Bull. Min. Res. Exp. (2023) 171: 185-203

Bulletin of the Mineral
Research and Exploration

http://bulletin.mta.gov.tr

A brief overview on geothermal scaling

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Review Article

Keywords:
Antiscalants, Deposit,
Geothermal Energy,
Precipitation, Scaling.

Received Date: 10.08.2022
Accepted Date: 03.01.2023

ABSTRACT

Hot spring waters are rich in terms of minerals. Since there are dramatic changes in thermodynamic parameters in geothermal power plants, such as a decrease in temperature and pressure, severe precipitation occurs throughout the system components in an uncontrolled manner. There are three main chemistries in deposits: carbonates (mainly calcium carbonates), silicates (metal silicates), and sulphides (antimony sulphide-stibnite). Energy harvesting is remarkably reduced out of the insulating nature of the deposit. Various actions need to be taken to mitigate this undesirable issue of scaling in geothermal systems. Geothermal systems are in fact quite complex, and the composition of brine and, accordingly, the chemistry of the deposit are not identical. Therefore, each system should be studied individually, and a tailor-made remedy should be developed. In this overview, the types of deposits in terms of chemistry and the actions (pH modification or antiscalant dosing) that should be taken to reduce scaling are mentioned, and potential chemistries of antiscalants are given.

1. Geothermal Energy and Scaling

The energy demand of countries has been remarkably increasing in recent years due to the high rate of population growth and industrial activities. Fossil fuels are major sources of this global demand, but the increasing awareness about the environmentally hazardous effects of these sources put the usage of clean and renewable energy sources forward, such as geothermal energy, solar energy, wind energy, and hydro energy (Owusu and Asumadu-Sarkodie, 2016). According to the latest Intergovernmental Panel on Climate Change report, it has been decided to limit the global average surface temperature increase to 1.5°C by 2030, which means the utilisation of renewable sources should be promoted (Leitzell and Caud, 2021). In comparison with the other renewable alternatives, geothermal energy is a cost-effective, technically proven, reliable, clean, and safe one, and it has been operated in various fields and applications for many decades (Brophy, 1997; Çiçek, 2020). Geothermal systems can deliver hot water into the buildings, which enables a free water heating possibility during power generation. Besides, geothermal energy has the smallest footprint among other major energy sources due to the innovations in technology.

The repeated opening and closing of Paleozoic and Mesozoic oceans dominate the geological and tectonic evolution of Türkiye, which is one of the most seismically active regions in the world (Dewey and Şengör, 1979). It is located within the Alpine-Himalayan orogenic belt at the geological margin between the African-Arabian and Eurasian plates.

Citation Info: Isık, T., Baba, A., Chandrasekharam, D., Demir, M. M. 2023. A brief overview on geothermal scaling. Bulletin of the Mineral Research and Exploration 171, 185-203. https://doi.org/10.19111/bulletinofmre.1228900

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The young volcanic activities, hydrothermally altered areas, and block faulting bring forth a wide range of hot springs in Türkiye; there are a total of nearly 1000 hot water springs in the country (Mineral Research and Exploration Institute (MTA), 1980; Mutlu and Güleç, 1998; Öngen and Ergüler, 2021). The geothermal fields in Türkiye can be grouped into four regions: western Anatolia, the North Anatolian fault zone, eastern Anatolia, and central Anatolia (Baba and Ármannsson, 2006). Türkiye's electricity generation capacity and the total installed direct heat use reached 1663 MWe and 5113 MWt, respectively, in 2022 (Şener et al., 2022). With these values, Türkiye ranked 4th in energy production and 2nd indirect use worldwide (Baba and Chandrasekharam, 2022). Considering Anatolia's Curie depth and heat flux, the probable thickness of the batholith can be regarded as 10 km. For example, the total granitoid area of Western Anatolia is 4221 km^2, and at least 2% of these granitoid can provide approximately 810^7 MWh of electricity by enhanced deep geothermal systems (Chandrasekharam and Baba, 2022). This high thermal regime gave rise to a large number of hydrothermal provinces throughout Türkiye. Moreover, the hydrogeochemical properties of the resources in Anatolia, which are so rich in geothermal resources, are quite different from each other. Moreover, each geothermal field shows different chemical composition from the others due to the complex lithology, tectonics, volcanic activities, and the structure of surrounding rocks. The majority of thermal waters in Türkiye are Na^+ - Ca^{2+} - HCO_3^- type, but on the coasts of western Anatolia, Na^+ - Cl^- type is also observed. The Argavlı and Sazlıköy springs are characterized as low-temperature springs, and Ca^{2+}, Mg^{2+} and HCO_3^- ions are dominated. On the other hand, the Gümüşköy region contains high-temperature wells with Na^+, K^+, Cl^-, and HCO_3^- predominant ions (Baba and Sözbilir, 2012).

Although its numerous advantages, such as energy harvesting and heating houses, geothermal energy has a serious obstacle. Because geothermal brine is composed of a mixture of minerals and gases, the high-temperature brine may cause operational limitations in geothermal systems called scaling and eventually corrosion (Figure 1) (Doğan et al., 2014). Scaling may result in plugging the wells and lines, and power plants face curtailment of production. In addition, the existence of scale on the wall of pipelines reduces both the steam or brine flow and effective heat transfer, which reduces the efficiency of geothermal plants and causes financial losses (Baba and Ármannsson, 2006). There are many studies to prevent the scaling problem in geothermal systems and treatment either with acids or organic antiscalants. However, acid treatment is a tedious process and requires more attention because the dosage and placement of the dosage in the system are highly critical; that high level of dosing may result in serious corrosion. On the other hand, increasing the solubility of ions/stability of colloids that are precursors of deposit by using antiscalants is a promising approach to minimize the scaling problem (Demir et al., 2014).

2. Scaling and Formation Mechanism

From the chemical point of view, scaling is nothing but the precipitation of compounds from aqueous solutions. Precipitates (deposits) are formed when certain cations and anions are combined and produce an insoluble ionic solid. Solubility guidelines give an essential impression about deposit formation (Petrucci et al., 2011). Petrucci et al. (2011) summarize the

Figure 1- a) Scaling examples from some geothermal fields (Doğan et al., 2014), scale formation in b) Tuzla geothermal field and c) antimony sulfide (stibnite) scaling examples from geothermal fields obtained from Kübilay geothermal power plant.

solubility rules for common ionic solids as follows: i) Group 1 cation and NH_4^+ form soluble salts, ii) the salts of nitrates, acetates, and perchlorates are soluble, iii) silver, lead, and mercury (I) salts are insoluble, iv) chlorides, bromides, and iodides are soluble, v) carbonates, phosphates, sulfides, oxides, and hydroxides are insoluble with some exceptions, and vi) sulfates are soluble apart from calcium, strontium barium. According to this guideline, the potential precipitation reactions could be predicted, and required precautions could be taken. All carbonates and silicates, which are, the main chemistry of geothermal scaling, insoluble in aqueous systems (Petrucci et al., 2011).

