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Experimental Fluid-Rock Interaction Simulating Reinjection of Cooling Tower Condensate in Andesitic-hosted Reservoir of Southern Negros Geothermal Field, Philippines

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ABSTRACT

The fluid-rock interaction of geothermal steam condensate and andesitic rock was studied experimentally at 230^{o}C and 20bars using a high temperature-pressure flow-through simulator. The experiment was designed to reproduce the reinjection of cooling tower condensate into the andesitic reservoir of Southern Negros Geothermal Field, Philippines. Effluent fluid samples were analyzed using IC and ICP-OES while rock samples were analyzed using XRD and SEM. Under geothermal conditions, the rapid equilibration of quartz increased SiO2 concentrations in reacted fluid up to 400mg/kg. Quartz crystals and feldspars are largely dissolved in the most reacted rock. The deposition of secondary mineral anhydrite, chlorite, and zeolites was observed in the run products. These occur mainly in the most reacted rock. The mineral deposition caused a drop in Ca, SO4, and Mg concentrations in the effluents and the buffering of Na and Al. Fluid pH rose slowly from 7 to 9 but did not reach a steady state indicating that andesite-fluid equilibrium was not achieved. The results of the fluid-rock interaction experiment afford understanding of the alteration processes occurring in the condensate fluid-injected reservoir and the permeability improvement of TWD with time.

1. INTRODUCTION

In 2011, the Southern Negros geothermal field began disposing cooling tower condensate through deep reinjection well TWD. In just a few months of injection, TWD injectivity increased at an average rate of 0.3kg/s per day at 1MPag WHP. In order to gain understanding on the nature and extent fluid mineral interactions contributing to the observed permeability increase, a laboratory simulation experiment was conducted simulating the travel of condensate fluid from the injection well to the identified well formation at 230^{o}C and 20bars (2MPag). The study is important to determine whether or not the technique can be extended to low permeability wells within Southern Negros geothermal field.

This report describes the method and the analytical techniques used in the experiment. The results obtained are presented and discussed with the aim of understanding the hydrogeochemical processes associated with TWD permeability improvement with time.

2. METHODOLOGY

2.1 Experimental

The flow through simulation was conducted using a plug-type flow through simulator capable of operating in geothermal conditions reaching 400^{o}C and 500 bars. Figure 1 shows the schematic diagram and photograph of the simulator. A computer-controlled double–piston metering pump allows fluid to flow through the system at a rate of 0.001-15ml/min.

Prior to the start of the experiment, oxygen was removed from the condensate fluid by bubbling with nitrogen gas for about 45 minutes. This process prevents unwanted oxidation reactions of Si and S. Likewise, the Ti-separator was emptied, cleaned and vacuumed to remove air in the tube connecting the Ti-separator. The separator was then filled with condensate fluid at a rate of 15ml/min using the double-piston metering pump.

For the simulation study, 27.7g of crushed drill core with 0.5-1mm sizes were used. The condensate fluid is allowed to flow through the rock cell containing the sample contained within an aluminum-lined externally-heated pressure vessel. The temperature inside the vessel was measured by a thermocouple located on top of the reaction cell while a computer controlled pressure regulator maintained the pressure in the system. Effluents were collected in an airtight syringe inserted into the back pressure regulator and analyzed using ICP-OES, IC, and UV-Vis. The experiment was kept running for 42 days, initially at room condition (27^{o}C), then stepped up to reservoir conditions at 230^{o}C and 20bars with flowing fluid rate of 1ml/hr. The flow rate was later reduced to 0.5ml. After the experiment, the run products were removed for SEM and EDX mineral identification.

