

# The injection of CO<sub>2</sub> to hypersaline geothermal brine: A case study for Tuzla region



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## ABSTRACT

Scaling is a serious issue for geothermal power plants since it remarkably decreases the harvesting of energy. The reduction of pH by organic acids whose structure is close to CO<sub>2</sub> for instance formic acid has been an effective solution for the minimization of scaling. Herein, the effect of CO<sub>2</sub> injection on the formation of scaling particularly metal-silicates was investigated for the model case of Tuzla Geothermal Field (TGF) located in the northwest of Turkey. CO<sub>2</sub> has an acidic character in aqueous systems because it leads to the formation of carbonic acid. The injection of 20.6 m<sup>3</sup>/s CO<sub>2</sub> (approximately 88 ppm) to hypersaline brine of TGF is a promising green approach for both mitigation of scaling by reducing pH from 7.2 to 6.2 at the well-head and the minimization of potential corrosion compared to the use of formic acid (55 ppm).

## 1. Introduction

Geothermal energy is a sustainable resource by which electricity can be generated from the heat stored by water reservoirs (Lund and Boyd, 2016). The most important operational handicap of power plants is the scaling by components such as calcite, silicate, metal-silicates, and sulfides (Gallup, 2002; Potapov et al., 2001). CO<sub>2</sub> that is an acidic gas is separated from the brine due to the decrease in pressure and temperature (Baba et al., 2015; Duan and Sun, 2003). This elimination leads to an increase in the pH of the brine, hence decreasing the solubility of minerals, particularly silica, in the water. As the geothermal fluid is transported to the power plant through the well, minerals with low solubility begin to precipitate in an uncontrollable manner on the equipment, called scaling (Demir et al., 2014). This phenomenon causes a blockage in the pipes of the heat exchangers, where the energy transfer of the system takes place. Furthermore, this deposit formation reduces the inner width of the system and prevents heat transfer, thereby reducing the efficiency of electricity production.

For the cleaning of metal silicate scaling, the production system is closed for a while and the system is washed with acids to dissolve silica and eliminate the metal-silicate deposit, which has high mechanical resistivity and stable chemical nature (Demadis et al., 2011a). For instance, hydrofluoric acid (HF) disintegrates the Si-O bonds are replaced by Si-F bonds. (Knotter, 2000) Nevertheless, the acid treatment increases the operating cost of the system; moreover, this operation leads

to the loss of production during a period of stoppage. In addition, the installation of the plant, which is costly and laborious, is damaged by this process because these chemicals increase the risk of corrosion in pipes (Demadis et al., 2011b; Zhang et al., 2011). In this wise, a number of the study was performed in the literature to mitigate the metal-silicate scaling using various strategies involving the use of inhibitors and regulation of water (Demadis et al., 2012; Gallup and Barcelon, 2005; Topcu et al., 2017). For the former method, organic molecules are commonly employed to eliminate the scaling using either chelating or dispersion mechanisms. In general, these compounds include protonated primary, secondary or tertiary amines (Danilovtseva et al., 2011; Demadis et al., 2008; Spinde et al., 2011), amide moieties (Demadis and Neofotistou, 2007), phosphonate (Spinthaki et al., 2018), ether (Preari et al., 2014), or alcohol functional groups (Topcu et al., 2019). For the latter, the brine is regulated using weak organic acids to reduce pH and increase the solubility. For instance, the acidification of high salinity brine to mitigate silicate scaling has been examined in our previous study. The scaling was remarkably prevented by reducing the pH of brine to < 6 using 55 ppm formic acid (HCOOH) (Baba et al., 2015). Formic acid is the simplest organic acid, whose structure is close to CO<sub>2</sub>. Moreover, it is a ferric iron reducing agent, and ferric silica scale may be more insoluble than ferrous silicate scale.

The acidity of the additive is quite an important parameter for preventing the formation of the geothermal deposit. Carbonic acid (H<sub>2</sub>CO<sub>3</sub>) has moderate acidity and simple chemical structure, compared

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to formic acid (Greenwood and Earnshaw, 1984; Riddick et al., 1985). The amount of  $\text{H}_2\text{CO}_3$  in nature may arise as a result of the thermal change in the rocks and minerals having releasing a carbonate ion or the decomposition of organic matter in the sedimentary rocks at shallow depths. Carbonic acid in a liquid state is released as  $\text{CO}_2$  gas due to the change in the solubility of brine. The dissociation of  $\text{H}_2\text{CO}_3$  into  $\text{CO}_2$  may be due to magmatic process or physical processes in solutions of meteoric waters. Therefore, considering, the use of a gas having the geological origin and acidic characteristic may be a possible remedy to mitigate metal-silicate scaling (Hibara et al., 1990).

