Environmentally Friendly, Rheoreversible, Hydraulic-Fracturing Fluids for Enhanced Geothermal Systems

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Abstract

Cost-effective creation of high-permeability reservoirs inside deep crystalline bedrock is the primary challenge for the feasibility of enhanced geothermal systems (EGS). Current reservoir stimulation entails adverse environmental impacts and substantial economic costs due to the utilization of large volumes of water “doped” with chemicals including rheology modifiers, scale and corrosion inhibitors, biocides, friction reducers among others where, typically, little or no information of composition and toxicity is disclosed. An environmentally benign, CO₂-activated, rheoreversible fracturing fluid has recently been developed that significantly enhances rock permeability at effective stress considerably lower than current technology based on laboratory-scale tests. In the present work we evaluate the potential of this novel fracturing fluid for application at geothermal sites under different chemical and geomechanical conditions, by performing laboratory-scale fracturing experiments with different rock sources under different confining pressures, temperatures, and pH environments. The results demonstrate that CO₂-reactive aqueous solutions of environmentally amenable Polyallylamine (PAA) represent a highly versatile fracturing fluid technology. This fracturing fluid consistently and reproducibly creates/propagates fracture networks through highly impermeable crystalline rock from Coso EGS and Newberry EGS sites at significantly lower effective stress as compared to conventional fracturing fluids. In addition, permeability was significantly enhanced (several orders of magnitude). This was evident in all laboratory-scale experiments, including variable rock source/type, operation pressure and temperature (over the entire range for EGS applications), as well as over a wide range of formation-water pH values. This effective, versatile, and environmentally- friendly fracturing fluid technology represents a significant advancement

39 compared to industrially available fracturing fluids for cost-effective and competitive geothermal
40 energy production.

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42 **Keywords:** Environmentally-friendly, rheoreversible, fracturing fluid, expansion, enhanced
43 geothermal systems

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1. Introduction

Enhanced geothermal systems (EGS) are considered a promising alternative for energy production for the United States and worldwide.^{1,2} With its negligible CO₂ 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.² The primary limitation for commercial EGS is the lacking 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 °C.^{2,3}

Recent advances in hydraulic fracturing techniques and horizontal drilling represent a key driver for EGS and subsurface energy development, in general. As conventionally recoverable resources decline, hydraulic fracturing in unconventional oil and gas exploitation has been implemented in over 52,000 oil and gas wells across the U.S.^{4,6} However, the fracturing fluids used in the oil and gas industry are problematic for EGS. First, the macropolymers developed to modify fluid rheology in oil/gas standard hydraulic fracturing may not be applicable at geothermal temperature ranges (150-400°C) due to their thermal decay.⁷⁻⁹ Second, these macropolymers are difficult to remove from the formation after fracture creation. The so called “fracture skin”, which is the residue of injected polymers and drilling mud not removed during fracture cleanup, limits effectiveness of hydraulic fracturing, because it decreases flow rates and heat transfer in EGS. There is also increasing concern over induced seismicity potential and how it may be associated with reservoir stimulation practices.^{6, 10} In addition, the most challenging issue is the large volumes of water used and wastewater generated during hydraulic fracturing that must be treated and disposed of. Finally, the contamination of soil and drinking water

resources have raised both environmental and economic concerns.¹⁰ Thus, to address these issues and advance the economic viability of EGS, the development of effective and environment-friendly hydraulic fracturing fluids is needed.

We recently developed a new fracturing fluid that can mediate a stimulated expansion and provide a controllable increase of hydraulic pressure to aid in fracturing processes.¹¹ Triggered by reaction with CO₂, this novel fracturing fluid [poly(allylamine) aqueous solution, referred as PAA hereafter] can undergo chemically-induced reactions to form a hydrogel with concomitant large and rapid volume expansion and viscosity increase (Fig. S1 in supporting information).¹¹ We reported that in the presence of CO₂ under 135 atm and 190 °C (the maximum temperature and pressure attained by the instrument), the viscosity of PAA solution was 15 cP, as compared a 1-2 cP on the control experiment under identical conditions.¹¹ Although a comprehensive study on the fracturing mechanism is planned and will be the subject of a coming publication, the authors believe that the volume expansion would generate a significantly increased mechanical stress in the confined environments of the fracture networks propagating fractures at effective stress significantly lower than currently used methods.

