

Evaluating the Efficiency of Scaling Inhibitors in Geothermal Fluids at High Pressures and High Temperatures

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ABSTRACT

Mineral precipitation (scaling) such as sulfates and carbonates is a well-known phenomenon in geothermal plants. Scaling can damage plant equipment (e.g. heat exchangers) or reduce the injectivity of the reservoirs and thus the operation lifetime of such installations. Reduction or prevention of scaling is commonly achieved by injecting scaling inhibitors into the geothermal circuit. However, most highly efficient scale inhibitors are toxic and persistent in the reservoir. In this context, the use of environmental friendly, non-toxic, and degradable scaling inhibitors has become attractive.

In this study, a scale inhibitor based on ecologically friendly polycarboxylates was examined with respect to its efficiency to inhibit calcite scaling under high pressure/high temperature (HPHT) conditions. Efficiency tests were carried out in a static batch experiment applying an autoclave system equipped with a sensor monitoring the pH-value. This system allows measurements at pressures and temperatures up to 150 bar and 125 °C. The results were compared with those from efficiency tests under normal ambient conditions.

1. INTRODUCTION

In geothermal applications the produced fluids will encounter considerable temperature and pressure changes when removed from the reservoir. This can lead to oversaturation of dissolved minerals and the well-known problem of mineral precipitation (scaling) within the geothermal fluid loop or in the reservoir after reinjection. Scaling can severely damage geothermal installations such as pipes, pumps, heat exchangers or decreases the injectivity of the reservoir (Saadat et al. 2010). Scale inhibitors have been applied very successfully over many years. Developed for application in oil field production, water heating facilities, and circulating cooling systems they prevent the formation of mineral scales such as calcite and barite effectively (Collins et al 2004, Sullivan et al. 1996, Choi et al. 2002). However, the commonly used inhibitors based on phosphates or phosphonates are known to have toxic effects on aquatic organisms or cause eutrophication problems (Hasson et al. 2011, Lattemann and Höpner 2008). Environmental concerns of the governmental authorities are increasing and force the companies operating geothermal applications toward the usage of “green” inhibitors that are non-toxic and biodegradable. Several new anti-scaling chemicals meeting these requirements were lately tested with regard to their inhibitory efficiency (Reddy and Hoch 2000, Baraka-Lokmane et al. 2008, Choi et al. 2001).

The performance of scaling inhibitors can be evaluated by the following two kinds of tests. The jar or bottle test is a static test of a fluid batch in a reactor (static batch test) and is widely used for inhibitor efficiency testing. The tube blocking test is carried out under dynamic conditions within a tube (Bazin et al. 2005). These tests result in the quantification of the inhibitory effect by determining the minimum inhibitor concentration (MIC), which is defined as the concentration of the inhibitor required to prevent a predefined change of a scaling indicating physical quantity over a certain time. In batch tests this quantity can be a broad variety of measurable fluid properties such as the pH value, the electrical conductivity, the concentration of certain ions or the amount of solid precipitation. In tube blocking tests it is the differential pressure over the tube. Applying a given test procedure, the lower the MIC for a scaling inhibitor, the higher is the inhibition performance. However, different ranking orders of scaling inhibitors were obtained when different efficiency test methods were applied (Bazin et al. 2005).

To our best knowledge, in inhibitor efficiency investigations for geothermal purposes, the static batch test was so far only carried out under ambient conditions or moderately elevated temperatures at normal pressure. However, for geothermal purposes the inhibitor will be added to the geothermal fluid under reservoir conditions, which are characterized by high pressure and high temperature (HPHT). Especially the temperature influences the performance of the inhibitors. Mineral saturation and most of the relevant chemical equilibria are temperature dependent and the thermal stability of an inhibitor also influences its performance. Therefore, it is necessary to determine MIC values under HPHT conditions (Sorbie and Laing 2004; Inches et al. 2007). In order to determine and compare the MIC values of inhibitors in geothermal fluids experimental methods are needed that allow the measurement of the inhibitor efficiency under HPHT conditions.