In this study,  $\text{CO}_2$  gas is injected to the geothermal system to prevent the formation of metal silicate scaling and compared with formic acid, which is currently employed in the Tuzla Geothermal Power Plant (TGPP) for pH modification. In this wise, the injection system was performed from the wellhead at various rates of  $\text{CO}_2$  flow. Corrosion of both  $\text{CO}_2$  and formic acid on two naked metal pieces from separator and vaporizer was examined.

## 2. Study area

The Tuzla Geothermal Field (TGF) is located in northwestern Turkey and is closely related to active tectonic zones of the North Anatolian Fault Zone (Fig. 1). TGF is in the settlement near the Aegean Sea. This geothermal field has two binary geothermal power plants (Tuzla and MTN Energy). The installed capacity of the Tuzla Geothermal Power Plant (TGPP) is 7.5 MWe and the annual energy production capacity is 51 GW h. The installed capacity of the MTN Energy Geothermal Power Plant is 8 MWe. This study was conducted in the TGPP.

## 3. Methods and materials

### 3.1. The gas injection system

To inject industrial  $\text{CO}_2$  into the system, a  $\text{CO}_2$  mobile heater tank, a text static mixer, a check valve, a flow meter, a solenoid valve, a regulator, a safety valve, and a pH meter were used.  $\text{CO}_2$  kept under a certain pressure is in a solid and gaseous state in the mobile heater tank. As a result of decreasing the pressure in the tank,  $\text{CO}_2$  transforms into the solid form that causes clogging in the injection system (Fig. 2). Therefore,  $\text{CO}_2$  is heated with the mobile tank heater and transferred to

the dosing system. The static mixer is designed and employed to the system for the homogeneous mixture of  $\text{CO}_2$  (gas) and brine. The static mixer with a  $\text{CO}_2$  diffuser was added to the outlet of the brine pumps after the separators. After the liquid  $\text{CO}_2$  from the tank is gasified in the evaporator and the pressure is regulated, it is loaded to the static mixer diffuser and mixed with brine and the pH is measured at the mixer outlet. A check valve is added to the system for operational safety after the  $\text{CO}_2$  (gas) dosing point. The flow meter was added to the system to measure the volumetric flow rate of  $\text{CO}_2$  (gas). The solenoid valve is an electromechanical valve that controls  $\text{CO}_2$  (gas) flow. The regulator allows the  $\text{CO}_2$  (gas pressure) to exceed the brine pressure while the safety valve keeps the pressure below 25 bar. After the pump, a set of samples is regularly collected from the measurement point with the help of the pH probe and sends the valve opening or closing command according to the set values.

### 3.2. Characterization

Geothermal fluids were collected from three production and one-reinjection wells, in the Tuzla Geothermal Field in October 2018. Electrical conductivity (EC), temperature ( $^{\circ}\text{C}$ ) and pH values were recorded in situ with a multi-parameter instrument. Water samples for major ions and for trace metal analysis were filtered using filter papers having a  $0.45\ \mu\text{m}$  pore size. The trace metal analysis was carried out by ICP-MS (inductively coupled plasma mass spectrometer) in the ALS Chemex Lab. The concentrations of bicarbonate ( $\text{HCO}_3^-$ ) and chloride ( $\text{Cl}^-$ ) were determined by titration while the sulfate ( $\text{SO}_4^{2-}$ ) concentration was characterized by ion chromatography (Table 1).