The goal of the present study is to demonstrate the versatility of this novel fracturing fluid for fracture creation/propagation under different EGS-relevant conditions. Specifically, this work: (1) conducted hydraulic fracturing experiments on rock cores collected from two EGS sites at different pressure, temperatures, and formation fluid pH, (2) characterized the fracture networks and determine overall permeability and (3) performed computational fluid dynamics modeling on two representative EGS rock cores to evaluate the spatial distribution of the fracture networks and compute individual fractures permeabilities as well as bulk post-fracturing

permeability. This work provides qualitative and quantitative basis for the potential application of our new fracturing technology in EGS operations to advance sustainable EGS-based energy production.

2. Materials and Methods

2.1 Chemicals and rock samples

Poly(allylamine) solution (average MW ~17,000, 20wt% in H₂O) was obtained from Sigma Aldrich. This polymer solution was diluted with deionized water (DIW) for 20 times and the diluted solutions were used for hydraulic fracturing experiments as described below. In some experiments, pH 7 and pH 10 buffer solution (Sigma-Aldrich) was used for sample preparation to characterize the effect of reservoir fluid pH on the ability of the PAA-based fracturing fluid to create/propagate fractures.

There were two rock cores used in this work. One was collected from the Coso geothermal field in California at depth of ~490 m. Coso Rock samples consisted of Mesozoic diorite metamorphosed to greenschist facies. The second rock cores were obtained from Newberry Crater, Oregon, at depth 706 m. These samples consist of siliceous volcanic rocks formed from massive to very vesicular lava flows, pumice, lahars, vitrophyre, cinders, lithic tuff, and interflow breccia. These raw sample materials were cut into small cylindrical rock cores (1.59 cm diameter and 5.08 cm length) and a centered hole (0.32 cm diameter and 2.54 cm deep) was drilled from the top of the cylinder. The top and bottom of the cores were polished to ensure the sealing with an O-ring (see next section).

2.2 Hydraulic fracturing experiments

Laboratory-scale hydraulic fracturing experiments were performed using the rock cores prepared from rock samples collected from the aforementioned two field sites. A schematic diagram for the hydraulic fracturing experimental setup is shown in Fig. 1. Each rock core was placed in a state-of-the-art cradle designed to expose the entire sample to the desired confining pressure while isolating the central hole drilled to introduce the fracturing fluid (Fig. S2).

Fig. 1. Schematic diagram for the hydraulic fracturing experimental setup.

Stainless steel tubing (0.16 cm OD) was introduced 0.5 cm into the hole leaving an internal dead volume of $\sim 200 \mu\text{L}$ in the rock core. Teflon O-ring was used on the top of the cradle to ensure sealing of the connections and avoid 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 fracturing experiment. The rock core in the cradle was then connected to the head of a high pressure vessel (High Pressure Equipment Company, Erie, PA), and the cradle was introduced to the pressure vessel. A 3-way valve was used to deliver polymer solution and CO_2 . The temperature of the reactor was controlled with heating tape, a thermocouple, and a temperature controller. After the target temperature was reached, water was injected into the pressure vessel using a syringe pump to increase confining pressure. The confining pressure was first increased to either 68 atm, immediately followed by introduction of $200 \mu\text{L}$ 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 in 3.4 atm (50 psi)

intervals until the target pressure was achieved. Subsequently, the rock core internal pressure was gradually increased in intervals of 1 atm with the fracturing fluid while maintaining the confining pressure constant, until an increase in the confining pressure was observed. This pressure equilibration indicates communication between the internal and external fluids as a result of fracture formation/propagation. The pressure difference between the applied fracturing fluid pressure required for rock core fracturing and the confining pressure is defined as “effective pressure” or “effective stress.” After pressure equalization was observed, the system was cooled to room temperature and the pressure was released before the pressure vessel was opened and the rock core retrieved. For comparison, control fracturing experiments using DIW/CO₂ were also performed at identical experimental conditions for comparison purposes. The rock cores retrieved from the high pressure vessel after fracturing experiments were subjected to a series of tests to examine the formation and distribution of fractures as described below. Hydraulic fracturing experiments were performed at 150 °C and 250 atm as well as at 300 °C and 330 atm with 1 wt% PAA solution to evaluate the fracturing fluid technology at low and high EGS temperature and pressure limits. In addition, we also conducted the fracking experiments with PAA solution prepared in pH 7 and 10 buffer solutions to test the effect of reservoir fluid pH on the effectiveness of the fracturing fluid to enhance permeability. Experiments at pH =7 and pH=10 were conducted at 300 °C and 333 atm with rock from the Coso site.