Precipitation of scales on the surface of heat exchanger tubes is a well-known problem called as fouling (Bott, 1995). Fouling decreases the thermal conductivity and overall heat transfer coefficient, which reduces the performance of heat exchangers due to the pressure drop in the fluid flow rate (Tubular Exchanger Manufacturers Association, 1952). This fouling layer increases in thickness with time until the heat exchanger loses its performance, whereby shutting down the system becomes a must. Geothermal fluids comprise several soluble species and dissolved gases with various concentrations. During the operation of geothermal systems, any change in the thermodynamics of the system, such as pressure and temperature thermodynamic change, may result in scaling or corrosion. The composition of geothermal fluids varies from site to site that there are various types of scale compositions due to the varied elemental constituents, and their composition depends on many parameters such as temperature and pressure of the fluid and water-rock interactions (Karabelas et al., 2002). Calcium carbonate and calcium silicate are the major constituents in geothermal fluids, while calcium sulphate, calcium carbonate, barium sulphate, calcium oxalate, strontium sulphate, and colloidal iron oxides are seen in some sites (Zhang et al., 2011). Generally, brines with a low and moderate temperature (<150 °C) end up the formation of calcium carbonate whilst high-temperature ones with high Total Dissolved Liquid (TDS) content yield siliceous scales (Owen and Michels, 1984; Corsi, 1986; Zhang et al., 2011). The term scaling generally refers to the formation and precipitation of inverse solubility salts when the salt exceeds its equilibrium solubility. The basic concept of scale formation is based on the solidification of an ionic substance that the change in Gibbs free energy transfers the substrate from a supersaturated state to an equilibrium state (Karabelas et al., 2002). For nucleation and growth, the driving force is needed that in geothermal systems, the change in temperature and pH is the most notable parameters. Figure 2 demonstrates a representative deposit developed in various geothermal fields.

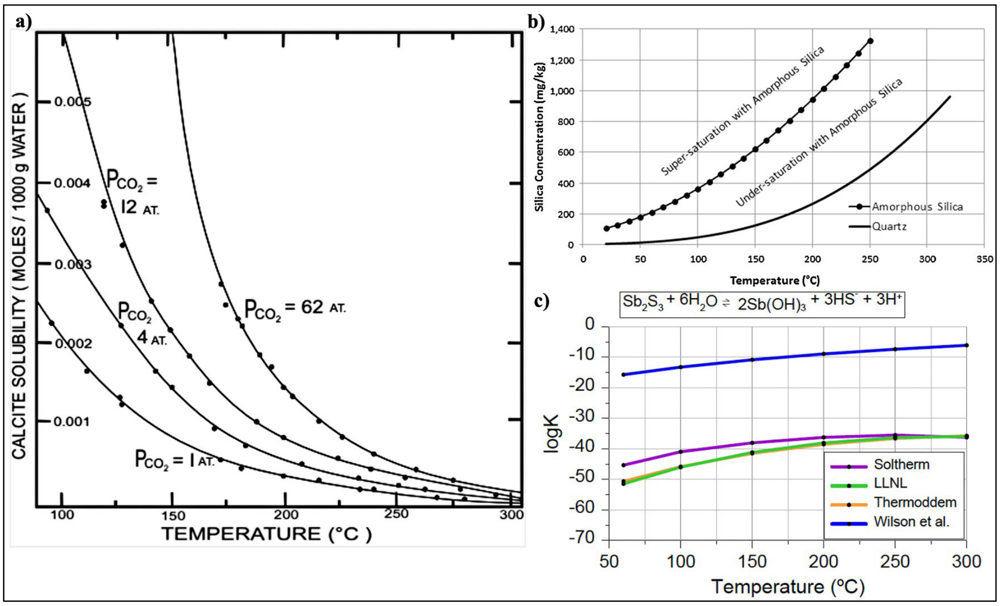

Figure 2- Effect of temperature on; a) calcite ($CaCO_3$), b) silica and c) stibnite solubility (Zarrouk and Purnanto, 2014; Buscarlet et al., 2016; Deendarlianto and Itoi, 2021).

The parameters pH, temperature, and pressure are the crucial ones that affect scaling in geothermal fluids. A high pH increases the concentration of carbonate ions and therefore induces scaling, whilst silica dissolution shows a different trend by changing pH (Kaypakoğlu et al., 2012). Calcite solubility increases as temperature decreases (Figure 2a) (Zarrouk and Purnanto, 2014; Deendarlianto and Itoi, 2021). Similar to the solubility of CO_2, increasing pressure improves the solubility of calcite. Silica, on the other hand, shows opposite behaviour against temperature (Figure 2b). Increasing temperature increase the solubility of silica and silica-containing deposits, for example, metal silica. Figure 2c demonstrates the dissolution of stibnite under the temperature effect. There is an increase in solubility as the temperature increases (Buscarlet et al., 2016).

2.1. $CaCO_3$

Calcite ($CaCO_3$) is the most abundant mineral in geothermal waters. There are different forms of calcite, such as aragonite and vaterite. However, since vaterite is not stable, it turns into calcite. Therefore, calcium carbonate precipitates mostly in calcite and aragonite forms. The factors affecting calcite scaling in geothermal waters are temperature, pH, and partial pressure of CO_2. As geothermal waters rise from the depths, their temperature and pressure decrease. CO_2 dissolved in the geothermal water due to the high pressure in the depths tends to escape from the geothermal water due to the decrease in pressure. At this time, the pH rises, and calcite scaling begins. This point where calcite scaling starts is called the flashing point or boiling point. Calcite scaling can be explained by Equation 1.

$$Ca^{2+}(aq)+2HCO_3\text{-}(aq) \leftrightarrow CaCO_3(s)+CO_2\uparrow(g)+H_2O)(l) \quad (1)$$

Calcite solubility is inversely proportional to temperature. In other words, calcite solubility decreases as the temperature increases. Therefore, in geothermal power plants, calcite scaling should not be expected in regions where cooling starts, such as heat exchangers, transmission lines, and reinjection wells. Calcite scaling is more common in production wells where the temperature is higher. In geothermal power plants calcite scaling can be controlled if the pressure of the geothermal fluid is kept above the partial pressure of the CO_2. On the other hand, using chemical inhibitors is another method to prevent calcite scaling.