The concentration of  $\text{SiO}_2$  was determined by measuring the molybdate-reactive silica (Icopini et al., 2005). This method is based on the measurement of monomeric silica such that an ammonium molybdate addition causes a reaction between monomeric and dimeric silica species and a phosphate group in an acidic medium resulting in a yellowish solution. The molybdophosphoric acid concentration is reduced by adding oxalic acid to eliminate color interference from the phosphates, thus the resulting color arises from the silicomolybdate complex. Hence, the stated silica concentration throughout the text is molybdate-reactive silica. In addition, the total silica concentration in natural brine was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS; Agilent 7500 CE Octopole instrument, Santa Clara, CA, U.S.A.). Note that the acidification of the brine for total silica concentration was carried out by  $\text{HNO}_3$ , not HF, which in fact would be better for dissolution of silica, to avoid damage to quartz apparatus of ICP-MS. Therefore the total silica concentration expressed in the text may be relatively lower than the exact result.

## 4. Results and discussion

### 4.1. Hydrogeochemical properties of the geothermal fluid

Tuzla Geothermal Field, whose fluid is rich in NaCl, has a very complex structure in terms of hydrogeochemistry. NaCl/water composition indicates a marine origin and also water-rock interaction. The origin of this fluid was studied by (Mützenber, 1997), (Balderer, 1997), (Vengosh et al., 2002), and (Baba et al., 2015). It was mentioned that geothermal fluid of Tuzla is fossil saline water that has been stuck between Miocene sediments. Further, it has been predicted that the geothermal fluid of this site is formed by dissolution of marine evaporites (Vengosh et al., 2002).

The fluid from the production wells is acidic due to an excess of free  $\text{CO}_2$ , which is the result of the high partial pressure of this gas in the well. The reservoir temperature of geothermal fluid is  $173\ ^{\circ}\text{C}$ . The wellhead temperature in production wells T9, T16 and T18 are  $149.1\ ^{\circ}\text{C}$ ,  $150.6\ ^{\circ}\text{C}$ , and  $150.6\ ^{\circ}\text{C}$ , respectively. The wellhead pressure ranges from 3.61 to 3.74 bar in production wells (Demir et al., 2014). All samples have the same reservoir and the  $\text{Na}^+/\text{Cl}^-$  water

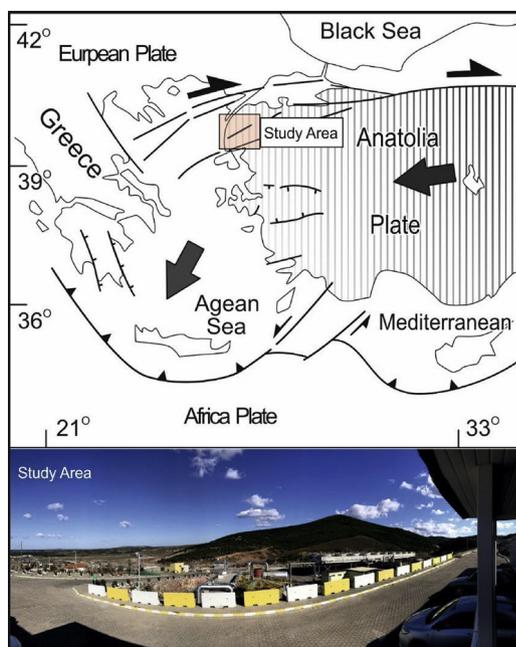
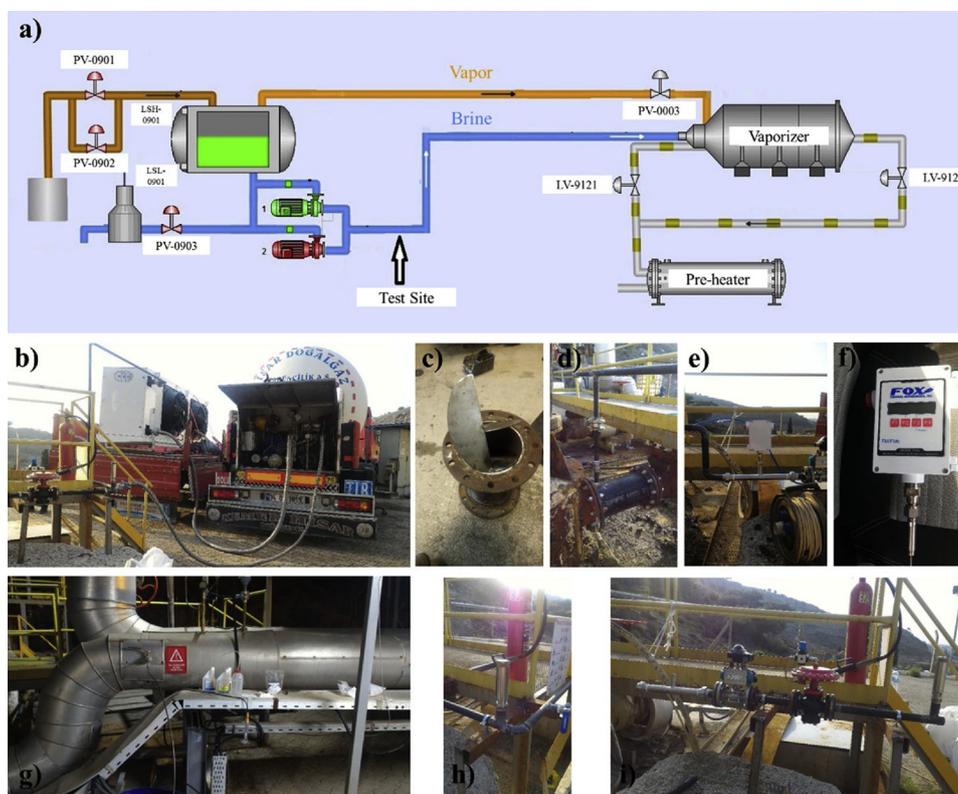


