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Stimuli-Responsive/Rheoreversible Hydraulic Fracturing Fluids for Enhanced Geothermal Systems

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ABSTRACT

Cost-effective and safe creation of high-permeability reservoirs inside deep crystalline bedrock is the primary challenge for the application of enhanced geothermal systems (EGS). Current reservoir stimulation processes entail adverse environmental impacts and substantial economic costs due to the utilization of extremely large volumes of water and a concomitant high amount of chemicals which can potentially contaminate deep aquifers. In this work, we report an environmentally benign, CO_2-activated, rheoreversible fracturing fluid that significantly enhances rock permeability at effective stress orders of magnitude lower than current technology. This novel hydraulic fracturing technique dramatically reduces water usage and the environmental impact of fracturing practices, potentially making geothermal energy production cost-effective and cleaner.

1. INTRODUCTION

Enhanced geothermal systems (EGS) are a promising alternative for energy production for the United States and worldwide (Blackwell et al., 2006; Duffield and Sass, 2003). With its negligible CO_2 emissions, EGS can help to mitigate climate change. However, this renewable energy alternative faces challenges. To our knowledge, no prior EGS project has sustained production at rates greater than 50% of what is needed for economic viability. The primary limitation for commercial EGS is the lack of suitable technologies to cost-effectively create high-permeability reservoirs from impermeable crystalline rock within the 900–4000 m depth in a temperature range of 150 - 400 ºC (Duffield and Sass, 2003; Pruess, 2006).

Recent advances in hydraulic fracturing techniques and horizontal drilling implemented first on unconventional oil and gas exploitation (Kargbo et al., 2010; Kerr, 2010; Tester, 2006) represented a key driver for EGS development. However, some of the fluid components used in hydraulic fracturing for recovery of tight oil and gas cannot be employed for EGS due to the high subsurface temperatures. First, the macropolymers developed to modify fluid rheology in oil/gas standard hydraulic fracturing degrade at geothermal temperatures above 150°C. Second, these macropolymers are difficult to remove from the formation after fracture creation/propagation. The so called "fracture skin", which is the residue of injected polymers and drilling mud not removed during fracture cleanup, limits the efficiency of hydraulic fracturing because it decreases flow rates and heat transfer in EGS. In addition, the most challenging issue is the large volume of wastewater generated, which may include radioactive and toxic elements extracted at EGS temperatures (150 °C – 380 °C), and that needs to be treated and disposed of. The contamination of soil and drinking water resources have raised both environmental and economic concerns (Tester, 2006). Thus, to enhance the economic viability of EGS, the development of more effective and environment-friendly hydraulic fracturing fluids is in urgent need.

The objective of this work is to report a novel CO_2-activated hydraulic fracturing fluid for reservoir stimulation. This fluid is environmentally friendly and potentially recyclable due to its rheoreversible properties. The fluid can undergo a chemically-induced large and rapid volume expansion triggered by CO_2 at temperatures relevant for reservoir stimulation in EGS. The volume expansion generates an exceptionally large compression and mechanical stress in fracture networks of highly impermeable rock propagating fractures at effective stress orders of magnitude lower than current technology.

2. MATERIALS AND METHODS

To select a polymer that can react with CO_2 in aqueous media and transition to a volume-expanding viscous hydrogel at conditions found in EGS, four polymers (from Gelest Inc. and Sigma Aldrich) were tested over a range of high pressure (HP) and high temperature (HT) conditions. The tested polymers include 3 [(2-Aminoethyl)amino] propylmethoxysiloxane dimethylsiloxane copolymer with 2–4% amino content, 3 aminopropylmethylsiloxane-dimethylsiloxane copolymer with 6–7% amino content, 3 aminopropyl-terminated polydimethylsiloxane with 3.2–3.8% amino content, and poly(allylamine) solution (referred as PAA hereafter, average MW ~17,000, 20 wt% in H_2O). These polymers solutions were diluted with deionized water (DIW) about 20 times their original concentration and the diluted solutions were reacted with CO_2 at different temperatures and pressures to learn about their potential volume expansion and how this increase in volume could be used in a confined environment to create/propagate fractures. Volume-expansion experiments were conducted in a pressure view cell equipped with sapphire windows. Wide ranges of pressure (110-300 atm) and temperature (60-400 °C) were tested for polymer volume expansion. Hydraulic fracturing experiments were conducted at 300 °C and 333 atm with rock cores collected from an EGS field site using the best polymer candidate. This selection was based on the volume expansion properties of the polymer solution upon reaction with CO_2.