Calcite scaling has been studied by different researchers around the world. Arnorsson (1989) studied calcite scaling theoretically and observed a decrease in the partial pressure of CO_2 due to boiling. This supported the supersaturation state and scaling of calcite. Akhmedov (2009) developed a kinetic model to calculate the calcium carbonate formation rate in his study. Ryley (1980) studied the relationship between wellhead pressure and mass discharge based on reservoir lithology and friction losses in a geothermal well. Barelli et al. (1982) focused on a two-phase flow model to understand the effect of heat exchange with height, non-condensable gases (NCGs), and salts in geothermal wells. A mathematical model for the estimation of calcite formation rates and analysis of the effect of calcite formation on flow rate were investigated by Satman et al. (1999). Patzay et al. (2003) simulated the flashing depth, temperature/pressure, and partial pressure profiles of non-condensable gases with the help of computer software. Wangen et al. (2016) considered the reduction problem in porosity due to scaling in the radius of the geothermal well with an analytical estimation. Siega et al. (2005) conducted a study on chemical inhibitors that prevent scale formation in the Mahanagdong geothermal field. Rangel et al. (2019) studied a chemical inhibitor in the Ribeira Grande geothermal field and concluded that this inhibitor was effective for 25 years in preventing calcite scaling. Lee et al. (2015) studied the effectiveness of two types of chemical inhibitors in the Chingshui geothermal field, whose production has decreased due to calcium carbonate scaling. Ramos-Candelaria et al. (2000) studied an inhibitor to prevent calcite scaling in the Mindanao geothermal field, which causes a production loss of 0.6 Mw per month. Calcium carbonate crystallization can be seen in many piping systems, and it is a common problem in low and medium-temperature geothermal systems. The crystallization occurs through three stages: supersaturation, nucleation, and crystal growth. The first stage, supersaturation, is the driving force of the crystallization process and directly affects the nucleation rate (Sousa and Bertran, 2014). The nucleation stage depends on the supersaturation level of the solution, but the diffusion of atoms and ions on the surface of nuclei governs the crystal growth. There are mainly three polymorphs of calcium carbonate, which are called calcite, vaterite, and aragonite (Rafferty, 1999; Karabelas et al., 2002). Whilst high-concentration gradients favour the calcite crystallization, high temperature promotes aragonite crystallization (Ueckert et al., 2020). Among the other polymorphs, calcite is the thermodynamically most stable form at any temperature but least soluble in water (Putranto et al., 2018). Aragonite and calcite have similar structures, and carbonate ions are formed in a staggered arrangement relative to each other with the inter-planar structure that electrostatic repulsion can be reduced. Vaterite is the less dense form of calcium carbonate polymorphs, and carbonate ions are eclipsed relative to each other. However, the transitions between these forms are possible under specific conditions, e.g., the required temperature is 0 – 30 °C from vaterite to calcite and 60 - 80 °C from aragonite calcite (Boulos et al., 2014). The magnesium ion favours the precipitation of aragonite rather than calcite, and inhibits the nucleation and growth stages of calcite (Nancollas, 1982).

In geothermal systems, reinjection of brine into subsurface formations results in calcium carbonate scale formation. The formation mechanism occurs that the presence of CO_2 release during the flashing of vapour phase results in a pH increase in the geothermal systems, and supersaturation conditions deposit the $CaCO_3$ solid (Rafferty, 1999; Karabelas et al., 2002). Calcite is one of the most abundant minerals in drilled geothermal systems and hydrothermally altered rocks, and aragonite has also been reported in some fields. However, vaterite formation has not been identified in geothermal systems (Arnorsson, 1989).

2.2. Silica

Silica is considered one of the essential elements due to its abundance in the earth's crust and its important role in a variety of different processes (Petkowski et al., 2020). Silica scaling is a problem that can occur in medium and high enthalpy geothermal fields. In hydrothermal fields, silica occurs in different forms at different depths. These are generally in the form of amorphous silica, chalcedony, cristobalite, and quartz. Quartz is the most stable form of silica with the lowest solubility among these forms. The solubility of amorphous silica in geothermal waters decreases with temperature and creates a scale problem in regions where steam separation and cooling occur. Therefore, transmission lines, heat exchangers, reinjection wells, and in some cases, production wells in geothermal power plants are the riskiest equipment in terms of amorphous silica scaling (Utami, 2000; Gunnarsson and Arnórsson, 2005; Mundhenk et al., 2013; Demir et al., 2014; Baba et al., 2015; Pambudi et al., 2015).

Silica scaling is more complex than other types of scaling and has not been fully understood until now. For example, unlike calcite scaling, silica scaling is controlled by the polymerization kinetics of silicic acid [$Si(OH)_4$] (Ellis and Mahon, 1977). This silica polymerization is expressed by Equations 2 and 3.

$$2\cdot Si(OH)_4 \rightarrow (OH)_3SiOSi(OH)_3 + H_2O \qquad (2)$$

$$Fe^{3+}\, H_2O + Si(OH)_4 \rightarrow Fe(OH)_3\cdot SiO_2 + 3H^+ \qquad (3)$$

These reactions define the first step of silica polymerization. In some geothermal fields, amorphous silica is found together with Al and Fe to form metal silicates (Gallup, 1993). Fe-O-Si bonds seen in Equation 3 are one of these metal silicates. Another metal silicate group is the Al-O-Si group. Al and Fe concentrations in geothermal waters lead to amorphous silica scale. Although Al concentrations in geothermal waters rarely exceed 5 mg/kg, the contribution of this value to scale formation is 10% by weight (Al_2O_3-SiO_2) (Ichikuni, 1983; Gallup, 1997; Yokoyama et al., 2002; Ueda et al., 2003; Ikeda and Ueda, 2017).

Silica scaling is the most challenging scale problem to remove and is complex to other scale types. This is because the silica scale is inert to many chemicals and resistant to mechanical cleaning. There are different studies on silica scaling in the literature (Gallup, 2002; Brown, 2011; Tobler and Benning, 2013; Andhika et al., 2015). Kristmannsdóttir mentioned that silica scaling caused a general problem in reinjection wells in 1989. On the other hand, significant silica (SiO_2) scaling in heat exchangers of binary geothermal power stations has been encountered in; Rotokawa and Ngawha, New Zealand (Wilson et al., 2007), Blundell, Utah (Gallup, 2011), two fields in the Imperial Valley, California (Gallup, 2011) and most likely many other plants around the world. One of the main contributors is that binary plants generally operate at lower geothermal fluid reinjection temperatures than flash plants (Zarrouk and Moon, 2014) with a correspondingly higher silica saturation index. Investigating the efficiency of pH modification and the use of organic inhibitors have been the solution methods for reducing and preventing silica scaling (Gallup, 2002; Gallup and Barcelon, 2005; Baba et al., 2015).

For silica dissolution, aqueous hydrofluoric acid (HF) solutions have been studied for many years for wet chemical etching. F^-, HF, and HF_2^- species in solution attack the glass and adsorbed on surface siloxane, vicinal silanol and silanol groups, respectively (Demadis et al., 2012*b*). Thus, chemical cleaning by means of HF treatment, either in the form of pure HF or in situ creation by combining HCl and ammonium bifluoride (ABF) is accepted as silica scale dissolution method for decades (Mccartney et al., 2017). In an aqueous solution, HF acts as a weak acid, and there is an equilibrium between H^+ and F^- ions. Then, F^- attacks undissociated HF to form bifluoride anion (HF_2^-), which is responsible for the attack of the silica matrix and etches the silica surface (Wong et al., 2009) Whilst HF is effective for the dissolution of silicate scaling, it is not as effective in dissolving metal silicates. Note that, F^- forms precipitation with Ca^{2+} and Mg^{2+}. Therefore, HF is a toxic chemical once it touches the human skin, it penetrates to the skin and causes the destruction of the deep tissue layer (Schwerin and Hatcher, 2022).

Amorphous silicate formation is based on the condensation polymerization of the silicic acid in acidic or basic environments (Figure 3) (Nassif and Livage, 2011). In most of the geothermal systems, dissolved CO_2 is found in $CO_{2(aq)}$ and HCO_3^- forms. Dissolved CO_2 is available in the geothermal hot water reserves. The temperature of geothermal fluid decreases while it moves through the well to the surface, and CO_2 is released into the vapor phase due to the pressure decrease. When the CO_2 amount in the geothermal fluid decreases, the water loses its acidity, the solubility of silicate decreases, and the fluid becomes over-saturated. When the steam flushes, the temperature of the brine drops and becomes even more saturated. In that case, the silica content, which is already unstable, becomes even more unstable (Demadis, 2010).