Fig. 1. Location Map of Tuzla Geothermal Field.



**Fig. 2.** Photographs of the pilot system in the TGF; (a) scheme of the system, (b) Mobile heater tank, (c) static mixer, (d) check valve, (e, f) flow meter, (g) pH meter controller, (h) safety valve, and (i) solenoid valve.

composition indicates a marine origin. The Piper and Schoeller diagrams show that the geothermal brine is of the NaCl facies (Fig. 3a and b). According to Giggenbach plot, Tuzla geothermal fluid appears to have equilibrated with the reservoir rocks (Fig. 3c). The geothermal fluids from the field plot in a linear array with a full equilibration temperature of 140 °C.

Many minerals found as hydrothermal minerals such as calcite, dolomite, chalcedony in the geothermal fluids are not known to form scales in wellbores although the fluid becomes oversaturated with respect to these minerals as a consequence of boiling and cooling. According to the Saturation Index (SI), all the waters are undersaturated with respect to calcite and wollastonite. The SI shows that the formation of silica and chalcedony minerals increases as the temperature decreases (Fig. 3d). A direct correlation is observed between the saturation of chrysotile/talc minerals and temperature.

#### 4.2. Effect of pH modification on solubility

The geothermal fluid of the study area has high silicic acid concentration; generating an insoluble Fe, Mg-silicate deposit via polycondensation. Since the solubility of silicic acid is a function of pH (Ketsetzi et al., 2008), the regulation of fluid properties can enhance the

solubility. The increasing pH may cause additional chemical reactions involving metal-hydroxides and oxyhydroxides, therefore the acidification of the fluid is a well-known method to mitigate metal-silicate scaling rather than alkali additives. Even though there are a number of organic soft molecules reported as metal-silicate inhibitors in the literature, they are still far from being applied on a large-scale due to high cost and difficulties in synthesis. Hence, the CO<sub>2</sub> that is already emitted from the system was employed to regulate the geothermal fluid.

The effect of CO<sub>2</sub> injection was characterized by considering the pH of brine-gas mixture and the concentration of the major components such as soluble SiO<sub>2</sub> and Fe<sup>2+/3+</sup> in the fluid. In Fig. 4, these three major parameters are represented as a function of CO<sub>2</sub> flow. In the absence of CO<sub>2</sub> the fluid pH is observed around 7.4, which is slightly alkaline and causes minimum solubility. The increased CO<sub>2</sub> flow lowers the pH exponentially and causes saturation at approximately 5.95 while the flow reaches 20.6 m<sup>3</sup>/s. This saturation behavior can be assigned to the solubility limit of CO<sub>2</sub> at the field condition. Not surprisingly, the concentration of soluble SiO<sub>2</sub> in the fluid has a reverse relationship with the pH (Fig. 4b). The concentration of the SiO<sub>2</sub> increases from 187 ± 3.8 to 203 ± 2.2 ppm as the CO<sub>2</sub> flow increases. Note that the solubility of SiO<sub>2</sub> is 172 ± 3.4 ppm in the absence of CO<sub>2</sub>. Therefore, the injection of CO<sub>2</sub> enhances the solubility of SiO<sub>2</sub> by approximately

**Table 1**

Chemical properties of the geothermal fluid (the concentrations are given as ppm).