2.1 Measurements of CO_2-Activated Volume Expansion of Selected Polymers

The experimental system for volume expansion measurements consisted of a HP cell (internal volume: 11 mL), a HP generator, a syringe pump, a camera, and a monitor (Figure 1). The HP cell was covered by insulation and was heated using a hot plate. The temperature was monitored using a thermocouple inside the cell and connected to a temperature controller. The pressure of the cell was monitored using two pressure gauges, which were connected to the HP generator and the HP cell. A stir bar was placed inside the HP cell to mix the polymer solution. The HP cell was equipped with three sapphire windows, one on the top and two on the opposite sides to allow the camera to monitor the phase behavior of the aqueous polymer solutions after CO_2 injection.

Before adding a polymer aqueous solution to the HP cell, the cell was heated to the desired temperature. The diluted polymer solution was then added to the HP cell to fill 40–50% of total cell volume. After the temperature reached equilibrium, CO_2 was injected into the cell from a syringe pump at 110 atm. The CO_2 pressure was increased stepwise every 110 atm until the pressure in the cell reached 300 atm. After equilibrating the system at 300 atm for 10 minutes, the heat was turned off. As the temperature decreased to below 200°C, the venting valve connected to the pressure cell was slowly opened and the reacted polymer solution was collected into a 20-mL vial for further analysis.

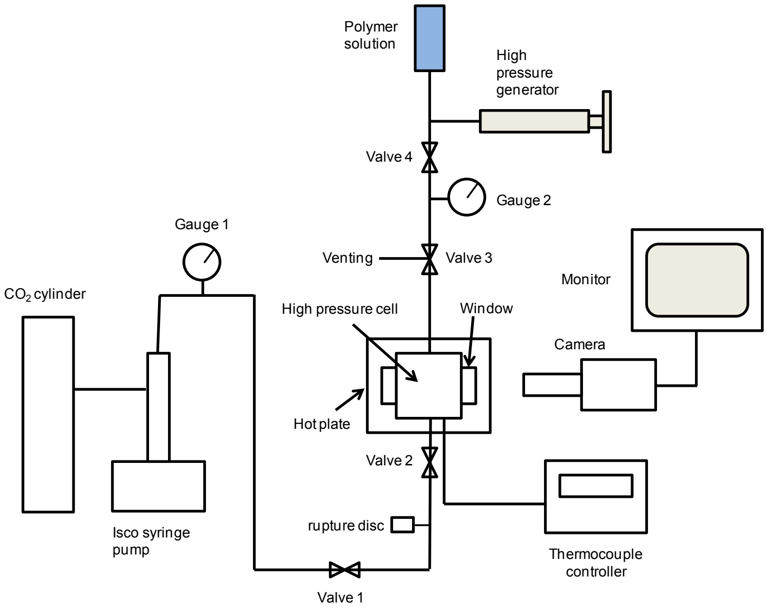

Figure 1. Schematic diagram of high P-T experimental setup for fluid volume expansion studies.