After the removal of CO_2 from the system, the pH of the system rises, and the major ions in geothermal fluid (such as Fe^{2+}, Mg^{2+}, Ca^{2+}) precipitate in the hydroxide form. Moreover, increased pH and the presence of Fe^{2+}, $Fe^{3+}$and Al^{3+} ions stimulate the silica polymerization simultaneously, and metal hydroxides interact with silica polymers to form metal silicate compounds, which are very hard to dissolve. These compounds are comprised of various oligomeric structures in amorphous form and have similarities with colloidal silica (Gallup et al., 2003). During polymerization, there is a need for a balance between

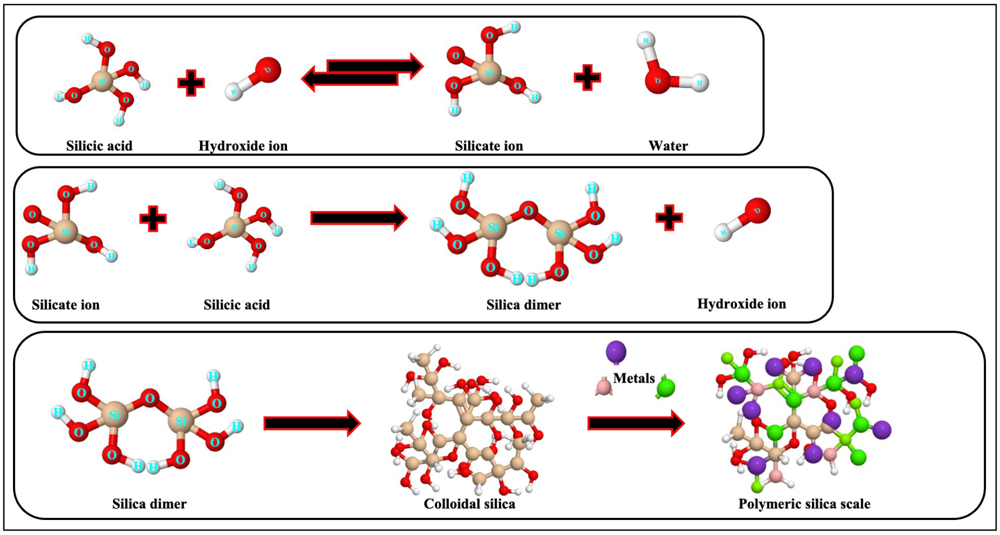

Figure 3- Polymerization reaction of ortho silicic acid (red: oxygen, white: hydrogen, nude: silicon, purple and green: metal ions).

unionized and ionized silica species. At high pH, the formation possibility of metal silicates increases because ionization of silicic acid is favoured, and silica polymerization slows down (Gill, 1993; Demadis and Mavredaki, 2005). Metal silicates can form in metal-rich geothermal brines, and commonly presented metal ions are aluminum (Al), magnesium (Mg), and iron (Fe). Metal silicates have much lower solubility than bare silica and have complications during the cleaning processes (Gallup, 2011).

Metal silicate scaling is probably the most difficult scale in geothermal systems because silica is found abundantly in all geothermal fluids, and its concentration increases with temperature. The formation of scale has economic sevre consequences such as increased costs for pumping, cleaning, and maintenance, loss or abandoning and reinjection of system due to clogging (Karabelas et al., 2002). Furthermore, the deposit formation reduces the inner width of the pipes and prevents heat transfer and the efficiency of production drops (Topçu et al., 2019*a*).

Thus, there is an increased need to understand the scaling and mitigate this problem. Generally, the elimination of silica deposition before it is formed is one of the frequently used methods (Demadis, 2005). However, silica polymerization has not been completely understood yet because every geothermal fluid has unique characteristics due to different environmental conditions such as salinity, temperature, and water-rock interactions. On the other hand, the removal of silica scaling by using acid treatment is another point of research. Water-rock interactions have been conducted by several researchers, and the chemical composition of geothermal brines is determined by their origin, the lithology of interacted rocks, and the temperature of the system (Gören et al., 2021).

2.3. Stibnite (Antimony Trisulphide)

Antimony-rich sulphide deposits have been observed in several geothermal plants, and their formation mechanism has drawn attention in the last years due to the dissimilarities from those carbonates and silicates. Antimony is found in sulfide derivatives such as stibnite and sulfosalts and forms stable interactions with sulphur. There are two oxidation states of antimony, which are trisulphide (Sb^{3+}) and pentasulphide (Sb^{5+}). Stibnite (Sb_2S_3), also known as antimony trisulphide, is a mineral with an orthorhombic crystal lattice. It has been observed in various power plants, and also it is the main component of hydrothermal systems. Stibnite dissolution occurs in water as hydroxide forms and hydrogen sulphide formation increases during the storage of stibnite. Equation 4 shows the dissolution of stibnite in water.

$$Sb_2S_3 + 6\,H_2O \rightarrow 2\,Sb(OH)_3 + 3H_2S \qquad (4)$$

In geothermal reservoirs, in which H_2S is already present, stibnite can form sulfosalts of antimony after dissolution (Equation 5). At this stage, $H_2Sb_2S_4$ is a significant problem when H_2S concentration is high, or the system temperature is relatively low (Kevin, 2013; Haklıdır and Balaban, 2019).

$$Sb_2S_3 + H_2S \rightarrow H_2Sb_2S_4 \qquad (5)$$

However, stibnite causes corrosion in geothermal systems and its mitigation is vital for the efficient running of the system (Ellis and Mahon, 1977). Stibnite precipitation can be controlled by pH and temperature. Because in condensers and heat exchangers, pH and temperature play an essential role such that the deposition of sulphur-based scales has been observed in these parts of the system. Although antimony is found in low concentrations in brine, stibnite formation is a major problem at low temperatures and pH. Wilson et al. (2007) reported that stibnite forms in the heat-exchanger units of New Zealand binary geothermal power stations, Rotokawa and Ngawha, and has developed into an ongoing problem. They determined the conditions to produce stibnite scaling and quantified the rate of deposition in each system. Also, they determined the Sb routes through geothermal fluids. Reyes et al. (2003) and Raymond et al. (2005) claimed that Sb is found not only in brine fraction but also may be transported in the vapour phase. A similar problem has been reported in an exploration well in Italy and in a pipe fragment in a Berlin station (Cappetti et al., 1995; Raymond et al., 2005). In Türkiye, stibnite scaling is a growing problem in many geothermal plants and is observed in the Germencik Geothermal Field (GGF) of the Büyük Menderes Graben (BMG) system. Tonkul et al. examined the stibnite scaling on the preheater of GGF and determined the optimum reinjection temperature as 95 °C to prevent the stibnite scaling (Tonkul et al., 2021). Avoiding of low pH and temperature, caustic dosing, chemical inhibition by antiscalants, chemical removal and mechanical removal such as high-pressure water blasting are possible methods to mitigate stibnite scaling (Kevin, 2013) Figure 2b shows the stibnite scaling from geothermal fields obtained from Kübilay geothermal power plant. Moreover, hot caustic soda (NaOH) circulation has been used in New Zealand and is considered as the most effective method for the dissolution of stibnite deposits in heat exchangers (Brown, 2011). Inanli and Atilla also utilised hot NaOH and found it successful to remove magnesium – iron silicates (İnanli and Atilla, 2011).

