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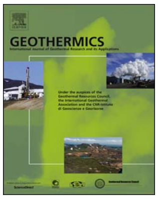

Experimental modeling of silicate-based geothermal deposits

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ABSTRACT

Scaling by metal silicates represents a major obstacle for geothermal systems. A composition that enables the fabrication of artificial deposits is necessary for the rapid testing of potential inhibitors. In this work, artificial deposits were synthesized by employing experimental conditions similar to those in the Tuzla Geothermal Field in Turkey. Although refluxing enabled the formation of a precipitate that was similar to naturally formed deposits in color and texture, their elemental composition and morphology showed a mismatch. An autoclave enabled the production of a precipitate that more closely resembled naturally formed deposits in color, texture, elemental composition, and structure.

1. Introduction

Geothermal energy is a renewable and sustainable energy source. However, the deposition of scale such as silicates and calcite is one of the main handicaps in many geothermal systems, such as the Tuzla Geothermal Power Plant (TGPP), which is located 5 km from the Aegean Sea and 80 km south of the city of Çanakkale, near the ancient city of Aleksandra Troia in northwestern Turkey (Fig. 1). The TGPP has an installed power generation capacity of 7.5 MWe and an annual energy production capacity of 51 GWh and is a closed-cycle system. Significant amounts of seawater enter the fault system such that the water is saturated with atmospheric oxygen. Moreover, the power plant experiences stoppages five times per year, and the system is opened for cleaning and maintenance during this process. Therefore, the system is not free from oxygen.

Scaling problems substantially reduce the efficiency of geothermal power plants and cause financial losses (Baba et al., 2015; Demir et al., 2014). The deposition of scale and related phenomena are considered to be major constraints on the improvement of geothermal energy. Among the different minerals liable to be deposited, silica is a common component and is difficult to remove. Silica precipitates in many different forms in nature (e.g., quartz, tridymite, cristobalite, amorphous silica, etc.) (Ehrlich et al., 2010; Ghouil et al., 2015). Although quartz is mainly observed in nature, extensive deposits of amorphous silica are found to have formed in the Tuzla Geothermal Field (TGF). Amorphous silica precipitates in the form of metal silicate deposits that contain iron and magnesium ions, which are very hard and dense and are difficult to remove from geothermal systems.

The modification of pH using organic acids appears to provide the best short-term remedy. However, corrosion remains a potential risk to the long-term sustainability of geothermal plants. Attempts have been made in the literature to screen potential organic inhibitors to minimize scaling by metal silicates (Demadis et al., 2012, 2007; Demadis and Neofotistou, 2004; Gallup, 1997, 1998, 2002).

The association of silicate solutions with metal salts has been documented in the literature. Saishu et al. (2013), for instance, examined the effect of a mixture of Na^+ and Al^{3+} on the morphology and precipitation rates of silica deposits. The experiments were performed with a constant Na/Al ratio of 1.48 and increasing Al^{3+} concentrations from 0 to 6.7 ppm. According to the results, the precipitation rate and the amount of silica precipitated increased with increases in the concentration of Al^{3+} and Na^+. These ions might promote the formation of Na-Al-Si complexes in solution. Moreover, with increases in the amount of these ions the morphology of the precipitates was found to be modified. Although at low Al^{3+} concentrations amorphous silica was formed, at higher concentrations of Al^{3+} the amorphous structure was transformed into quartz. This result was attributed to a reduction in the energy barrier required for the nucleation of quartz to occur. In another study, Icopini et al. (2005) investigated the effects of various parameters, such as ionic strength, pH, and different initial concentrations of silica, on the rate of oligomerization of silica. The ionic strengths of all solutions were obtained using a mixture of Na^+, K^+, Ca^{2+}, Cl^-, and HCO_3^- solutions. Test experiments were carried out at ionic strengths of 0.01 and 0.24 molal (m), pH values ranging from 3 to 11, and initial concentrations of silica of 250, 750, and 1250 ppm. The results showed that silica