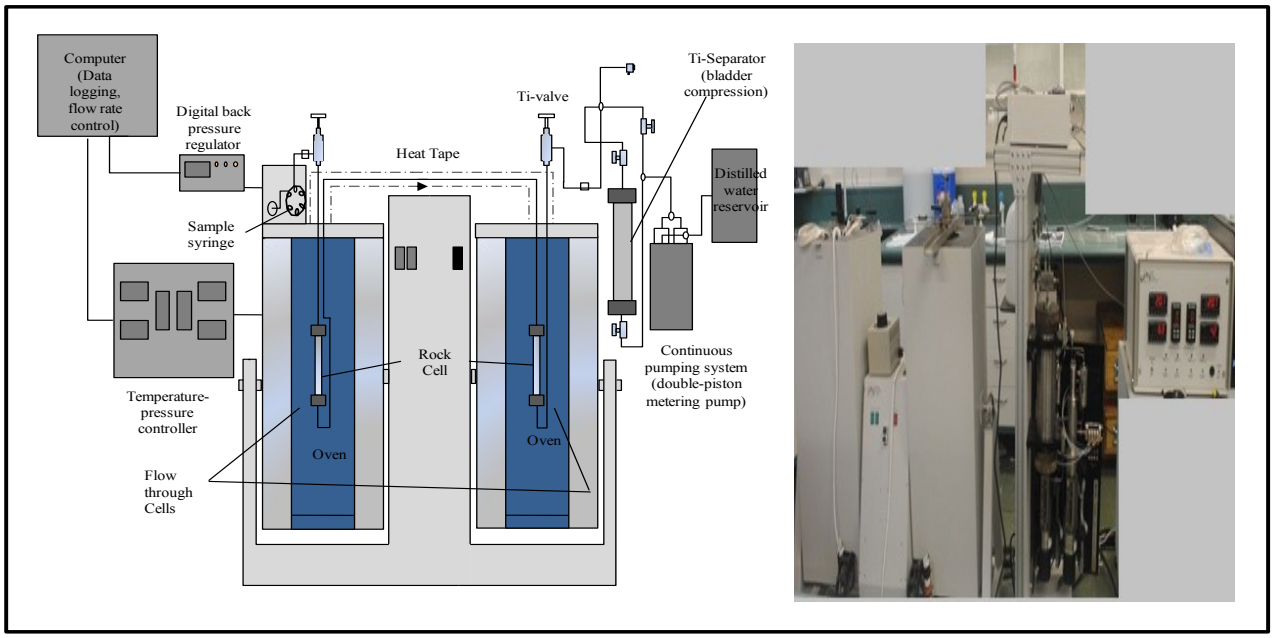


Figure1. Schematic diagram (a) and photograph (b) of dual cell flow through simulator

2.1 Fluid Chemistry

Table 1 presents the chemical composition of the fluid. The elemental concentrations in the fluid are generally low except for sulfate which was significantly high because of condensed H_2S resulting from the preferential partitioning of the gas in geothermal steam (Giggenbach, 1980).

Table 1. Chemistry of Cooling Tower Condesate

Lab Measurement	Values
pH	7.80
Temperature	22°C
Cations	mg/L
	<0.15
As	<0.015
Ca	1.1140
Cu	0.0426
Fe	<0.08
K	<0.90
Li	<0.01
Sr	<0.003
Mg	0.1001
Mn	<0.007
Na	<2.50
S (total)	69.3
Anions	
SO_4	82
Cl	0.8400
Undissociated	
SiO_2	0.79
B	1.34
Others	
Biocides (Bulab 8057, Bulab 1174, Bulab 8054)	

2.2 Andesite Composition

Using X-ray diffraction Spectrometer, the mineral and chemical composition of the rock sample was defined. The XRD analysis revealed presence of quartz (40%), calcite (20%), feldspar (albite-20%), clinochlorite (15%), and pyroxene (5%) in (Figure 2).