Sample Number	Type	Ca <sup>2+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>
T9	Production well	2370	220	110	19280	34500	200	2
T16		2400	230	114	19400	34450	190	1
T18		2570	240	94	20170	37110	230	1
T15	Re-injection well	2400	230	104	19210	35040	195	1
T7	Observation well	30	17	1	1090	1660	110	5
T8		20	3	1	210	290	30	50
TA1		2460	230	78	19500	35450	140	1

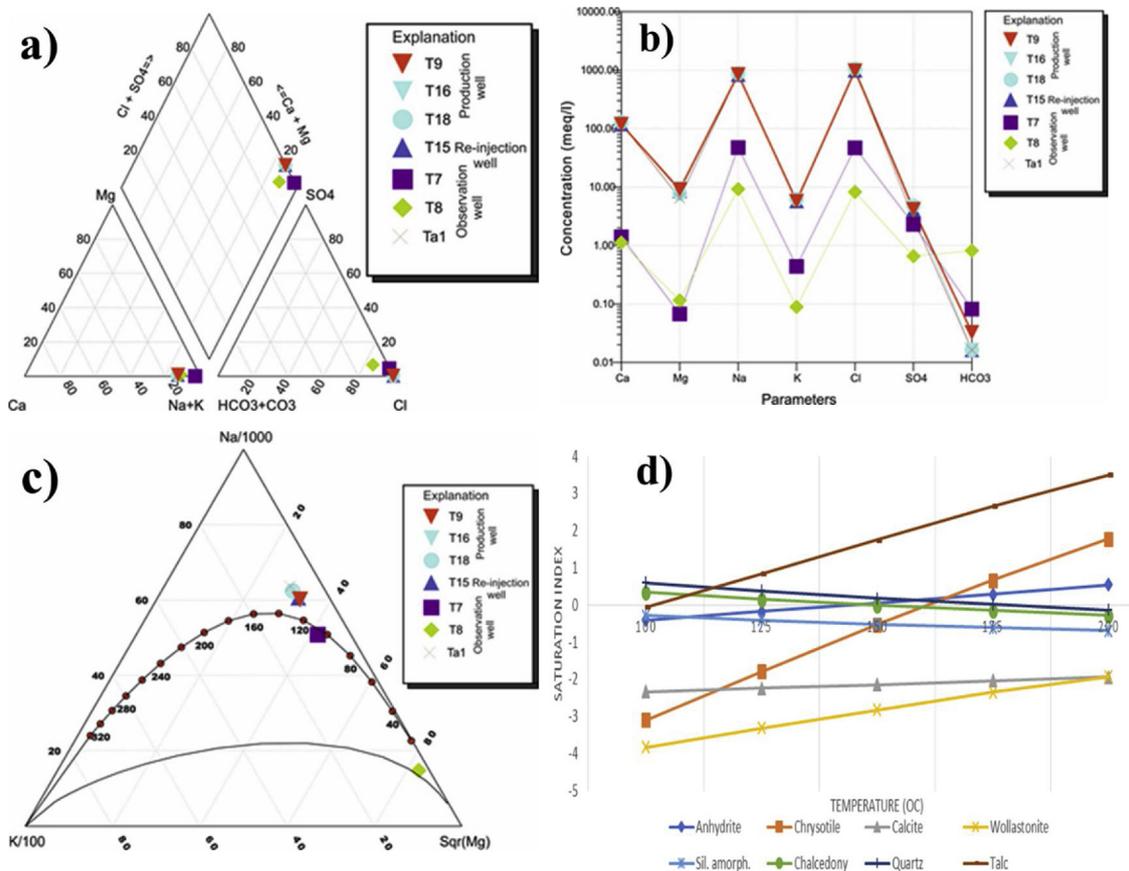


Fig. 3. (a) Piper Diagram, (b) Schoeller Diagram, (c) Giggenbach Na-K-Mg Diagram, and (d) Saturation Indices for some minerals in the geothermal fluid.