2.2 Hydraulic Fracking Experiments

Laboratory-scale hydraulic fracturing experiments were performed using rock cores from the Coso geothermal field (~490 m depth) in California. Rock samples consisted of Mesozoic diorite metamorphosed to greenschist faces. The raw sample was cut into small cylindrical rock cores (1.59 cm diameter and 5.08 cm length). A centered hole (0.32 cm diameter and 2.54 cm deep) was drilled from the top of the cylinder. Stainless steel tubing was introduced 0.64 cm into the hole leaving an internal dead volume of ~200 µL in the rock core. The connection was sealed with Portland cement slurry (water-to-cement ratio = 0.4), and was cured for over a week. The cement sealing was to prevent any communication between the external fluid (water) used to apply the desired confining pressure and the internal dead volume in the rock core during the course of the experiment.

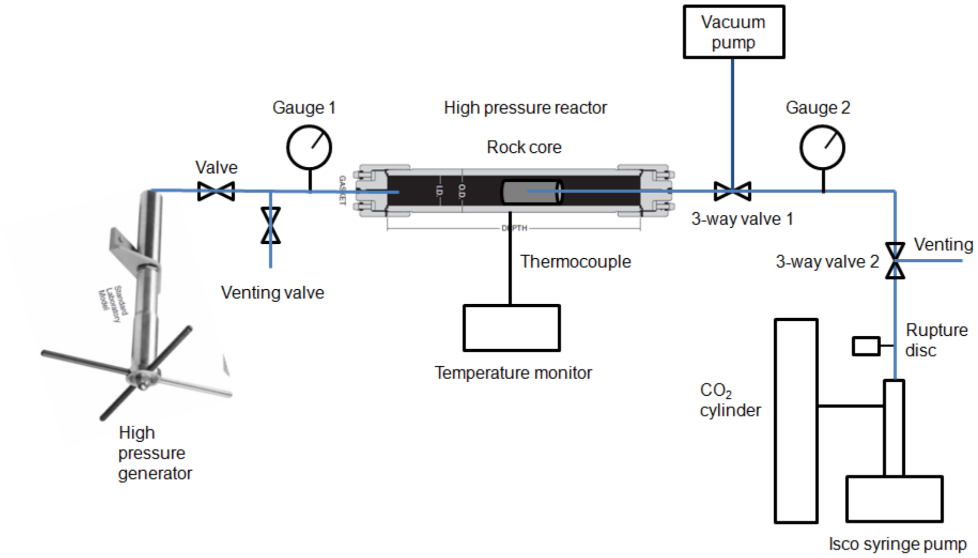

Figure 2. Schematic diagram for the hydraulic fracturing experimental setup.

The hydraulic fracturing experiment was conducted with a HP flow reactor (Figure 2).The cemented rock core (total diameter ~2.4 cm) was introduced into the HP reactor. A 3-way valve was used to deliver polymer solution or CO_2. The temperature of the reactor was controlled with heating tape, two thermocouples, and two controllers. After the target temperature was reached (300°C), water was injected into the reactor using a pump to increase confining pressure. The confining pressure was first increased to 68 atm, immediately followed by introducing 200 µL of 1 wt% PAA solution and 68 atm of CO_2 inside the core sample via the three-way valve. Then, the confining pressure and rock core pressure were increased step by step at increments of 6.8 atm (100 psi) until reaching a target pressure of 333 atm. Then, at a constant confining pressure of 333 atm, the rock core pressure was gradually increased from 333 atm in intervals of 1 atm until we observed an increase in the confining pressure equalizing the internal rock core pressure. This was indication that there was communication between the internal rock core and the external confining fluid (water). Finally, the system was slowly depressurized and cooled before the rock core was removed from the pressure vessel. For comparison, a control fracturing experiment using DIW/CO_2 at identical conditions was performed. The rock cores retrieved from the HP vessel after fracturing experiments were subjected to a CO_2 leakage test at 5 atm to determine the existence of fractures.

3. RESULTS AND DISCUSSION

3.1 Rheological Property Changes of Polymer under EGS Conditions

In this work four polymers were proposed as potential candidates for reversible CO_2-expanding hydrogels at geothermal temperatures. Aqueous solutions of PAA were the only polymer solutions that successfully formed a viscous hydrogel with corresponding volume expansions in the range of 80–150% during their reaction with CO_2 (Figure 3).