In this study we investigated a calcite inhibitor based on phosphorus free polycarboxylates with regard to its potential for geothermal application. This inhibitor was developed for calcium enriched industrial wastewater only. A static batch test system was established and evaluated applying the calcite scale inhibitor to a synthetic solution of calcium and bicarbonate. The MIC of this inhibitor was determined at HPHT conditions and compared with the MIC at ambient conditions monitoring the decrease in pH during precipitation. With these experiments it was intended to ascertain firstly if the established HPHT system and applied test method were suitable for the determination of scale inhibitor MIC and secondly to which extent the MIC under HPHT conditions differs from the MIC determined under ambient conditions.

2. MATERIALS AND METHODS

A batch reactor consisting of a stainless steel laboratory autoclave system (250 mL reaction chamber) with heater/stirrer and temperature control unit (Berghof GmbH, Eningen, Germany) was applied for the inhibitor efficiency experiments. The autoclave was equipped with a temperature sensor, an antimony solid phase pH-electrode, and a reference electrode. Both electrodes are especially designed to enable measurement conditions up to a pressure of 150 bar and a temperature of 125 °C (Kurt Schwabe Institut, Meinsberg, Germany). A picture of the autoclave setup is shown in Figure 1.



Figure 1: Laboratory autoclave setup including (from bottom to top) heater/stirrer, stainless steel autoclave in thermal insulating sheath, clamp, autoclave lid with electrodes, manometer and inlets for gas feed, liquid injection and temperature sensor.

Synthetic fluids were prepared by adding a NaHCO_3 -solution to a CaCl_2 -solution to result in final concentrations of Ca^{2+} and HCO_3^- of 200 mg/L and 305 mg/L, respectively (5 mM each). These concentrations are in the range of those known from the natural fluids exploited from the low enthalpy geothermal systems in Germany, i.e. the South German Molasse Basin and the Upper Rhine Graben (Schellschmidt et al. 2010, Stober et al. 2013, Saadat et al. 2010). In both regions problems in the geothermal facilities arise due to calcite scaling.

In a HPHT experiment the calcium chloride solution was heated to 120 °C within the autoclave. After reaching the temperature a pressure of 10 bar was applied by loading nitrogen into the autoclave. The inhibitor was always added to the sodium bicarbonate solution before the injection into the reactor. Injection was realized by using a stainless steel syringe and a high pressure syringe pump (Nexus 6000, Chemyx Inc., Stafford, Texas). The calcite precipitation started immediately after the injection. The decrease in pH value was monitored using a signal measuring device (LM2000, Kurt Schwabe Institut, Meinsberg, Germany) connected to a personal computer where all the data were recorded and analysed. After approximately 12 hours reaction time the autoclave was slowly cooled down to RT and the pressure was unloaded.

The experiments at ambient conditions were carried out at normal pressure and 30 °C. Since the room temperature could fluctuate between 20 and 25 degrees, the temperature of 30 °C was chosen in order to keep it constant without the necessity to cool the reactor. At these conditions the pH value of the solution is in the range of 8 to 8.5 and calcite precipitation occurs very slowly. Therefore, after injection of the sodium bicarbonate solution and 15 min equilibration time 0.1 mL of a 1 mol/L NaOH solution was added in order to elevate pH value and accelerate the precipitation. The mixture was allowed to react for at least 4 hours.

HPHT experiments started with injection of the NaHCO_3 /inhibitor-solution and experiments under ambient conditions with the addition of NaOH ($t = 0$). In all experiments the pH value was recorded and analysed over a time period of 240 minutes. ΔpH values were calculated by subtraction of the maximum pH value from the pH value at 240 min. The MIC was determined as the concentration of inhibitor that was necessary to reduce the change in pH to at least half the value obtained without inhibitor within the 4 hour time frame.