18%. On the other hand, the total  $\text{SiO}_2$  concentration, i.e. the summation of monomeric and oligomeric silica, was found to be 320 ppm. Therefore, the difference between total  $\text{SiO}_2$  and the monomeric  $\text{SiO}_2$  concentration gives a colloidal  $\text{SiO}_2$  concentration in the brine (nearly 148 ppm difference). In an acidic environment, colloidal  $\text{SiO}_2$  can be solubilized (Demadis and Mavredaki, 2005), thus the increase in molybdate reactive  $\text{SiO}_2$  may be attributed to the dissolution of colloidal  $\text{SiO}_2$  by the addition of  $\text{CO}_2$ . In addition, the total concentration of  $\text{Fe}^{2+/3+}$  does not show a remarkable difference as the flow rates vary. It remains unchanged between 6–8 ppm (Fig. 4c).

The pH of the fluid can be readily regulated in the field using formic acid due to ease of supply and low cost. Therefore, the use of formic acid in the same production well may provide further insight into the performance of  $\text{CO}_2$  as a benchmark. Since the most effective dosing range of formic acid is between 45 and 80 ppm, it was employed for well T16 fluids and characterized in terms of pH,  $\text{SiO}_2$ , and  $\text{Fe}^{2+/3+}$ . In Fig. 5, detailed information regarding with formic acid trials is given. pH of the fluid decreases as the applied acid concentration increases. Compared to the  $\text{CO}_2$  injection, the pH decrease is more dramatic and it falls to 5.3 at 80 ppm dosage. Additionally, the decrease follows a linear pattern due to the better solubility of formic acid. In fact, the concentration of ions shows a fair degree of increase as a result of the partial dissolution of the metal-silicate deposit. The solubility of  $\text{SiO}_2$  gradually increases with the addition of formic acid and reaches to  $196 \pm 3.2$  ppm at 55 ppm dosage. Nevertheless, the solubility starts to decrease after further addition of formic acid. On the other hand, in a similar to  $\text{CO}_2$  treatment, the  $\text{Fe}^{2+/3+}$  solubility exhibits a minor increase to  $6.0 \pm 1.1$  ppm for all dosages of formic acid.

The inhibition of metal-silicate scaling was also examined with weighed coupons that are exposed to brine in the power plant for 168 h by using the most efficient dosage of the inhibitors. In the case of  $\text{CO}_2$  addition, the accumulation on the coupon is found to 210 mg while this

level reaches 240 mg by adding formic acid. This weight difference consistent with the increase in solubility and shows that  $\text{CO}_2$  is effective alternative to formic acid.

#### 4.3. Discussion of corrosion

The corrosion by chemical additives in the geothermal system is a substantial issue as well as their inhibition performance. Therefore, the dosage of inhibitors having an acidic character is determined meticulously to avoid harm to the geothermal system. To quantify the corrosion for comparison, a set of experiments was carried out in a lab-scale autoclave reactor using a synthetic brine at similar field conditions for both  $\text{CO}_2$  and  $\text{HCOOH}$ . The two different metal pieces (pipe and block) were supplied by the TGF and subjected to  $\text{CO}_2$  and formic acid, respectively. The dosage of inhibitors was fixed to the values showing the best inhibition performance, which are  $20.6 \text{ m}^3/\text{s}$  of  $\text{CO}_2$  and 55 ppm of formic acid. The amount of brine in one-hour passes from the system is 250 tons. For the calculation of  $\text{CO}_2$  solubility, the result of (Duan and Sun, 2003) was employed. According to the model the authors propose that, the solubility of  $\text{CO}_2$  is  $0.0020 \text{ mol/kg}$  at  $150^\circ\text{C}$ , 5 bar, and  $1.0 \text{ mol/kg}$  NaCl concentration. This calculation suggests the solubility of the  $\text{CO}_2$  that is 88 ppm. Note that the values for Tuzla are  $143^\circ\text{C}$  and  $0.5 \text{ mol/kg}$  NaCl that may show softer condition and therefore higher solubility of  $\text{CO}_2$ .