Karaburun et al. (2022) and Çiftçi et al. (2020) studied the solubility of stibnite in the presence of potential antiscalants containing various functional groups such as acrylic acid, sulphonic acid, and phosphonic acid under both in the lab (reflux and autoclave) and in the field. Both testing pointed out that sulphonic acid containing antiscalants were found to be the most effective ones in mitigation of the sulphide-rich deposits.

3. Sources supplying materials for scaling

Geothermal waters generally contain large amount of dissolved minerals and gases. These minerals and gases precipitate when the geothermal waters move from hot environment to cooler environment and get deposited in almost ll the appliances that carry the fluids. Types of scaling depend on the geothermal reservoir composition. The types of reservoir rocks widely depending on the geographic location of the geothermal systems. There are three main reservoir rocks that are commonly encountered. There are sedimentary rocks such as sandstones, volcanic rocks such as basalts and andesites and plutonic rocks like granites.

Silica is the most common dissolved mineral in high temperature geothermal systems (250 °C) occurring in countries like Iceland and New Zealand. The dissolved silica is usually in amorphous form. When the geotheral fluid cool, the steam separates thereby making the liquid supersaturated in silica, resulting in precipitation (Mahon, 1966; Gunnlaugsson et al., 2014). The reservoir rocks are volcanic, like basalt and andecite.

Iron siliate sacling occurs commonly in geothermal waters where the reservoir rocks are ultramafic rocks like peridotite, dunite and pyroxenite where Mg-Fe silicte minerals dominate in these rocks. These geothermal systems are found in Indonesia and New Zealand (Gunnlaugsson et al., 2014). They are commonly associated with iron sulphide scales.

Sulphide scaling is common in geothermal systems rich in H_2S gas, that are commonly associated with active volcanic regions (like Iceland) or in geothermal systems where the reservoir rocks are rich in sulphide minerals like galena (PbS), covellite (CuS), chalcopyrite ($CuFeS_2$), stibnite (SbS_2). These minerals are common in geothermal systems in Iceland, Italy, Indonesia and Türkiye (Ármannsson and Hardardóttir, 2010; Gunnlaugsson et al., 2014; Tonkul et al., 2021).

Calcite scaling is very common, especially when the reservoir rocks are of limestone or dolomite such a those found in Italy (Montanari et al., 1994) and Türkiye and volcanic rocks such as those found in Iceland and New Zealand (Simmons and Christenson, 1994; Gunnlaugsson et al., 2014).

4. Methods to Prevent Scaling

For several years, the methods to control geothermal scaling have been investigated. pH modification and utilisation of scaling inhibitors are common remedies for the prevention of scaling in geothermal systems.

4.1. pH Modification

As a fruitful approach, pH modification has been used to reduce the scaling in geothermal power plants. Manipulation of the chemical composition of geothermal fluids can be performed by modifying the pH of the system. pH modification can be applied either by increasing pH to increase the solubility of the deposits (Lichti and Brown, 2013).

The addition of hydrochloric acid (HCl) into the geothermal fluids is a common strategy, and even a subtle decrease in pH below a certain value, at which the formation of carbonate scaling becomes impossible, results in the prevention of scaling. Hoyer et al. (1991) controlled the ferric silicate scaling at the Salton Sea by brine acidification. A small amount of HCl is injected into the brine to lower the pH by up to 0.3 units and this little pH change inhibits the ferric silicate formation (Hoyer et al., 1991). The optimisation of acid dosage and choosing the acid injection point are two significant parameters. However, the main drawbacks of this approach using inorganic acid are the cost of consumed acid during the pH modification, corrosion and as well as health issues. Because most geothermal liquids have extremely large buffer capacity, even for a small decrease, a large amount of acid is required (Topçu et al., 2019*b*). There is a need for an alternative approach to prevent scaling and remediate the scaling problems in geothermal systems. For the mitigation of amorphous silica and metal silicates, pH modification with concentrated sulphuric acid (H_2SO_4) has been used in Mak-Ban (Bulalo, Philippines) geothermal field (Gallup, 2011). Similarly, concentrated H_2SO_4 is injected into the brine in Hatchobaru, Japan, and at pH 5-6, the silica scaling rate was reduced significantly (Kiyota and Uchiyama, 2011). Moreover, H_2SO_4 application contributes to the reduction of hazardous hydrogen sulphide emission from geothermal power stations that produced hydrogen sulphide gas was converted to H_2SO_4 by the help of a sulphur oxidising bacteria *Thiobacillus thioparus* (Hirowatari, 1996). Corrosion is a serious issue, particularly in the elbow part of the pipeline, when such inorganic acids are dosed in the system.

Since CO_2 removal triggers the formation of stibnite-based deposits, the application of organic acid R-COOH is a wise approach for pH modification. The smallest organic acid with one carbon atom and structure is similar to CO_2 in formic acid and is environmentally benign. Formic acid (H-COOH), the smallest organic acid with a single carbon atom, has been used to minimize silicate scaling in Tuzla regions successfully. The brine has pH of 7.2 and is reduced to 6.2 by the injection of CO_2 (Topçu et al., 2019*b*). It is the simplest organic acid with a similar chemical structure of CO_2 that removal of CO_2 from the system causes an increase in pH and results in silicate formation. This simple organic acid is able to inhibit the colloidal silica formation and enhances the dissolution of already formed scales. Baba et al. (2015) studied the required dosage and optimum conditions for formic acid treatment and reported that 55 ppm formic acid is a required concentration for the minimization of silicate scaling. However, formic acid offers a short-term solution to the scaling problems.

The use of gas having geological origin and acidic characteristics might be a possible solution to reduce the meta-silicate scaling in geothermal systems. Carbonic acid (H_2CO_3) has moderate acidity and a simple chemical structure. Carbonic acid dissociates into CO_2 which changes the solubility of brine and it comes from the magmatic processes or decomposition of organic matter in sedimentary rocks (Hibara et al., 1990; Topçu et al., 2019*b*).

Formic acid shows the most similar chemical structure to CO_2 and the acidity of the geothermal fluid can be modified via formic acid to bring back the optimum conditions and enhance silica dissolution. In Tuzla Geothermal Power Plant (TGPP), formic acid has been adopted to minimize the amorphous silica and metal silicate deposition. The optimum condition for formic acid dosage was determined as 55 ppm and the stand time is retarded from 1 to 6 months (Baba et al., 2015). Moreover, CO_2 injection is another approach to prevent metal silicate scaling. Topçu et al. (2019) injected CO_2 gas into to the TGPP with various flow rates, and the results emphasized that 20.6 m^3/s CO_2 injections showed a better performance than 55 ppm formic acid injection, and less corrosion is observed in CO_2 gas injection (Topçu et al., 2019*b*). In this way, a sustainable route can be achieved in geothermal systems by capturing the released CO_2 from the system and injecting it through the wells. As a new perspective to the pH modification and antiscalant application in geothermal systems, there is a patent application for the usage of CO_2 as an antiscalant (Baba et al., 2020).