Temperature plays an important role in controlling the rheology of aqueous PAA-CO_2 fluid system. At 58°C and 127°C, upon CO_2 introduction at 110 atm, the volume expansion of PAA solution was not obvious (Figure 3). As CO_2 pressure increased to 300 atm, the volume increased slightly. At 196 and 265°C, ~75 % of volume expansion was observed upon CO_2 injection at 110 atm. As CO_2 pressure increased further, the PAA solution volume increased up to 85% (300 atm). In the case of 333°C, the volume increase of the PAA solution was 100% and 150% when CO_2 pressure was 110 and 200 atm, respectively. Similar volume expansion was observed at 402°C. It is worth mentioning that (1) at 333 °C volume expansion was observed only a few seconds after introducing CO_2 at 110 (or 170 atm for 402 °C), and (2) a corresponding increase in the viscosity of the fluid was observed. Viscosity increase was obvious at low temperature (58 to 265°C) when fluid flow was diminished after CO_2 introduction. At even higher temperatures, the PAA solution transitioned to a hydrogel upon CO_2 injection. These results suggest that CO_2 pressure can be employed to precisely control the rheology of PAA solutions, with the potential to create additional stress in confined environments such as during geothermal reservoir stimulation.

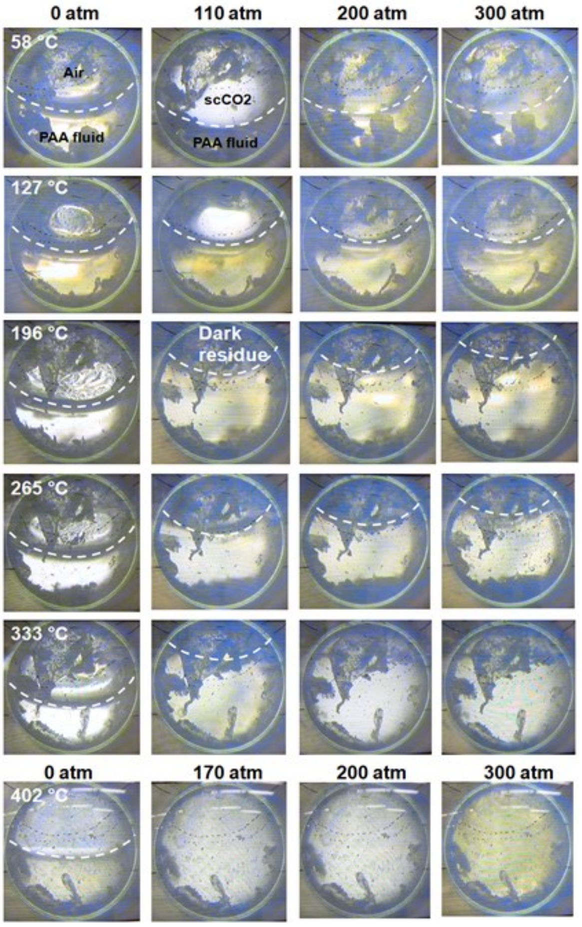

Figure 3. Volume changes of PAA solution reacted with CO_2 as a function of temperature (58–402°C) and CO_2 pressure (0–300 atm). CO_2 pressure was increased from 110 to 300 atm, except for the experiment at 402°C (170–300 atm), where the initial pressure of PAA solution at 402°C was 150 atm before CO_2 injection. The dashed lines indicate the boundary between PAA fluid and supercritical CO_2 (after CO_2 injection) or air/water vapor (before CO_2 injection). The window is partially covered by some residual PAA.

