulator. *Geothermal Research Council Transactions, 11*, 503-507.

Bödvarsson, G., 1964: Physical characteristics of natural heat sources in Iceland. *Proceedings UN Conference on New Sources of Energy, Volume 2: Geothermal Energy, Rome, Italy*. United Nations, New York, 82-89.

D'Amore, F., Truesdell, A.H., and Haizlip, J.R., 1990: Production of HCl by mineral reaction in high temperature geothermal systems. *Proceedings 15th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, California, United States*, 23-25.

Eliasson, E.T., Thorhallsson, S., and Steingrimsson, B., 2014: Geothermal power plants. *Presented at "Short Course on Utilization of Low- and Medium Enthalpy Geothermal Resources and Financial Aspects of Utilization, organized by UNU-GTP and LaGeo, in Santa Tecla, El Salvador*, 16 pp.

Ellis, A.J., and Mahon, W.A.J., 1977: *Chemistry and geothermal systems.* Academic Press, New York, NY, United States, 392 pp.

Fournier, R.O., and Rowe, J.J., 1966: Estimation of underground temperatures from the silica content of water from hot springs and wet-steam wells. *Am. J. Sci*., *264*, 685-697.

Giggenbach, W.F., 1991: Chemical techniques in geothermal exploration. In: D'Amore, F. (coordinator), *Applications of geochemistry in geothermal reservoir development.* UNITAR/UNDP publication, Rome, 119-142.

Giroud, N., Ármannsson, H., and Ólafsson, M. 2008: *Well KJ-35, Krafla. Chemical composition of liquid and steam during a flow test in autumn 2007.* Iceland GeoSurvey, report ÍSOR-08056 (in Icelandic), 8 pp.

Gíslason, G., and Arnórsson, S., 1976: *Framvinduskýrsla um breytingar á rennsli og efnainnihaldi í borholum 3 og 4 í Kröflu (A progress report on flow and chemical compostion of fluids from boreholes 3 and 4 in Krafla).* Orkustofnun, report OS-JHD-7640 (in Icelandic), 14 pp.

Gudmundsson, Á., 2001: An expansion of the Krafla Power Plant from 30 to 60 MW_e. Geothermal considerations. *Geothermal Research Council Transactions, 25*, 741-746.

Gunnarsson, I., Arnórsson, S., and Jakobsson, S. 2005: Precipitation of poorly crystalline antigorite under hydrothermal conditions. *Geochim. Cosmochim. Acta, 69*, 2813-2828.

Gunnarsson, I., Arnórsson, S., and Jakobsson, S., 2005: Precipitation of poorly crystalline antigorite under hydrothermal conditions. *Geochim. Cosmochim. Acta*, *69*, 2813-2828.

Gunnlaugsson, E., 2004: Examples of chemical monitoring of geothermal water used for district heating in Reykjavík. *International Geothermal Days, Poland 2004*.

Gunnlaugsson, E., and Einarsson, Á., 1989: Magnesium silicate scaling in mixture of geothermal water and deaerated fresh water in district heating system. *Geothermics*, *18-1/2*, 113-120.

Gunnlaugsson, E., and Ívarsson, G., 2010: Direct use of geothermal water for district heating in Reykjavík and other towns and communities in SW-Iceland. *Proceedings World Geothermal Congress 2010, Bali, Indonesia,* 6 pp.

Hardardóttir, V., 2002: *Sudureyri district heating system. Borehole water chemistry 2000-2001*. Orkustofnun, report OS-2002/028 (in Icelandic), 10 pp.

Hauksson, T., 1979: *Well KG-12*. Orkustofnun, Well Letter No. 11 (in Icelandic), 5pp.

Hauksson, T., 1980: *Krafla. Calculated chemical composition of liquid and steam in boreholes*. Orkustofnun, report OS-80018/JHD10 (in Icelandic), 30 pp.

Hauksson, T, and Benjamínsson, J., 2005: *Krafla and Bjarnarflag. Borehole production and the chemical composition of water and steam in boreholes and production equipment in 2004*. Landsvirkjun, report (in Icelandic), 78 pp.

Hauksson, T., and Gudmundsson, 2008: *Krafla. Acid wells*. Landsvirkjun, report, 17 pp.

Hauksson, T., Thórhallsson, S., and Guðmundsson, Á., 1999: *Calcium carbonate deposits in Krafla boreholes. Chemical inhibition of deposition.* Orkustofnun, report OS-99033, 48 pp.

Hauksson, T., Thórhallson, S., Gunnlaugsson, E., and Albertsson, A., 1995: Control of magnesium silicate scaling in district heating systems. *Proceedings World Geothermal Congress 1995, Firenze, Italy*, 2487-2490.

Lund, J.W, Freeston, D.H., and Boyd, T.L., 2010: Direct uses of geothermal energy 2010 worldwide review. *Proceedings World Geothermal Congress, Bali Indonesia,* 23 pp.

Mahon, W.A.J., 1966: Silica in hot water discharged from drillholes at Wairakei, New Zealand. *New Zealand Jour. Sci., 9*, 135-144.

Miller, R.L., 1980: Chemistry and materials in geothermal systems. In: Casper, L.A., and Pinchback, T.R. (editors), *Geothermal Scaling and Corrosion. ASTM STP 717*. American Society for Testing and Materials, 3-9.

Ólafsson, M., 1999: *Sudureyri district heating system. Borehole water chemistry 1998.* Orkustofnun, report OS-99011 (in Icelandic), 13 pp.

Swanteson, J., and Kristmannsdóttir, H., 1978: *The chemical composition of altered rock in Krafla*. Orkustofnun, report OSJHD-7822 (in Icelandic),

Thórhallsson, S., 2012: *Common problems faced in geothermal generation and how to deal with them.* Presented at "Short Course on Geothermal Development and Geothermal Wells, organized by UNU-GTP and LaGeo, in Santa Tecla, El Salvador, 14 pp.

Truesdell, A.H., Haizlip, J.R., Ármannsson, H., and D'Amore, F., 1989: Origin and transport of chloride in superheated geothermal steam. *Geothermics*, *18*, 295-304.

Wangyal, P., 1992: *Calcite deposition related to temperature and boiling in some Icelandic geothermal wells.* United Nations University Geothermal Training Programme, report 11, 33 pp.