4.2. Dosing of Antiscalants

Antiscalant utilisation is the most promising and eco-friendly method to struggle with the scaling problems, and there is a wide variety of inhibitor chemicals in the market according to the encountered problems. They are commercial products and have been used to ruin the crystal structure of scale minerals. Their application is carried out to prevent the calcite, silica, stibnite, and other possible scale formations, and inhibitors are picked up according to the reservoir temperatures of geothermal wells.

Various polymeric macromolecules have been used as antiscalants in geothermal systems, and commercially, there is a wide range of antiscalants in the market (Çiftçi et al., 2020). However, the vital point is to test and choose the proper antiscalant for the field according to the physical conditions (pH, temperature, pressure, etc.) and chemical composition of the field. Performing the tests to choose the potential commercial antiscalants in the field conditions is a tedious and costly process. Therefore, the synthesis of geothermal deposits artificially in the laboratory under desired conditions (either with reflux or autoclave type pressurized reactor) is a more practical and economical way to perform the tests for antiscalant performances. Çelik et al. (2017) employed a reflux and autoclave reactor system to synthesize artificial metal silicate deposits in the laboratory (Figures 4a and 4b).

The reflux includes a round-bottom flask heated to 90 °C under atmospheric conditions. On the other hand, the autoclave reactor is comprised of a closed container, liquid and gas inlets, a magnetic mixing monitor, and temperature – pH probes. Hot silicone oil circulates throughout the closed container and heats the device up to 250 °C and the magnetic mixing motor stirs the reaction solution up to 3000 rpm (Çelik et al., 2017). By this way, the conditions of a real geothermal well can be mimicked under laboratory conditions without using large amounts of chemicals during the optimisation of antiscalant parameters.

There are two main mechanisms for the mitigation of deposits. The first one is stabilization of colloidal particles occurring in the brine. Colloids are accepted as the precursor of the deposit, .e. initial solid particles precipitated in the system. Since they have a submicron diameter, they have the large surface area to volume ratio. A strong tendency exists for aggregation and agglomeration, eventually deposit formation. Against the aggregation process, dispersion agents are applied to the system to coat the colloid surface such that the surface energy of the particles is reduced and the undesirable aggregation is prevented. The second mechanism is chelation. A Coulombic interaction

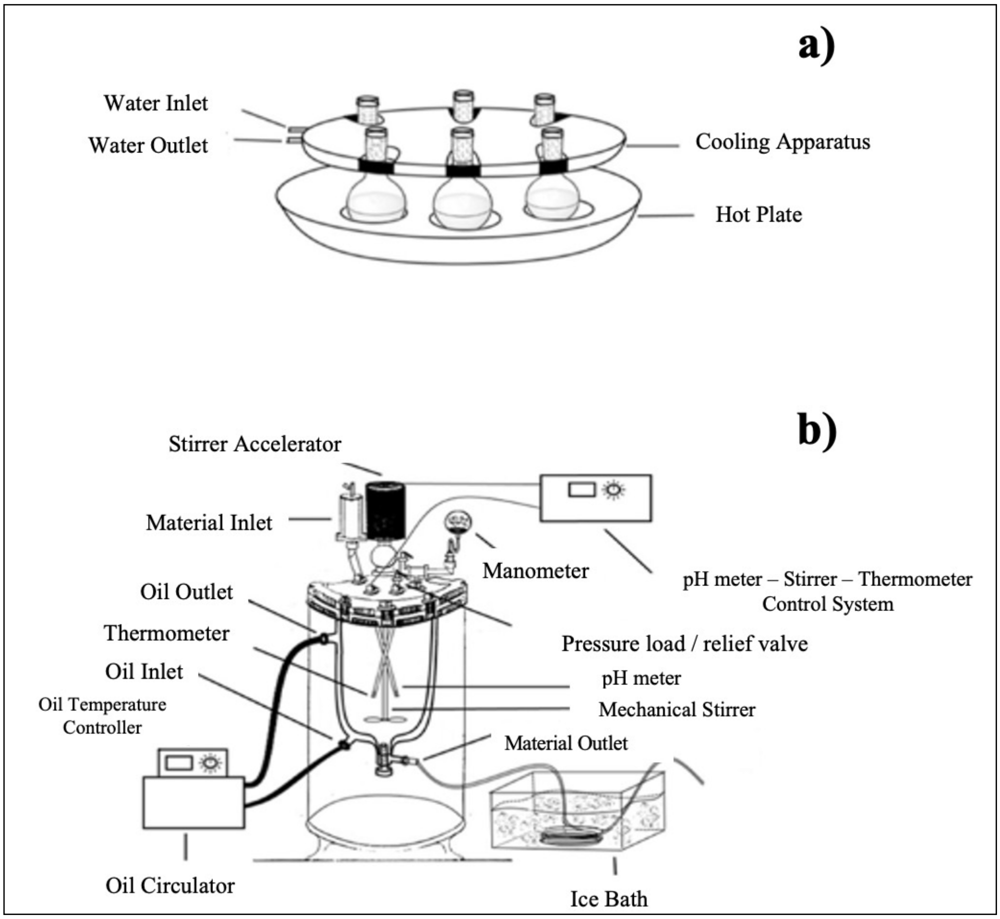

Figure 4- Schematic view of; a) reflux and b) autoclave reactor systems (Çelik et al., 2017).

takes place between electron-rich functional groups and a metal cations. This interaction prevents the metal to contribute the formation of a deposit. The cartoon demonstration given in Figure 5b shows interaction with one cation and one carboxylic acid group. However, there may be a higher number of cations for one negative central organic group. For comparison of both dispersion and chelation mechanisms, note that the colloids are large submicrometer structures containing more than thousands of atoms; on the other hand, chelation prevents one or several number of cation.

Figure 6 demonstrates the monomers of artificially synthesized antiscalants in an autoclave reactor system (Topçu et al., 2017). The antiscalants can work either by chelation or dispersion mechanism, and these monomers are able to work in both chelation and dispersion mechanisms.

Topçu et al. (2017) developed four different co-polymers by merging three different monomers with different combinations that have various chelating groups for metal cations. They synthesized homo and copolymers of acrylamide (AM), the sodium salt of vinyl sulfonic acid (VSA), and vinyl phosphonic acid (VPA) monomers via free radical polymerization and investigated their antiscaling performance against metal-silicate scaling was examined in an autoclave system to stimulate the real field conditions. The performance of synthesized antiscalants was evaluated by monitoring the ion concentration in the decantate solution after the removal of precipitates by centrifugation. They reported that VSA-rich copolymers showed the most promising antiscalant performance for Fe and Mg silicates. The solubility was improved to 225 ppm when 50 mL of 50 ppm antiscalant was employed at 137.6 °C and 3.2 bar for 45 min.

