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Mineral scaling in geothermal fields: A review

Yung Ngothai[1]*, Norio Yanagisawa[3], Allan Pring[2], Peter Rose[4], Brian O'Neill[1], Joël Brugger[2]
[1] School of Chemical Engineering, The University of Adelaide, SA 5005
[2] South Australian Museum, North Terrace, Adelaide, SA, 5000
[3] Institute for Geo-Resources and Environment, AIST, Tsukuba, 305-8567, JAPAN
[4] Energy and Geoscience Institute, The University of Utah, Utah 84109, USA.

*Corresponding author: yung.ngothai@adelaide.edu.au

Abstract

Geothermal power is an established energy source in several countries, for example New Zealand and Iceland. However the proposed geothermal operations in South Australia occurs at a much greater depth (5 km) and the heat source is radioactive decay rather than volcanism. A number of issues relating to the geochemistry of geothermal fluids are required to be considered and explored to ensure safe, economic energy production from geothermal fields. Low pH and saline waters, at temperatures much greater than 200°C, are highly corrosive, and it is vital to prevent the generation of scales as the brines are transported to the surface. This paper provides a review on silica, calcite and metal sulphide scaling at various geothermal fields. The solubility of silica and calcite as a function of temperature and/or pressure were discussed and how it affects scaling at various locations in the geothermal plant.

Keywords: silica scaling, calcite scaling, metal sulphide scaling, EGS, HDR.

Introduction

In many developed geothermal fields in USA, New Zealand, Indonesia, Japan etc., mineral scales tend to precipitate with change of fluid temperature and/or pressure, leading to fluid flow problems. To overcome the operational problems associated with this scaling, several methods have been developed to eliminate and/or reduce the amount of mineral deposition. It is however important that we further investigate the mechanisms involved and the relation between mineral scaling and the physical and geochemical characteristics of the rocks and fluids in the geothermal system under exploitation.

For future geothermal systems, research and development of Enhanced Geothermal System (EGS) is required at a rapid pace, especially in Australia.

The outline of EGS (or Hot dry rock – HDR) system is described as follow; injected water is heated in artificial reservoir constructed using hydrofracturing technology by flowing through a high temperature granite. The heated fluid produced in reservoir, is used for power generation.

The first EGS project was carried out at Fenton Hill, New Mexico (USA), which ran from 1970. After that other EGS projects were established in a number of countries e.g., Japan (at Hijiori), Soultz, France, etc. Metal corrosion and mineral scaling were observed at these EGS systems. For example, in Soultz, metal corrosion occurred due to high Cl concentrations (Baticci et al, 2010) while in Hijiori, anhydrite and calcite scaling occurred in the lower production wells and pipelines at ground level due to dissolution of anhydrite in the reservoir by the injected low temperature water (Yanagisawa et al., 2008). These problems are common to the well-developed conventional geothermal power plants and likely to feature in EGS systems.

This paper presents a brief review of mineral scaling in geothermal fields and discussion for future EGS development.

Mineral scaling

The fluid in a natural geothermal system has a long residence time (thousands of years) at a relatively high temperature (> 150°C – 300°C) which therefore indicates a significant rock-water interaction. Since the system has had a long residence time, it is often assumed to be in a state of chemical equilibrium (Grigsby et al., 1989). Therefore, when fresh water is introduced into the system to extract heat, the system is no longer in equilibrium, which leads to precipitation and dissolution of different parts of the mineral assemblage. Precipitation, or scaling, is one of the major problems in geothermal energy extractions. Minerals may precipitate depending on the compositions of the granite and the injected brine.

In geothermal fields, it has been reported that silica, calcium carbonate, anhydrite, metal sulphides and iron minerals scales precipitated around production and injection wells and in the piping.

Silica scaling

Silica scaling is a well known problem in conventional geothermal systems, which occurs due to the presence of amorphous silica, during heat extraction or partial flashing (Robinson, 1982). Amorphous silica can contain several metals such as iron, magnesium, and calcium, etc.

Silica scale precipitated in many geothermal fields due to its high solubility at high temperature in the reservoir through water-rock interactions and the solubility rapidly decreases with decreasing temperature. The solubility of silica is also strongly dependant on pH. For example, iron-beared amorphous silica tends to precipitated at fluid mixing points. At this point, temperature, pressure and pH of fluid change rapidly and leading to significant changes in solubility and chemical equilibrium leading to silica precipitation.