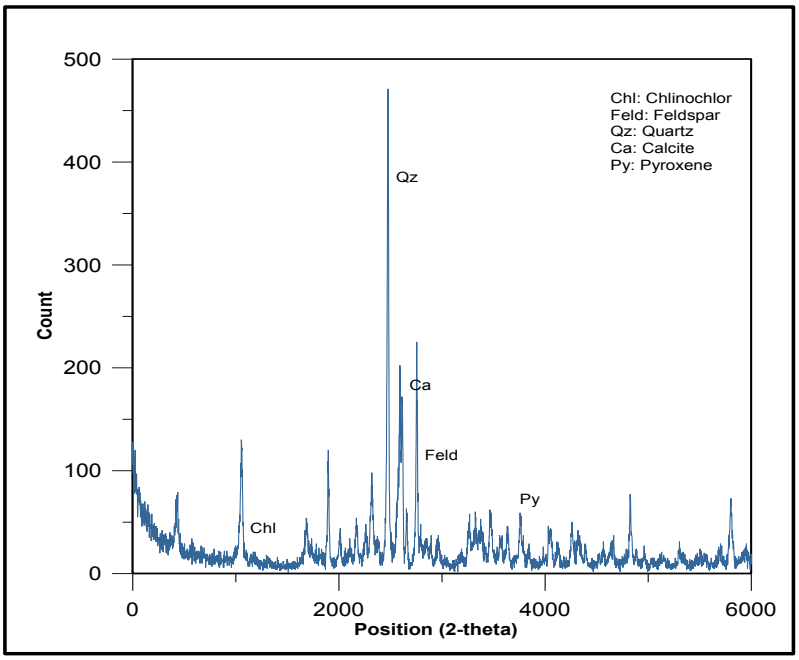


Figure 2. XRD Analysis of the Andesitic Rock

3. RESULTS AND DISCUSSION

Figure 3a and 3b presents fluid chemistry with pH, temperature and time. At room temperature, fluid pH increased from 7.8 to 8.31 and measurable concentrations of Ca, Mg, and Sr were obtained. This is due to dissolution of calcite (Equation 1). Calcite dissolution consumes protons which accounts for the pH increase in the fluid. Sr and Mg which are normally bound to Ca in nature are released to the solution as calcite is dissolved.

$$CaCO_3 + H^+ \Longrightarrow Ca^{+2} + HCO^{3-} \quad (1)$$

At elevated temperature of 230^{o}C, quartz is spontaneously dissolved (Equation 2) until its equilibration concentration of 400mg/L. Consequently, Na and K were quickly released into the solution resulting to increased Na and K levels in the effluent samples (Equation 3).

$$SiO_2 + H_2O \Longrightarrow H_2SiO_4 \quad (2)$$

$$\text{Na or K feldspar} + 4H_2O + 4H^+ \Longrightarrow Na^+ + Al^{+3} + 3H_4SiO_4 \quad (3)$$

The dissolution of quartz and feldspar are evident in the SEM photomicrographs taken for the most reacted rock as shown in Figure 4b. Feldspar and quartz crystals were totally dissolved in the most reacted rock, forming vugs and void spaces on the rock matrix. This is not apparent in the least reacted rocks (Figure 4c and 4d) wherein the SEM images resembled those of the unaltered rock (Figure 4a).

SEM photomicrographs and EDX analysis detected secondary mineral anhydrite ($CaSO_4$) (Figure 5). The mineral is formed as calcium from the host rock reacts with SO_4 in the condensate fluid (Equation 4). SEM analysis showed extensive deposition of the anhydrite crystals in the most reacted rocks. The deposition occurred instantaneously as the temperature is increased. The solution remained unsaturated until the end of the experiment suggesting that the Ca has been consumed in the single precipitation reaction (Brantley, 2008). However, the rate of formation of the mineral anhydrite is still lower compared to the rate of dissolution of silica as shown in Figure 3c.