To quantify the extent of corrosion for comparison, a simple mathematical formula was employed;

$$\%Corrosion = \frac{(m_0 - m)}{m_0} \times 100 \quad (1)$$

where  $m_0$  is the initial mass of the metallic object,  $m$  is the mass of the cleaned object after acid treatment. In a control trial, the corrosion was found to be 0.13% and 0% for the block and the pipe, respectively. It

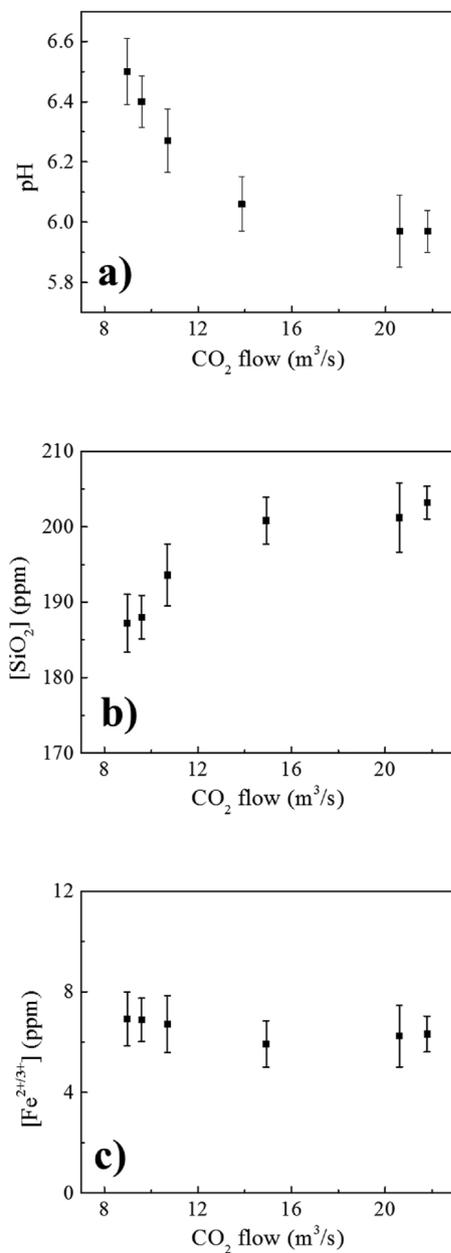


Fig. 4. The results of chemical analysis in the geothermal fluid in the T16 separator for the CO<sub>2</sub> trials; (a) pH, (b) [SiO<sub>2</sub>], and (c) [Fe<sup>2+/3+</sup>].

was 0.21% and 0.35% respectively for formic acid while it shows similar values to the control trial in the case of CO<sub>2</sub> injection (0.13% and 0.05%). The metal pieces were also examined by imaging. The images of metal pieces before and after the corrosion test are presented in Fig. 6. The appearance of the metal samples is consistent with the corrosion calculations. Initially, all the samples have smooth and bright surfaces. After 1 h acid treatment, the block is corroded with small rust spots. Similar imaging was applied to metal pipes taken from the vaporizer tubing of the TGPP. Note that the vaporizer is the most expensive part of the system. Upon acid treatment, the pipes have a dull surface; on the other hand, the CO<sub>2</sub>-treated pipe appears shiny, indicating no traces of corrosion at least the experimental conditions employed in this study. In the case of the metal blocks, the pieces subjected to formic acid and in the absence of an inhibitor (control) suggest a partial corrosion. It is observed that CO<sub>2</sub> does not cause a remarkable damage under these conditions.