Furthermore, silica has several structural phases, for example, quartz and amorphous silica while silica exists in solution both as a polymer and a monomer form. This variety leads to a complex array of mechanisms for silica precipitation, especially in lower temperature environment such as at the injection well.

The dissolution of solid silica phases (SiO_2) in water has been extensively studied (Mackenzie and Gees, 1971; Owen, 1975; Robinson, 1982). The solubility data for various silica phases (Rimstidt, 1980 cited from Robinson, 1982) are shown in Figure 1 where the solubility of different silica phases is plotted versus temperature. Quartz is thermodynamically the most stable phase of silica thus its solubility at any given temperature is lower relative to other silica phases.

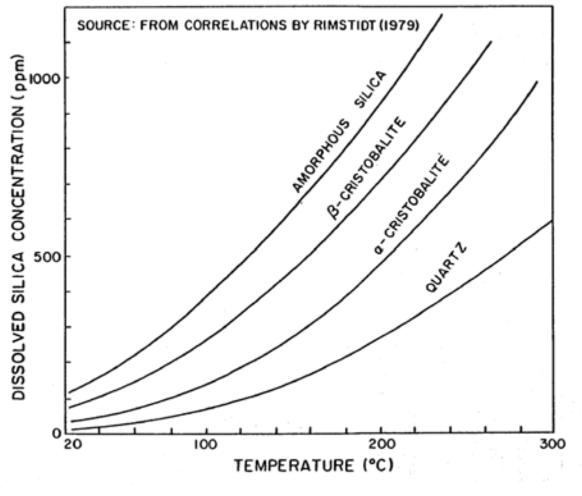

Figure 1: Equilibrium solubilities of silica phases

Silica concentrations in geothermal reservoir waters at 200-350˚C are approximately 300-700 mg/kg SiO_2 (Gunnarsson & Arnórsson, 2005). Fournier and Rowe (1966) state that the silica content in geothermal waters is controlled by the solubility of quartz at depth and not the solubility of amorphous silica at and near the surface of the ground. When hot brine is brought to the surface it is either flashed or cooled while passing through a power plant system to release its available thermal energy. Chan (1989) states that the dissolved silica in the brine may then become supersaturated. Depending on the degree of supersaturation the dissolved monomeric silica may nucleate and deposit as amorphous silica scale on equipment, such as heat exchanger surfaces (Chan, 1989). The factors which affect the solubility of amorphous silica in solution include temperature, pH, pressure and salt content (Chan, 1989). Gunnarsson & Arnórsson (2005) state that there are two processes involving aqueous silica that occur in an amorphous silica super-saturated solution. The first process is the direct precipitation of amorphous silica directly onto the surface of equipment. The second is the tendency for silica to polymerise and form colloids that remain in suspension for long periods of time. Polymeric silica has less tendency to precipitate from solution than monomeric silica.

Kinetics of silica dissolution needs to be established in order to evaluate the likelihood of silica scaling. Factors that control the rate of polymerization of dissolved silica are pH, salinity, degree of supersaturation, presence of solid substances, and temperature (Angcoy, 2010). Bethke (1996) compiled the rate constants for quartz and amorphous silica dissolution which were originally determined by Rimstidt and Barnes (1980), are shown in Table 1.

Table 1: Rate constants of quartz and amorphous silica dissolution

T(°C)	Quartz	α-Cristobalite	Amorphous silica
25	4.20×10^{-18}	1.71×10^{-17}	7.32×10^{-17}
70	2.30×10^{-16}	6.47×10^{-16}	2.19×10^{-15}
100	1.88×10^{-15}	4.48×10^{-15}	1.33×10^{-14}
150	3.09×10^{-14}	6.12×10^{-14}	1.49×10^{-13}
200	2.67×10^{-13}	4.81×10^{-13}	9.81×10^{-13}
250	1.46×10^{-12}	2.55×10^{-12}	4.43×10^{-12}
300	5.71×10^{-12}	1.01×10^{-11}	1.51×10^{-11}

Calcite scaling

Calcite or aragonite ($CaCO_3$) scaling is also a well known problem in conventional geothermal systems, Calcite scale occurs near the flashing point in the production wells due to decrease in calcite solubility.