To determine the rheoreversibility of PAA solution, a sequential volume expansion experiment was conducted with 1% PAA solution at 330°C and 300 atm. After each expansion experiment, the PAA solution was collected and reused for the next expansion experiment. The result indicates that PAA solution showed volume expansions of 80%, 85% and 60% after the first, second, and third experiments. The formation of hydrogel and volume expansion was observed when the pressure was as low as 150 atm for all three cases. A control experiment conducted with only DIW with no polymer produced no volume expansion. These results illustrate the rheoreversibility of PAA-CO_2 fluid. Thus, PAA can be recycled from a gel to an aqueous solution of PAA with relatively low impact on its rheological properties. This is a key feature of this new fracturing fluid for the following two reasons. First, the rheoreversibility of PAA-CO_2 fluid indicates that PAA can be removed as an aqueous solution after reservoir depletion and reused, thus dramatically reducing potential environmental impacts and costs during EGS reservoir stimulation. The traditional processes for hydraulic fracturing generate millions of gallons of wastewater with a large number of chemicals, including hydrocarbons such as benzene, inorganic acids, xantham gum, ethylene glycol, isopropanol, citric acid, N,N dimethylformamide, and ammonium perfulfate. Second, the new hydraulic fracturing fluid would accelerate energy production by increasing flow rates and heat transfer due to the additional stress that can be created confined environments by volume expansion.

To identify the reaction mechanisms for the CO_2-induced gel formation processes, in situ HP MAS-NMR analysis was conducted. The result indicates that, similar to the results from ex situ study at room temperature in organic solvents reported previously (Carretti et al., 2003), the reaction profile for gel formation is initiated when CO_2 reacts with the pendent amines in PAA to initially form carbamate salts, which then condense to form the corresponding urea, cross-linking the polymer chains. It is important to note that PAA has been previously reported to show no volume expansion in aqueous solutions unlike the case of organic solvents. Nevertheless, in this work it is shown for the first time the CO_2–triggered volume expansion of diluted PAA aqueous solutions at temperature.