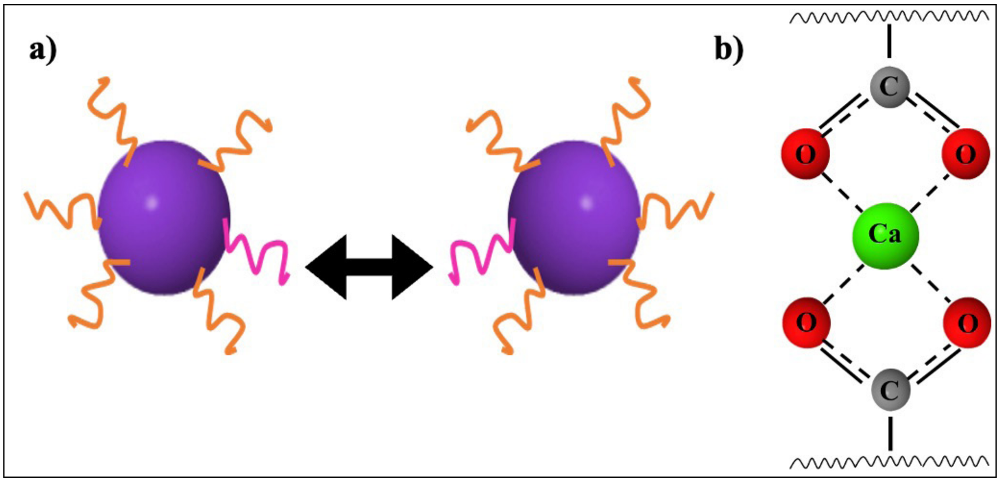

Figure 5- Main mechanisms of deposit formation; a) dispersion, steric stabilization of colloids against aggregation, b) chelation, chelation of Ca^{2+} with carboxylic acid group given as an example.

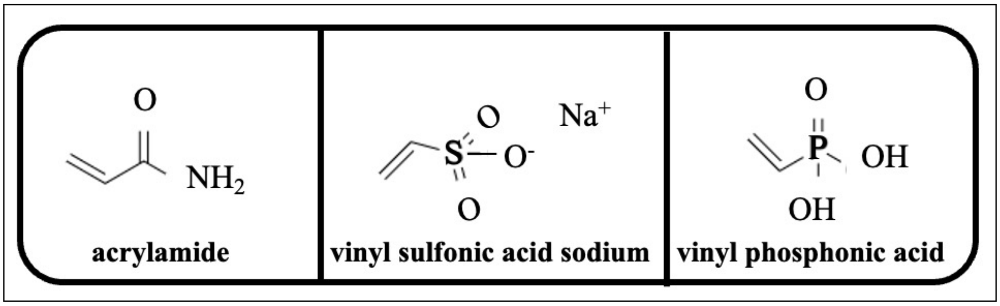

Figure 6- Molecular structure of monomers of artificially synthesized antiscalants (Topçu et al., 2017).

To get further understanding of the efficiency of metal-chelate agents without performing laboratory experiments, a complete information about the structural characteristics and selectivity performance of antiscalants may be provided by quantum mechanical calculations, and density functional theory (DFT) can be used to perform these first-principal calculations. Topçu et al. calculated the binding energies of antiscalant to the selected metal ions (Mg^{2+}, Ca^{2+}, and Fe^{2+}) and investigated the tendency of chelation performances (Topçu et al., 2019*b*). Using this approach, the chelating ability of molecules can be predicted before the tests, and the time and cost-efficient analysis can be performed (Figure 7).

Amine structural units have been proposed as potential silica inhibitors in the literature. Chauhan et al. (2014) synthesized a star-shaped polymer by using a polyacrylamide and polyacrylic acid modified bio-inspired algae core (Figure 8). The results of this study emphasized that experiments, which were carried out at a higher temperatures, have lower soluble silica levels and these star-shaped copolymers have nearly 95% inhibition performance at 55°C for 12 h of reaction time (Chauhan et al., 2014).

Chelating agents have been alternatively used for silica dissolution. (Fredd and Fogler, 1998) used ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA) to chelate or bind metals such as calcium. During the process, the chelating agent solvates the calcium ion and allows the calcite to be transported to the surface of the well or into the injection well. The rate of calcite dissolution by using chelating agents is lower than the utilisation of mineral acids which means the chelating agent moves through a longer path and dissolves more calcite along the way by entering all fractures (Rose et al., 2007).

The main idea of chelation is to entrap the sedimentary ions before their precipitation in the geothermal well and prevent their scale formation by stabilizing the silica colloids (Topçu et al., 2019*b*). Polymeric molecules have been used for the stabilization of colloidal silica particles either by van der Waals forces or hydrogen bonding. Preari et al. (2014) employed Polyethylene glycol (PEG), which has been used as non-ionic surfactant in the literature, and investigated the interaction between PEG and silica species at neutral conditions via hydrogen bonding. PEG is a typical dispersing agent this in fact, a surface active reagent. It adsorbs to

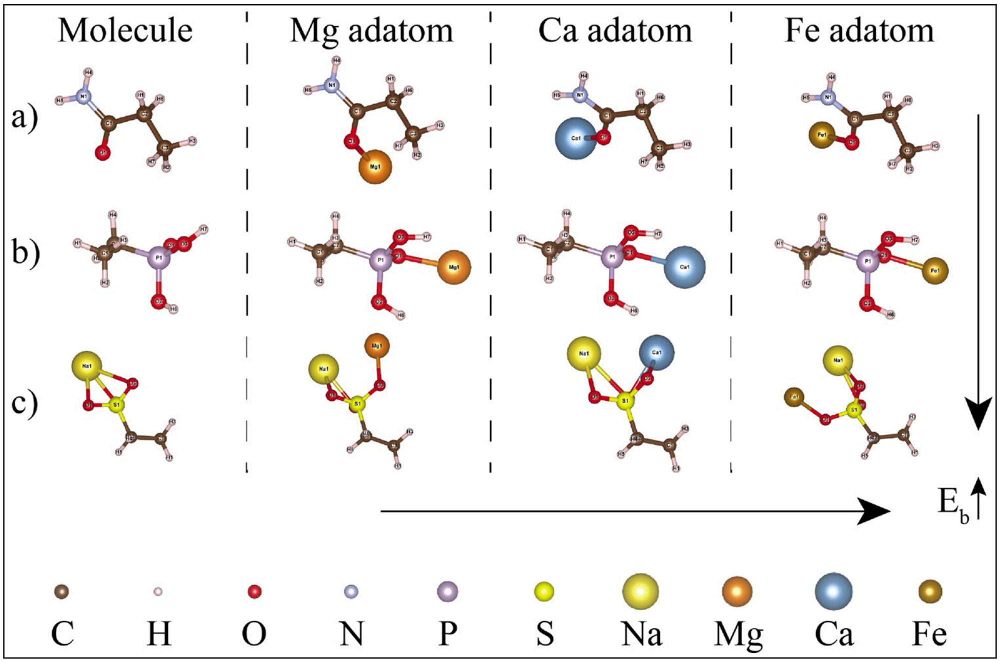

Figure 7- Schematic representation of the metal ions captured by antiscalant molecules; a) acrylamide, b) vinylphosphonic acid, and c) sodium salt of vinyl sulfonic acid (Topçu et al., 2019*b*).