Calcium solubility varies with the pressure of CO_2 (P_{CO_2}) and temperature of the fluid. Figure 2 shows the calcium solubility curve as a function of P_{CO_2} and temperature by Fournier (1985). It is noted from this curve that under the same temperature condition, calcite solubility is higher with respected to increase of P_{CO_2}. This explains why it is common to observe scaling at the flashing point. During flashing, where vapour release occurs causes the P_{CO_2} to decreases, calcite solubility therefore drops and calcite scale precipitates there. Furthermore, as calcite solubility is lower at high temperature conditions, calcite precipitation tends to occur at deep points in production wells and could be a serious problem. Many geothermal fields with high calcium or hydro-carbonate concentration experience calcite scale problems. In Japan, especially at the Mori and Oku-Aizu geothermal field calcite scaling is a serious problem.

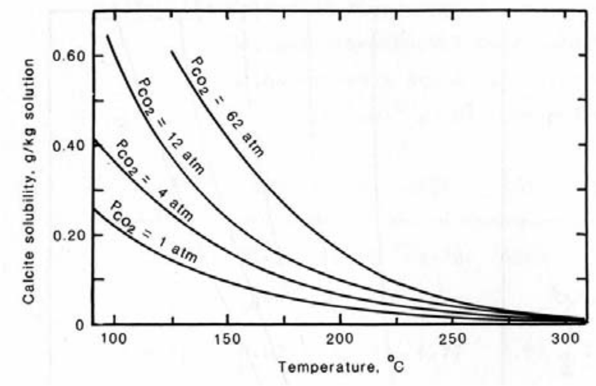

Figure 2: Solubilities of calcite as a function of temperature and pressure of CO_2

To prevent calcite scaling in wells, various chemical inhibitors have been used in many geothermal fields. For example, sodium polyacrylate, C_2H_3COONa, has been used for several Japanese geothermal fields and hot spas. Similar chemicals have been used around the world. At high fluid temperature, sodium polyacrylate reacts with calcium ion to make complex. Calcium complex cannot react with the bicarbonate ion (HCO_3^-) to precipitate calcium carbonate. Thus, this sodium polyacrylate inhibitor is effective to prevent calcite scaling. For a production well, a capillary tube is inserted into well until it reaches the depth of the flashing point and the chemical inhibitor is then injected directly at this point and prevents scaling.

Similarly the solubility of anhydrite ($CaSO_4$) is lower at higher temperature and tends to precipitate deep in the production wells and at the peak temperature point. In this case, with the temperature of fluid from deeper parts increases anhydrite precipitate due to its decreasing solubility. It has been reported that in Japan, Mori and Sumikawa geothermal fields experience anhydrite scaling.

Metal sulphide scaling

Metal sulphide scaling is often occurred in volcanic or high Cl environment. For example, at Salton Sea geothermal field, the salinity (35% NaCl) and metal concentrations (around 20% copper) in the fluid are very high (Skinner et al., 1967), many sulphide minerals form scales, such as bonite (Cu_5FeS_4), chalcocite (Cu_2S) have been found.

In Japan, metal sulphide scaling is found in Oku-Aizu (Nitta et al., 1991) and Yamagawa (Akaku, 1988). At Oku-Aizu geothermal field, the sulphur removal system near power plant has been built to prevent sulphide scaling.

The sulphide mineral scaling indicate the conditions in the deep-seated reservoir, especially in granitic rocks. For example, at the Kakkonda geothermal area, in north-eastern Japan, there is a 80 MW geothermal power plant using high temperature fluid from the reservoir at the boundary between the Quaternary Kakkonda granite and the Pre-Tertiary formations at about 3km depth. Metal sulphide minerals deposit in the production wellhead and pipelines (Yanagisawa et al., 2000).

The metal sulphide scales are classified into two types, based on sulphide mineralogy. These are Pb-Zn rich type and Cu rich type. Pb-Zn rich scale is found in Well-19 located at the marginal part of the Kakkonda granite as shown in Figure 3. It is mainly composed of amorphous silica, galena (PbS), sphalerite (ZnS) and pyrite (FeS_2). The brine of WD-1a at 3.7km depth, in the Quaternary Kakkonda granite rock, underlied Well-19, is rich in Pb and Zn and the scale in Well-19 is of similar composition.. Cu-rich scale is found in Well-13, located at the central part of the Kakkonda granite. It is mainly composed of amorphous silica, chalcocite (Cu_2S), bornite (Cu_5FeS4), loellingite ($FeAs_2$) and native antimony (Sb). It is also rich in Au, Ag, As, Cr, Ni and Mo compared to Pb-rich scale.