$$2Ca^{+2} + SO_4 \Longrightarrow CaSO_4 + Ca^{+2} \quad (4)$$

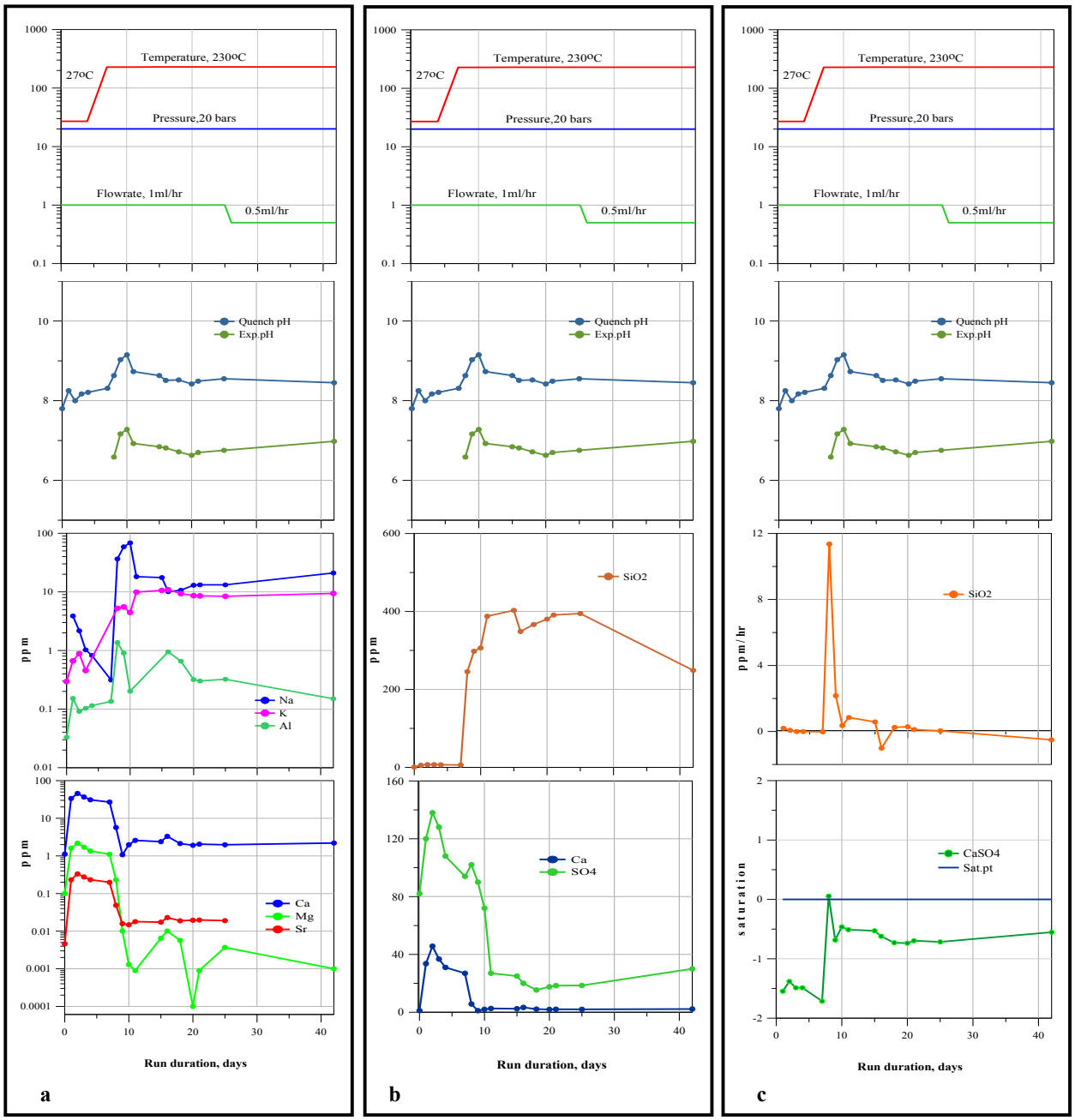


Figure 3. (a) and (b) The relationship of Na, K, Al ,Ca, Mg, Sr, Si, and SO4 concentration in the reacted fluid with pH, temperature, and time; and (c) the rate of solubility of SiO2 and saturation of CaSO4 as anhydrite.

Precipitation of Na-Ca bearing aluminosilicates, most likely plagioclase, was also observed in SEM photomicrographs. This caused a gradual decline in Na concentration and pH values in the fluid as described in Equation 5. A good growth of smectites, chlorites and zeolites were also found in the SEM photomicrographs. The mineralogy is in reasonable agreement with geothermal alterations of andesitic rocks at 230°C (Reyes, 1990).

$$xNa^{++}\ \ (1\text{-}x)Ca^{+2}\ +\ Al^{+3} + 3SiO_2 + H2O \Longrightarrow (Nax,Ca1\text{-}x)AlSiO_3O_8 + 4H^{+} \qquad (5)$$

Fe concentration in the effluent remained low throughout the duration of the experiment suggesting that any iron released to the solution by lower temperature Mg-Fe bearing silicates is quickly immobilized to high temperature Fe bearing silicates such as plagioclase or chlorite (Figure 4d). In the same way, Al is immobilized in the primary and secondary mineral throughout the experiment.