2.3 Post experiment fracture connectivity measurements

Gas leaking test (gas bubbling experiment) was performed for each core after fracturing experiment to verify the presence of fractures connected to the external surface of the sample (see Fig. S3 for an example of this test). This experiment was conducted by injecting N₂ gas at

6-10 atm into the center hole of the rock core. The core was placed inside water, so the fracture opening to the external surface of the rock cores can be identified by the appearance of gas bubbles. The pressure was maintained at low levels (6-10 atm) to minimize the potential creation of new fractures during the gas leaking tests.

2.4 Post experiment permeability measurement

Pre-experiment rock intrinsic permeability values were below the lower limit of measurement. However, the intrinsic permeability of the fractures formed after fracturing experiments were calculated from measurements of tracer travel time through fractured core within the high pressure vessel using 1 M copper acetate solution. The blue colored solution was injected into the fractured rock cores using a water-filled syringe pump to allow the application of a constant pressure gradient of 6-8 atm. The time when the blue colored solution was observed at the region where gas leakage occurred was used to calculate the seepage velocity, which in turn was used to calculate the permeability using Darcy's law (Equation 3). The time intervals recorded to estimate the permeability on post-fractured rock samples ranged from 1.5 to 240 sec with an error of 0.3 sec based on multiplying by a factor of 2 the minimum time required to start or stop the timer. Since we do not know explicitly the exact fracture pathway in the rock core, we assumed that the pathways of all the fractures were straight lines perpendicular to the central hole and extend directly from the central hole to the external surface (i.e., 0.635 cm). It is noteworthy that more than likely this assumption underestimates the actual fracture pathway. Therefore, the measured permeability represents the lower limit of the intrinsic permeability. The permeabilities obtained by this method are referred here in as *experimental* permeabilities to differentiate them from the permeability values obtained by computational fluid dynamics (CFD)

modeling in two representative rock cores which will be referred in the text as *model-estimated* permeabilities.

2.5 X-ray microtomography (XMT) analysis

XMT scanning was performed at 110 keV and 190 μ A for optimum image quality and contrast. The samples were rotated continuously during the scans with momentary stops to collect each projection (shuttling mode) and minimize ring artifacts. A total of 3142 projections were collected over 360 degrees with 0.5 second exposure time and 4 frames per projection. Image voxel size varied from 25–30 μ m depending on specimen dimensions. The images were reconstructed to obtain three-dimensional datasets using CT Pro 3D (Metris XT 2.2, Nikon Metrology, UK). For rock cores after fracturing experiment, pressurized scans were conducted using a cell containing the sample (Fig. S3) connected to a nitrogen tank regulated to 8 atm (similar to pressure gradient of permeability measurements). The cell was made of polyether ether ketone (PEEK) to minimize the adsorption of x-ray.

2.6 Computational Fluid Dynamics (CFD) modeling of hydraulic fractures

CFD simulations were performed in two representative post-fractured rock samples (Coso 1-10 and Newberry-4) to visualize flow characteristics in the hydraulic fractures and to compute bulk permeability, from herein *model-estimated* permeability. Detailed description of XMT image segmentation, mesh generation and fluid flow simulations can be found elsewhere.^{12, 13} Briefly, the XMT images were pre-processed in ImageJ to remove any low frequency noise. Intensity thresholds followed by manual validation were performed to identify the fracture boundaries. An isosurface from the segmented data was extracted using a variant of marching

cube algorithm¹⁴ and smoothed using volume conserving smoothing.¹⁵ The isosurface was imported in Magics (Materialise, Plymouth, MI, USA) to clean up any intersecting and overlapping triangles and also to create a flat inlet surface for boundary condition specification. The outlet boundary in this case was outside surface of the rock core. The final surface from Magics was imported, remeshed and volume meshes were generated using the standard tetrahedral meshing utility in STARCCM+ (CD-Adapco). The final volume mesh for the samples Coso -1-10 and Newberry 4 consisted of 516112 and 2762135 vertexes, 4678568 and 26021566 faces, and 2197594 and 12342917 tetrahedral elements, respectively. A mesh independence study was performed using hybrid prism/tetrahedral meshes generated in STARCCM+. The tightly packed boundary layer consisted of prismatic elements to accurately capture boundary layer formation at the fracture walls. Tetrahedral mesh elements constituted the core of the volume mesh. The simulation results from the tetrahedral meshes were considered independent of mesh density since the difference in flow field between the tetrahedral mesh and the hybrid prism/tetrahedral mesh were less than 6%.