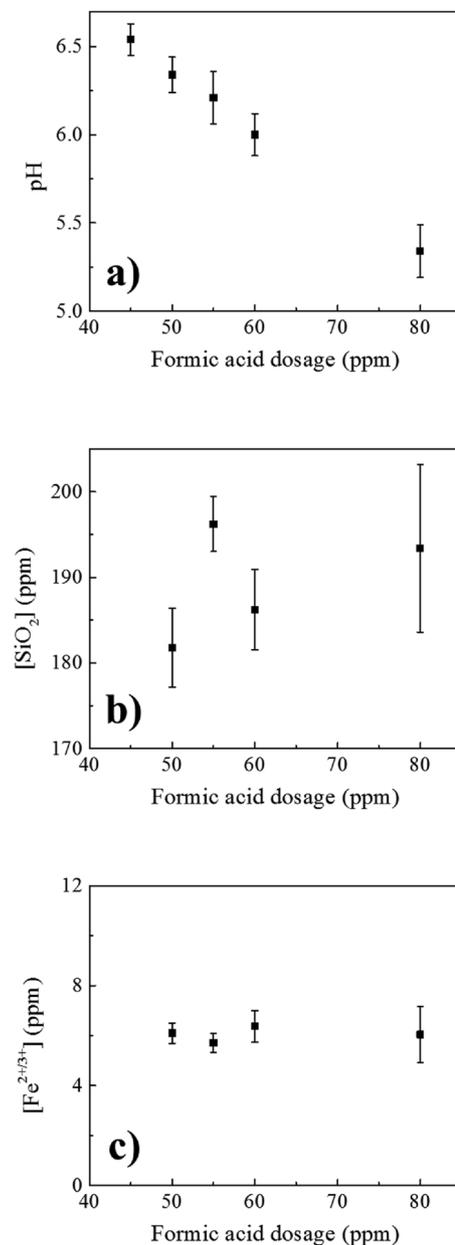


Fig. 5. The results of chemical analysis in the geothermal fluid in the T16 separator for the formic acid trials; (a) pH, (b) [SiO<sub>2</sub>], and (c) [Fe<sup>2+/3+</sup>].

## 5. Conclusions

Metal-silicate scaling is one of the major obstacles to geothermal power plants, particularly at the TGF. Scaling reduces the efficiency of the plants due to clogging of the transfer lines and reduction of thermal conductance. pH modification is a fruitful approach to mitigate scaling, therefore readily available organic acids particularly formic acid in the TGF have been used in large volumes. The study demonstrates a set of inhibition experiments using industrial CO<sub>2</sub> gas since this molecule has an acidic nature in aqueous systems. A series of tests was performed in the field using a variable flow rate of CO<sub>2</sub>. The formic acid trials were also carried out to compare as a benchmark. The inhibition of metal scaling and potential corrosion on the metal parts of the system was examined ex-situ. The injection of CO<sub>2</sub> at 20.6 m<sup>3</sup>/s showed a better performance than formic acid (55 ppm employed as usual) in scaling inhibition and less corrosion under the identical harsh conditions. Consequently, CO<sub>2</sub> can be employed instead of formic acid. The main intention of this study in future will be to capture the CO<sub>2</sub> of the system

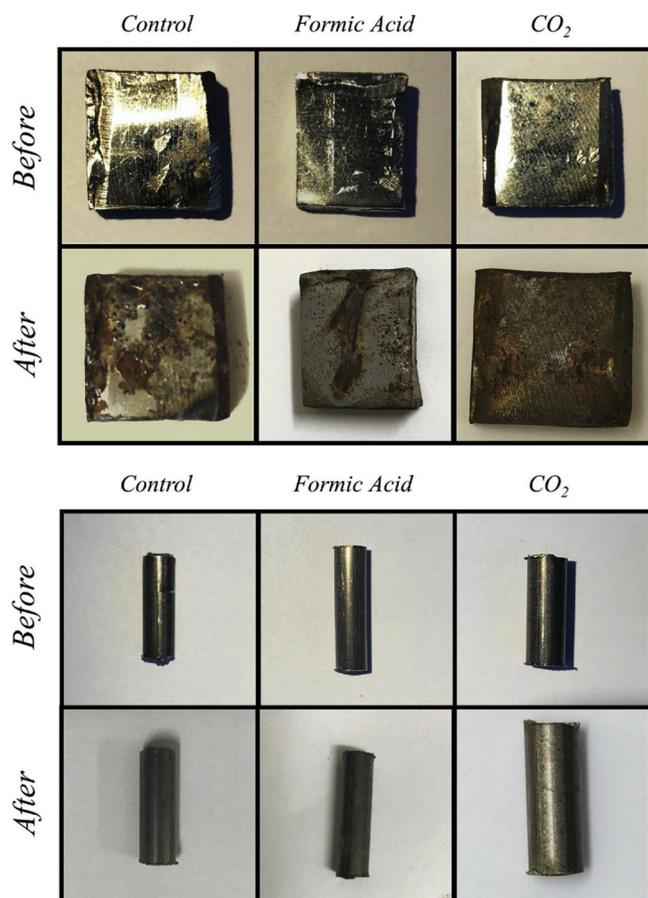


Fig. 6. Images of metal blocks and pipes sampled from the power plant system before and after acid treatment.

itself released during the production. The results reported here could be a basis for such a study that may develop the sustainability of geothermal power plants.

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