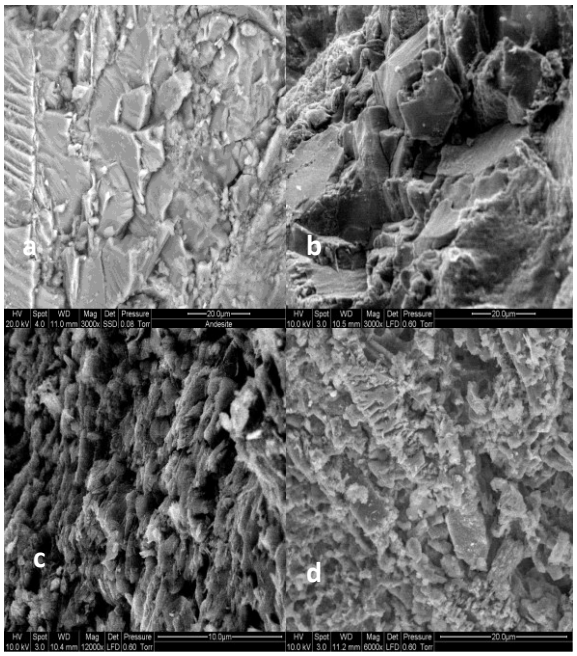


Figure 4. Scanning electron photomicrograph of the (a) unaltered andesite (b) most reacted (c) mid-reacted rock (d) least reacted at 230^{o}C and 20 bars.

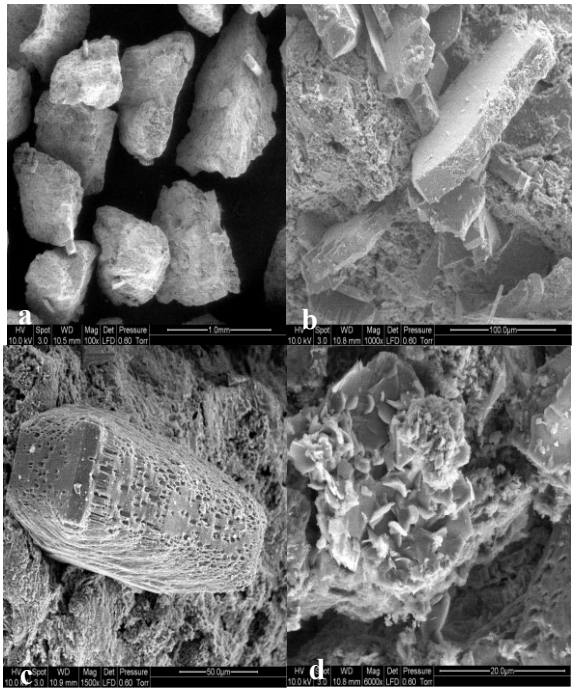


Figure 5. Scanning electron photomicrograph of the secondary mineral anhydrite (a)100x (b)800x (c)1200x and chlorite (d) formed at 230^{o}C and 20 bars

4. CONCLUSION

The experiment successfully elucidates the hydrothermal processes occurring in a geothermal steam condensate-andesite equilibria not accurately described in mathematical models. Based on the study, TWD fluid-mineral equilibria involve both dissolution of silica in the silicic rock and deposition of the secondary mineral anhydrite, with dissolution as the predominant process. Dissolution of silica is extensively occurred at the surface where the fluid passes through creating vugs, fractures, and void spaces on the rock. This accounts for the observed permeability improvement in well TWD.

The study conducted further showed that injection of condensate fluid can indeed improve well permeability. And under similar conditions, as in the case of Southern Negros Geothermal Field with similar rock formation, the technique may be extended particularly for low permeability wells.

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