The applied calcite scale inhibitor was based on poly(carboxylate)s and poly(amino acids) (Niederrhein Chemie GmbH, Kevelaer, Germany). The concentration unit ppm refers to the volume ratio $\mu\text{L/L}$.

3. RESULTS AND DISCUSSION

During calcite precipitation carbonate ions are removed from the solution. Consequently, the regeneration of the carbonate-bicarbonate equilibrium leads to a release of protons and thereby lowers the pH. By measuring the decrease in pH it was aimed to quantify the calcite precipitation. This equilibrium itself is strongly pH dependent, so that calcite precipitation could also be accelerated by increasing the initial pH value.

After the calcium chloride solution within the autoclave reached HPHT conditions (10 bar, 120 °C) the pH equilibrated at a value between 8.7 and 9.2. With injection of sodium bicarbonate solution to the reactor the pH value of the fluid was then elevated by 0.8 to 1.2 units. In HPHT experiments this leads to a pH value higher than 9.5 and instant calcite precipitation so that the pH value decreases fast within the first few minutes. Typical pH curves are shown in Figure 2.

In the experiments under ambient conditions the pH increases to a value around 8.5 after addition of the bicarbonate solution. Under these conditions it takes several hours until calcite precipitation becomes detectable. Increasing the pH value to 9 reduced this initial time to less than 1 hour, whereas the equilibrium was reached between 1 and 4 hours of reaction time. Exemplary pH curves of the experiments under ambient conditions are shown in Figure 3.

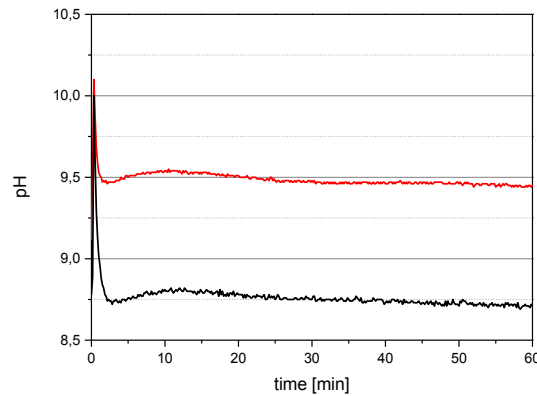


Figure 2: pH curves of HPHT experiments with different concentrations of scaling inhibitor (black: no inhibitor, red: 50 ppm) in dependence of reaction time.

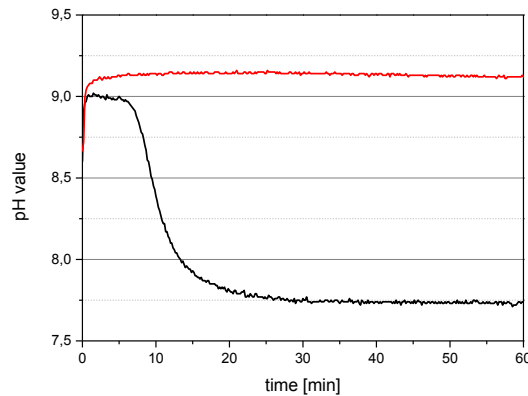


Figure 3: pH curves of experiments at ambient conditions with different concentrations of scaling inhibitor (black: no inhibitor, red: 10 ppm) in dependence of reaction time

The extent of precipitation was represented by the decrease in pH (ΔpH). HPHT experiments were carried out with 0, 10, 25, 50, and 100 ppm inhibitor. The decrease of the pH value due to calcite precipitation was highest when no inhibitor was added. The absolute value of ΔpH decreased with increasing concentration of inhibitor indicating that calcite precipitation was indeed inhibited. However, a sharp drop of the pH instantly after injecting the bicarbonate solution in all HPHT experiments as well as a ΔpH of -0.4 at a concentration of the inhibitor of 100 ppm showed that the inhibition was always incomplete. Since the precipitation started immediately after the injection it could have interfered with the equilibration of the pH sensor after increasing the pH due to the injection. In that case the decrease of pH could have been even more pronounced than actually measured and a systematic error of the measurements has to be taken into account. However, in this series the tendency of the ΔpH values over the experiments were of importance rather than the single values. Figure 4 shows the dependence of ΔpH from the inhibitor concentration.