OpenFOAM (OpenCFD Ltd., Reading, UK) was used to solve the steady state simulation. The flow predictions were based upon the laminar, 3-D, incompressible Navier-Stokes equations for fluid mass and momentum:

$$\nabla \cdot u = 0 \quad (1)$$

$$\frac{\partial u}{\partial t} + u \cdot \nabla u = -\frac{\nabla p}{\rho} + \nu \nabla^2 u \quad (2)$$

where ρ is the density, ν is the kinematic viscosity, u is the fluid velocity vector, and p is the pressure.

For Coso-1-10, water at 300°C temperature and 100 atm pressure was considered to be the working fluid, with a density of 712.04 kg/m³ and a kinematic viscosity of 1.2078×10⁻⁷ m²/s. For Newberry 4, water at 150°C temperature and 100 atm pressure was considered to be the working fluid, with a density of 918 kg/m³ and a kinematic viscosity of 2.069×10⁻⁷ m²/s. The proximal end of the drill hole was assumed the inlet and outside surface of the rock core was assumed to be the outlet. Both models were driven by a predetermined flow rate specified at the inlet and a zero pressure boundary condition at the outlet. A no-slip wall condition was applied to the fracture boundaries, which were assumed to be rigid and impermeable.

Using the model's specified pressure gradient, the spatial distribution of velocity was predicted and intrinsic permeability was also calculated using the Darcy's law as given below:

$$q = -k/\mu \times \nabla P \quad (3)$$

where q is the flux (m/s), μ is the dynamic viscosity of fluid, and ∇P is the pressure gradient vector (Pa/m).

3. Results and Discussion

3.1 Hydraulic fracturing experiments

It is well known that temperature and pressure in different geothermal sites varies with depth and the relationship between temperature and depth is significantly different for different US

Exp. No.	Core name	Temp. (°C)	Pressure (atm)	Fracking fluid	Effective pressure of rock fracking. (atm)	Permeability after fracking exp. (mD)	Gas leaking test
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geothermal sites as reported by the US-DOE Geothermal Technology Office (DOE-GTO). To evaluate fracturing applicability across this variability, a total of 13 rock cores from two geothermal sites were subjected to hydraulic fracturing under different experimental conditions spanning the known range of EGS site temperatures, pressures, and reservoir pH. The permeability values for each sample were determined experimentally with two exceptions (samples Coso 1-10 and Newberry-4) were both, experimental and model-estimated permeability were determined. The experimental conditions and the results, including experimental permeabilities, are summarized in Table 1. Model-estimated permeabilities for Coso 1-10 and Newberry-4 are discussed in section 3.2.

Table 1. Conditions of hydraulic fracturing experiments

1	Coso-1-10	300	333	PAA-CO ₂	17	8.8	Yes
2	Coso-1-19	300	333	DIW/CO ₂	>170 ^a	< 0.001 ^b	No ^c
3	Newberry-01	300	333	PAA-CO ₂	114	0.031	Yes
4	Newberry-03	300	333	PAA-CO ₂	82	0.032	Yes
5	Newberry-02	300	333	DIW/CO ₂	> 170 ^a	<0.001	No ^c
6	Coso-1-9	150	250	PAA-CO ₂	34	8.8	Yes
7	Coso-1-18	150	250	DIW/CO ₂	49	<0.001	Yes
8	Newberry-04	150	250	PAA-CO ₂	133	5.3	Yes
9	Newberry-08	150	250	DIW/CO ₂	>170 ^a	<0.001	No
10	Coso-1-14	300	333	PAA (pH7)-CO ₂	27	2.0	Yes
11	Coso-1-16	300	333	pH 7 buffer-CO ₂	45	0.60	Yes
12	Coso-1-15	300	333	PAA (pH10)-CO ₂	24	0.35	Yes
13	Coso-1-17	300	333	pH10 buffer-CO ₂	41	0.032	Yes