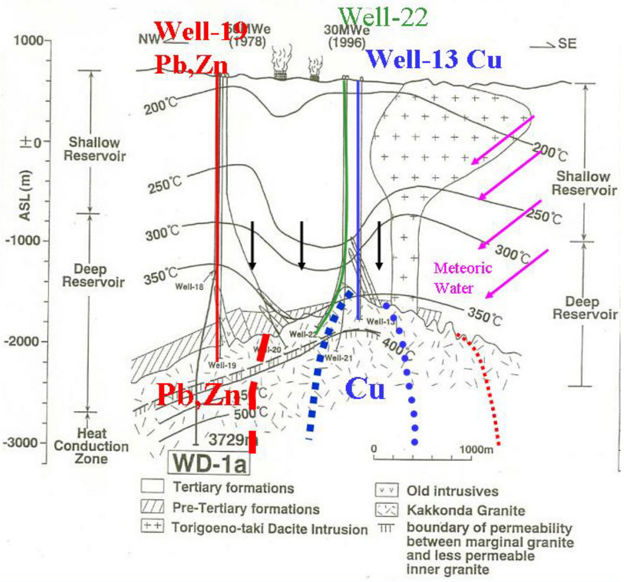

Figure 3: Schematic geothermal cross-section of the Kakkonda geothermal system including well name and metal in precipitated sulphide and brine in granite

Scaling in EGS system

In EGS system, several different types of scale mineral precipitated in the Hijiori system, located in Yamagata Prefecture of Japan (Yanagisawa et al., 2008). At the Hijiori field tests were undertaken using a series of hydraulic stimulation experiments. A heating reservoir was created at 2000m depth, after which river water was injected into the fractured reservoir, heated in reservoir and returned to installations on the ground level..

Scaling at surface installations and in deep wells (HDR-2 and HDR-3) are shown in Figure 4. Anhydrite deposited in the deeper parts of the production wells, while silica and calcium carbonate precipitated at the surface downstream of the wellhead. Amounts of precipitation depended on the temperature and chemical composition of the produced fluid. In HDR-2, which is closer to the injection well, most of the scale was calcium carbonate; in HDR-3, which is further away from the injection well, there was slight precipitation of amorphous silica. As fluid circulation progressed and temperature decreased, scaling in the flow line of well HDR-2 changed from amorphous silica to calcium carbonate.

Figure 5 shows the depth temperature profile. As water was injected anhydrite dissolved around the injection well, the water heated as it flowed through the reservoir, and anhydrite precipitated due to lower solubility at higher temperatures.

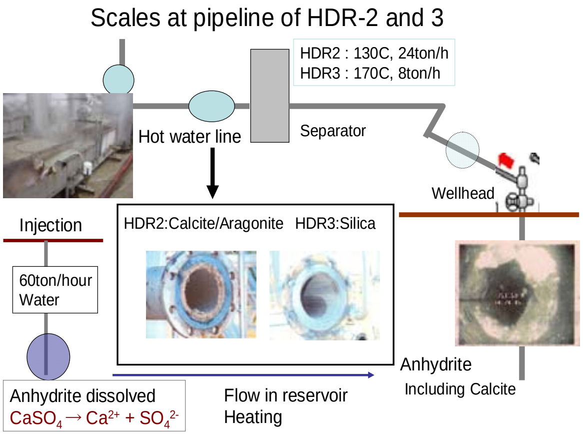

Figure 4: Scale sampling site and photo at Hijiori site

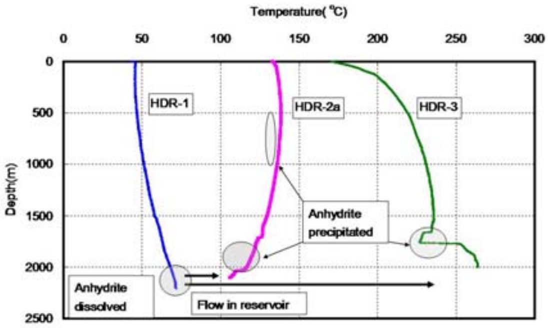

Figure 5: Temperature profiles in the Hijiori wells measured in July 2002

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