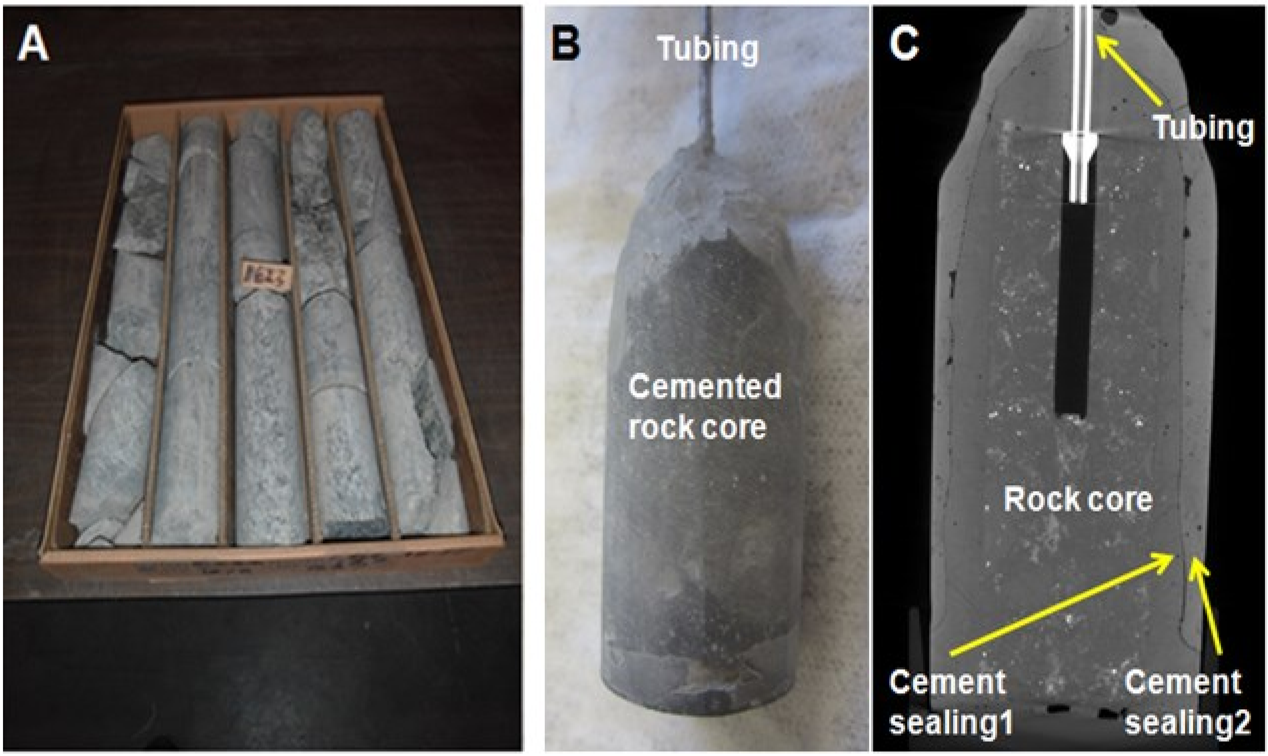

Figure 4. Left: Diorite samples from Coso EGS reservoir. Middle and right: Rock core/cement shell picture and X-ray micrograph showing no pre-existing fractures and the internal orifice to inject the fracturing fluid via 1/16" stainless steel tubing.

The discovery of this new rheoreversible hydraulic fracturing fluid is significant. It is the first time that a CO_2-triggered expanding hydrogel was obtained. More significantly, this hydrogel was stable at temperatures as high as 400 ºC. US EGS temperatures range between 160 ºC and 380 ºC. Our fluids then represent excellent candidates for reservoir stimulation in EGS since they reproducibly form hydrogels in a temperature range of 196–402°C and CO_2 pressures between 110–300 atm. The hydrogels formed with a concomitant volume expansion, which makes it an excellent hydraulic fracturing fluid in EGS, as will be demonstrated below.

3.2 Fracturing Experiments

Three rock cores from the Coso geothermal field were subjected to hydraulic fracturing experiments at 300°C and 333 atm using 1 wt% PAA and CO_2 (Coso 1-6 and Coso 1-8, duplicate experiments under the same experimental conditions), and DIW and CO_2 (Coso 1-7, serving as a control experiment). XMT analysis obtained on the total volumes of the rock cores prior to the experiment indicate that there was no preexisting fractures at the maximum resolution of the instrument (XMT image voxel size = 30-35 µm, Figure 4). Experiments performed on Coso 1-6 and Coso 1-8 employing 200 µL of 1 wt% aqueous PAA consistently showed fracture creation and propagation with resulting communication (fluid flow) between the internal fluid injected in in the rock core (aqueous PAA- CO_2) and the external confining fluid. Furthermore, the effective pressure (differential pressure at which the internal core pressure and the confining pressure equilibrated) was only 7 and 9 atm, respectively. After the rock samples were retrieved from the reactor, leaking tests were conducted by injecting CO_2 into the rock core at 5 atm to verify the presence of fractures connected to the external surface of the sample. CO_2 leakage was immediate and profuse on these two rock cores (Figure 5). The permeability estimated from flowing deionized water at room temperature and at a pressure of 5 atm was estimated in 200 mD when normalized to the volume of the rock sample. For the control experiment with core sample Coso 1-7 carried out at identical HP/HT conditions, no communication between internal and external fluids was observed even at differential pressures as high as 130 atm (Figure 5). PAA-CO_2 fluid generated fractures on this highly impermeable rock samples due to CO_2-induced volume expansion in a confined environment. Thus, in this work, it was successfully demonstrated that reproducible hydraulic fracturing at significantly lower effective stress can be performed at the lab scale, while conventional fluids were not able to create fractures at considerable higher pressures.