^a: No communication observed even at maximum pressure allowed by the pump. Also, gas leaking test and XMT analysis did not indicate any fractures on this rock core; ^b: no liquid was observed on the external surface even after applying 10 atm pressure to the center hole for 5 min, suggesting the permeability is lower than 0.001 mD. ^c: no gas flow observed

3.1.1 Effects of temperature and pressure

3.1.1.1 Fracturing experiments conducted at 300 °C and 333 atm conditions

Experiments #1 through #5 were conducted with rock cores from Coso and Newberry geothermal sites at 300 °C, which falls in the upper range of US geothermal sites and correspond to depth of 1585 m (5200 ft) below surface for Coso geothermal site^{2,3}. Rock core Coso 1-10 (Experiment #1) was fractured applying an effective pressure of only 17 atm with PAA-CO₂ fracturing fluid system, whereas Coso 1-19 (Experiment #2, a control experiment with DIW-CO₂) was not fractured even when the internal pressure was 170 atm higher than the confining pressure (note that at this effective pressure, the pressure of CO₂ was actually near the upper limit of the ISCO pump). Gas leaking test for Coso 1-10 showed that N₂ bubbles appeared immediately and profusely and occurred within the top 2.54 cm of the rock core, consistent with

the location of the center hole (2.54 cm depth) where the hydraulic fracturing fluid was injected (Fig. S4). XMT analysis showed no presence of preexisting fractures on Coso 1-10 before the fracturing experiment, while after fracturing experiment fractures can be clearly seen and extend approximately 2 cm longitudinally (Fig. 2).

Fig. 2. XMT images of Coso 1-10 before (left) and after (right) hydraulic fracturing experiment. Control experiment (#2, coso-1-19) did not show the presence of fractures even at differential pressures as high as 170 atm. The fractures extended ~0.5 mm above and ~17 mm below this transversal section.

The experimental permeability of Coso-1-10 after fracturing was determined to be approximately 8.8 mD, which is comparable to the typical permeability of sandstone reservoir rocks¹⁶. It is noteworthy that, as we discussed in Section 2.4, the actual intrinsic permeability could be higher than the experimental permeability reported in Table 1 due to the assumptions employed for its calculation. When we determined the experimental permeability for Coso 1-19, no liquid was observed on the external surface of Coso 1-19 after applying 10 atm pressure on the center hole for 5 min. Based on this result, we estimate that the permeability of Coso-1-19 after fracturing experiment is less than 0.001 mD. Thus, the permeability of Coso rock core fractured with a conventional fracturing fluid (Coso 1-19) is at least three orders of magnitude lower than the permeability of a Coso rock core fractured with PAA-CO₂ fracturing fluid (Coso 1-10). Previous studies have shown that Coso geothermal field rock consist mainly of diorite which is highly impermeable rock with compressive strengths in the range of 1500-2000 atm.¹⁷,¹⁸ Coso 1-10 was fractured with an applied effective stress of 17 atm when employing PAA-CO₂ fracturing fluid as compared to more than 170 atm for an identical rock core (Coso 1-19, control experiment), suggesting that the novel PAA-CO₂ fracturing fluid can create/propagate fractures

in highly impermeable crystalline rock. Additional fracturing experiments were conducted with rock cores collected from another geothermal site, the Newberry crater site, under identical conditions (300 °C and 333 atm). Newberry geothermal reservoir cores consist of highly impermeable (order of 10^{-6} mD) siliceous volcanic rocks obtained at 700+ m depth.¹⁹ For the control experiment conducted with DIW-CO₂ (Table 1), the rock core (Newberry-02) was not fractured even when internal pressure was 170 atm higher than the confining pressure. Similarly to the control experiment for Coso field rock core (Coso 1-19), no N₂ leaking was observed for Newberry-02 after the fracturing experiment. When employing PAA-CO₂ as a fracturing fluid, however, similar Newberry rock cores [Newberry-01(experiment #3) and Newberry-03(experiment #4)] were successfully fractured at significantly lower effective pressures (see Table 1). N₂ leaking test revealed the presence of connecting fractures and the experimental permeability of the two fractured cores was similar (0.031 and 0.032 mD, respectively) (Table 1), showing an increase in permeability with respect to the original unaltered Newberry rock samples of over four orders of magnitude (0.032 mD vs. 10^{-6} mD)¹⁹. Although both gas leaking tests and experimental permeability values suggest that fractures were successfully created for Newberry 01 and 03, results from XMT analysis indicate that the fractures obtained consist of micro-fractures with apertures equal or below the resolution limit of the instrument (voxel size = ~ 25-30 μ m, data not shown).