Within the HPHT series the MIC was determined as 25 ppm. It became evident that very high concentrations of the inhibitor are required to reach an inhibition efficiency higher than 75%. An acceptable level of inhibition (usually higher than 90%, Graham et al. 2006) by applying an economically efficient amount of inhibitor seems not feasible with the tested inhibitor at HPHT conditions.

The inhibitor efficiency tests at ambient conditions were carried out applying inhibitor concentrations of 0, 2, 5, and 10 ppm. Here, the MIC was determined as 2 ppm, being lower by more than one order of magnitude compared to the HPHT experiments. Figure 5 shows the dependence of ΔpH from the inhibitor concentration. Under ambient conditions the efficiency of the inhibitor is excellent. This result was expected since the inhibitor is already used as a calcite scaling inhibitor for industrial wastewater. However, it is remarkable by which extent the MIC under HPHT conditions differs from the MIC determined under ambient

conditions. The difference in MIC confirms the necessity to determine MIC values under HPHT conditions, when comparing the efficiency of scale inhibitors designed for geothermal application.

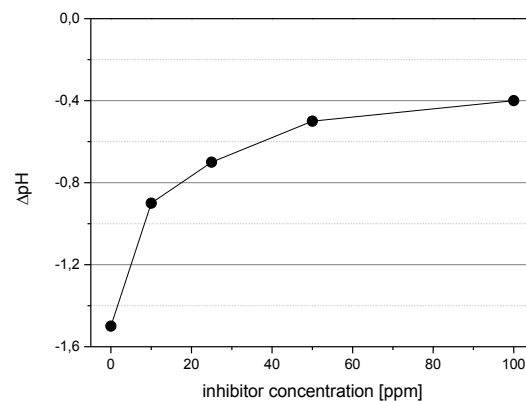


Figure 4: Decrease of pH (ΔpH) during precipitation in dependence of the inhibitor concentration in HPHT experiments.

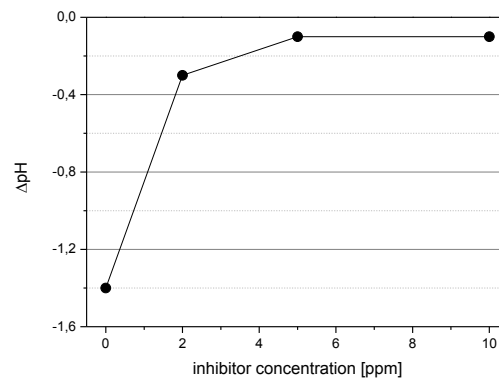


Figure 5: Decrease of pH (ΔpH) during precipitation in dependence of the inhibitor concentration in experiments at ambient conditions.

In order to explain the difference in MIC between the two experiment series, degradation of the inhibitor under HPHT conditions has to be taken into account. The thermal and hydrolytic stability of the inhibitor needs to be investigated. The time frame of this stability (and simultaneously inhibition performance) is of particular interest for environmental friendly inhibitors which are considered to be biodegradable. However, the influence of shifted equilibria due to higher temperature and pH value is expected to dominate over degradation effects within 4 hours of reaction time.

4. CONCLUSION

The results of the inhibition tests clearly show a decrease in the efficiency of the inhibitor at HPHT conditions compared with ambient conditions and thus demonstrate the requirement of HPHT tests. The experiments proved that the applied autoclave system was suitable for inhibitor efficiency tests at HPHT conditions. A robust testing system was established being able to determine the MIC of environmental-friendly scaling inhibitors under conditions prevailing in the respective geothermal reservoir. This system enables enhanced evaluating and comparing of scaling inhibitors for geothermal purposes.

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