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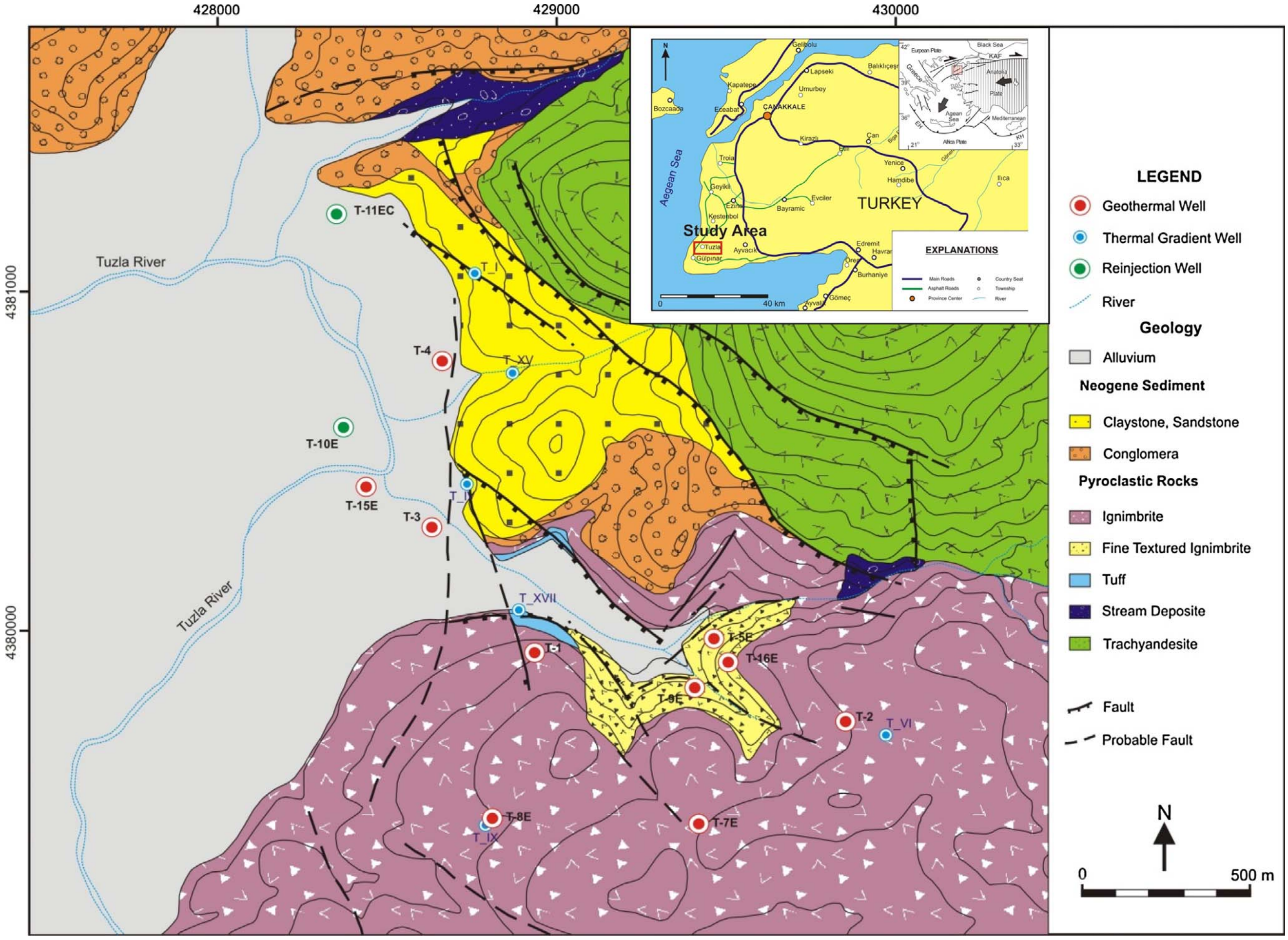

Fig. 1. Location and geological map of study area (WES JEC, 2006; Baba et al., 2015).

nanocolloids were stabilized at low pH and low ionic strengths but became unstable when the solution pH was near neutral and at higher ionic strengths and higher initial silica concentrations. The rate of oligomerization of silica was higher by six orders of magnitude in solutions with high ionic strengths than in those with low ionic strengths. Moreover, the rate increased with an increase in the initial concentration of silica. Chen and Marshall (1982) stated that Na_2SO_4, NaCl, $MgSO_4$, and $MgCl_2$ affected the concentration of dissolved silica. Increases in the salt concentration increased the amount of silica precipitated. In addition, the effect of temperature on scaling by silicates was examined, where the experiments were conducted at constant salt concentrations. The results showed that the solubility of silica increased with an increase in temperature. In addition, the effects of added salts and temperature were found to change the structure of the precipitate, which underwent a transformation from amorphous silica to cristobalite or quartz. Gallup et al. (2003) studied the desilication of geothermal water systems to obtain more commercially valuable minerals. The experiments were performed at 90 and 130 °C. Except for Mg^{2+}, other cations reacted with silica to give poorly crystalline metal-rich silicates and co-precipitated as metal carbonates at 90 °C. Raising the temperature to 130 °C resulted in an increase in the crystalline content of the precipitates, which suggested the formation of more commercially valuable minerals. The results of desilication tests showed that the most effective desilicating agents were Mn^{2+} and Fe^{2+}. Silica precipitated rapidly with the use of these cations, and a combination of Mg^{2+} and Fe^{2+} in solution reacted with silica to give saponite-type precipitates. Brown (2011) examined the thermodynamics and kinetics of scaling by silica. His group performed test experiments on scaling by silica using NaCl solutions. As the supersaturation index increased, the rate of precipitation of silica also increased. This result was explained by a reduction in the electrostatic attraction between Na^+ and monosilicic acid. Silica colloids in dilute solutions were very stable and had negative surface charges that prevented the agglomeration of silica particles. If the concentration of the solution reached supersaturation, cations surrounded the negatively charged silica particles, with the results that cations in saturated solutions and silica particles came together to form metal silicate precipitates, negatively charged silica particles approached closer to each other, and larger silica colloids formed.

A methodology for testing the performance of potential inhibitors in laboratory conditions is needed. In this study, synthetic precipitates were produced that had similar compositions and morphologies to those of the deposits collected in the vaporizer of the TGPP. Synthetic brine consisting of Cl-rich salts of the common metal ions Fe^{2+}, Mg^{2+}, and Ca^{2+} in the presence of Na silicate was prepared and reacted at high temperatures. Two types of apparatus (reflux and autoclave) were employed for the fabrication of metal deposits. Refluxing is a technique commonly used in chemistry laboratories and can be used as a screening technique for potential inhibitors. On the other hand, an autoclave is a more specialized apparatus in which it is possible to increase and control pressure, pH, and temperature during the synthesis of artificial deposits. The formation of deposits in the autoclave reactor was found to be close to the field conditions, which was a prerequisite for screening potential inhibitors of scaling by metal silicates. The resulting deposits were characterized in terms of elemental composition, morphology, crystal structure, and structural formation. The experimental conditions were adjusted to enable the fabrication of deposits of which the features closely resembled those of naturally observed deposits, to