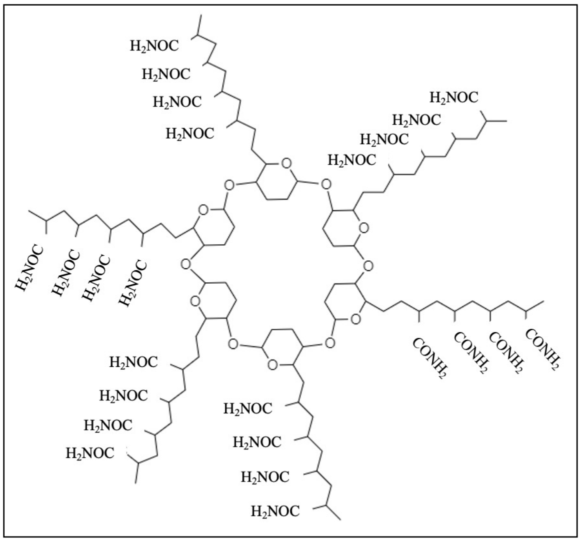

Figure 8- Structure of Algea core star shaped polyacrylamide dendrimer (Chauhan et al., 2014).

the surface of colloids and prevents aggregation and agglomeration of the individual silica particles (colloidal stabilization). The molecular weight of the dispersion agent is critical for the stabilization of the known size of the colloids. Note that smaller colloids need lighter molecular weight dispersing agents. Poly (vinyl alcohol) and poly (vinyl pyrolidone) are known examples of this group of agents.

Polymers with positively charged end-groups have been frequently preferred and compounds with protonated amines, amide moieties and phosphonium are promising candidates for silicate scale prevention applications (Demadis and Neofotistou, 2007; Spinde et al., 2011; Daniloytseva et al., 2011; Demadis et al., 2008; 2012*a, b, c*) Topçu et al. (2019*b*) employed polyethylene gloycol, polyvinyl alcohol, polyvinylsulfonic acid (PVSA), polyvinylphosphonic acid and polyacrylamide with various molecular weights as silica-targeted metal-silicate antiscalants. They provided evidence that orthosilicic acid polycondensation can be prevented by ether and alcohol moieties on polymer chains in the presence of various metal cations such as Fe^{2+}, Mg^{2+} and Ca^{2+}. Even these cations act as catalyst for polycondensation reaction, the silicate solubility is enhanced by using PEG and PVSA mixture not only in hot geothermal wells but also in cold industrial water systems. The dissolved silica concentration increased from 130 to 420 ppm when 100 ppm PEG and 25 ppm PVSA were employed as a mixture at 137.6 °C and 3.2 bar.

Dendrimers are another class of antiscalants that are repetitively branched globular molecules and some of them are effective silica inhibitors. Polyaminoamide (PAMAM) dendrimers have amine functional groups, and they are able to interact with negatively charged silica. Demadis et al. (2008) demonstrated the importance of ionic interactions over silica scaling and at high cationic charge densities, silica entrapment occurs due to the attack of $-NH_3^+$ groups (Neofotistou and Demadis, 2004; Demadis and Neofotistou, 2007). Different functional groups on PAMAM dendrimers have significant effects on silica scale prevention. Whilst -COOH groups were not efficient due to the repulsive forces between anionic silica and deprotonated COO^- groups, $-NH_2$ terminated dendrimers (Figure 9) have a remarkable effect on silica scaling (Neofotistou and Demadis, 2004). According to their results, 40 ppm $-NH_2$ terminated PAMAM increases silica concentration from 171 to 384 ppm. However, the dosage of these dendrimers is an important parameter, although they are promising solutions for silica scaling.

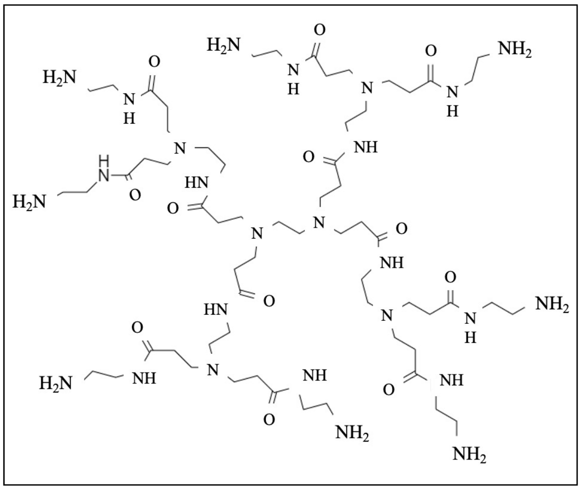

Figure 9- Chemical structure of $-NH_2$ terminated PAMAM (Neofotistou and Demadis, 2004).

During the application of antiscalants, white flocculant formation indicates the loss of inhibition performance of inhibitors in time because protonated $-NH_3^+$ groups entrap with anionic silica groups. Neofotistou and Demadis (2004) proposed the addition of an anionic polymer to prevent the flocculation effect of PAMAM-SiO_2 complex and Carboxymethylinulin (CMI) polymer was used as an anionic polymer. Hereby, anionic groups of deprotonated $-COO^-$ on CMI neutralizes the $-NH_3^+$ groups on PAMAM dendrimer and flocculation of $-NH_2$ and SiO_2 was prevented in the system. According to the results, a 40 ppm dosage of CMI is an adequate amount for inhibition performance. As an anionic polymer, polyepoxysuccinic acid (PESA) has been used by Zhang et al. (2011). to get rid of white flocculants, which were formed by the interaction between $-NH_2$ groups of adipic acid/ amine-terminated polyethers D230/ diethylenetriamine copolymer and silica particles. 20 ppm PESA neutralized the positive charges when 40 ppm copolymer was used. A copolymer of acrylic acid and hydroxypolyethoxy allyether was used by (Gill, 2011) to retard the silica polymerization and disperse the polymerized silica. Polyetyhelenemine has been also used as a scale inhibitor, and Demadis and Stathoulopoulou (2006) compared the efficiency of this $-NH_2$ terminated polymer with PAMALAM dendrimer. According to their results, both cationic polymers enhance the silica solubility, but high positive charge density results in inhibitor coprecipitation with anionic colloidal silica, whereas low charge densities render the inhibitor ineffective at lower dosages. 10 ppm PEI reaches 55% inhibitory efficiency at 24 hours, whilst 80 ppm PAMALAM dosage exhibits 60% inhibition.

5. Results

Scaling has been observed in all geothermal power plants to some extent, regardless of the chemistry of the deposit. The geothermal systems, particularly the ones electrical energy is harvested, are quite concentrated in terms of minerals. For instance, there are some distinct geothermal fields with highly corrosive fluids such as Tuzla (Çanakkale), Seferihisar (İzmir), Gülbahçe (İzmir) and Çeşme (İzmir). Total dissolved solid concentration usually exceeds 5.000 ppm which causes running and maintenance problems based on scaling and as well as corrosion (Baba, 2015). In addition to the high concentration of minerals, another issue that must be considered is the geothermal systems' dynamic nature. Power plants produce a large volume of brine so that the reservoir change over time, and new troubleshooting methods to the problems are required. Accordingly, the chemistry of the deposit is a subject to change. The formation of the deposition may not be entirely prevented; however, it can be minimized to an acceptable amount of time. Various potential chemistries have been mentioned in the text. Their performance varies depending on the temperature and salinity of the geothermal power plant of interest. A particular study must be performed for each field to find the best antiscalant or antiscalant composition for the increase of the performance of geothermal power plants. The performance of potential nominees commercial antiscalants can be tested by pressurized reactors readily employing field conditions. Moreover, computational tools can be used for the selection of the best functional group of antiscalant molecules.

Acknowledgements

DC thanks TUBİTAK (Project No: 120C079) for the support to participate in this work.

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