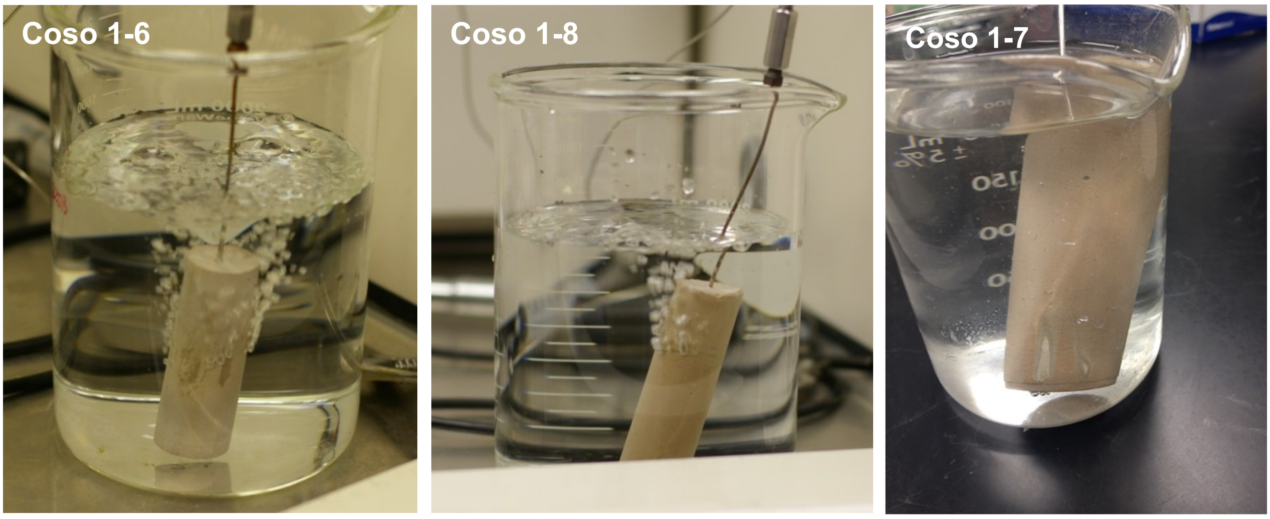

Figure 5. Pictures of CO_2 leakage experiment at ~5 atm CO_2 pressure. CO_2 bubbling from the rock surface was observed from the rock cores Coso 1-6 and Coso 1-8 after hydraulic fracturing experiment with 1 wt.% PAA and CO_2. The control experiment H_2O/CO_2 under identical conditions did not show fracture propagation even at differential pressures as high as 130 atm.

It is noteworthy to mention that the Coso geothermal field samples used in this work are mainly diorite rock which is one of the strongest rocks with compressive strengths in the range of 1500-2000 atm (Berkman, 2001; Davatzes and Hickman, 2006). Hydrated Portland cement has compressive strength of ~ 350 atm which, although lower than diorite, is still higher than most sedimentary rocks (Berkman, 2001; Guettala and Mezghiche, 2011). Therefore, the reproducible creation of fracture networks in Portland cement sealed Coso rock by PAA-CO_2 fluid indicates the exceptional potential of this fluid technology to increase reservoir permeability and enable the feasibility of EGS.

4. CONCLUSIONS

This work reports a hydraulic fracturing fluid that undergoes a large and fast volume expansion triggered by CO_2 at temperatures relevant for reservoir stimulation in EGS. The volume expansion will create a significantly large mechanical stress in the confined environments of the fracture networks and thus aid to the hydraulic pressures introduced enhancing, as a result, reservoir stimulation. This was demonstrated by performing high pressure/temperature experiments that simulated reservoir stimulation conditions on actual EGS reservoir samples. Fracture creation/propagation with the corresponding permeability enhancement was successfully achieved with minimum effective stress (7-9 atm). This environmentally benign, CO_2-activated, rheoreversible fracturing fluid significantly enhances rock permeability at effective stress orders of magnitude lower than current technology. This novel technology will dramatically reduce water usage and the environmental impact of fracturing practices, making geothermal energy production cost-effective and cleaner.

5. ACKNOWLEDGEMENTS

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