3.1.1.2 Fracturing experiments conducted at 150 °C and 250 atm conditions

A second set of experiments was performed at a lower limit of P/T conditions in US EGS reservoirs as reported by the DOE-GTO. These fracturing experiments were carried out at 250 atm and at a temperature of 150 °C, corresponding to some locations drilled at the Desert Peak

and Newberry EGS sites.^{2,3} Table 1 (experiment #6 through #9) shows that the effective stress required to create/propagate fracture network is significantly lower when employing PAA-CO₂ rheoreversible fracturing fluids to fracture both Coso and Newberry rock cores, and that the experimental permeability of the generated fracture networks is considerably and consistently higher than those obtained using DIW/CO₂ (control experiments). For example, using PAA-CO₂ fracturing fluid in a EGS Coso rock core (Coso 1-9) the sample was fractured with an effective stress of 34 atm while a nearly 50 % increase in effective stress was required to fracture an identical sample (Coso 1-18) when using a conventional fracturing fluid (control experiment). In addition, the experimental permeability value for the Coso sample fractured with the PAA-CO₂ fluid system was in the order of several mD, which is nearly four orders of magnitudes higher than the experimental permeability obtained in a Coso rock sample fractured with the conventional fracturing fluid (Coso 1-18). Fig. 3 shows the XMT micrographs obtained from Coso 1-9 showing fracture networks generated by the novel PAA-CO₂ fracturing fluid. On the other hand, no evidence of fractures (to the resolution limit of the instrument) was observed on XMT images of Coso 1-18 sample which was subjected to DIW/CO₂ hydraulic fracturing fluid (data not shown). Fracture micrographs of a Newberry sample (Newberry-04) fractured with PAA-CO₂ fracturing fluid at 150 °C and 250 atm are shown in Fig. 4 manifesting the presence of fractures that communicate the center hole of the rock sample with the external surface. Newberry samples subjected to DIW/CO₂ fracturing fluids (control experiment) show no observable fracture networks.

Fig. 3. XMT images of rock cores Coso 1-9 before (left) and after (right) hydraulic fracturing experiment. Control experiment (#8, Coso 1-18) did not show the presence of fractures. The fractures extend ~10 mm above and ~5 mm below this transversal section.

Fig. 4. XMT images of Newberry-04 rock core fractured with PAA-CO₂ fracturing fluid. The Figure shows sample micrographs before (left) and after (right) hydraulic fracturing experiment. The fractures extend ~0.4 mm above and ~1.5 mm below this transversal section. Control experiment (Newberry-08) did not show the presence of fractures.

The results from these experiments suggest that, 1) similarly to previous high temperature experiments, under low temperature and pressure conditions, PAA-CO₂ fracturing fluids can generate highly permeable fracture networks in highly impermeable crystalline rock cores from both Coso and Newberry geothermal sites at significantly lower effective stress than the cores subjected to hydraulic fracturing with DIW-CO₂ (control experiments); 2) the permeability of the fracture networks generated with PAA-CO₂ fracturing fluid is several orders of magnitude higher than the permeability of identical rock samples subjected to a conventional fracturing fluid independent of the experimental confining pressure and temperature. The versatility of these rheoreversible fracturing fluids at both low and high EGS temperatures is then demonstrated at the laboratory scale. It is important to notice that at lower confining temperature and pressure, the effective pressures needed to fracture these rock cores is higher than that required at higher confining temperature and pressure. For example, while only 17 atm of effective stress is needed to fracture Coso-1-10 at 300 °C-333 atm with PAA-CO₂ fluid systems, more than twice as high (effective) pressure (34 atm) was needed to create/propagate fracture networks when identical Coso rock cores are subjected to confining P/T of 150 °C and 250 atm. The higher effective pressures required for PAA-CO₂ fluid system to generate similar fracture

networks at lower T/P conditions as compared to experiments performed at confining P/T of 333 bar and 300 °C is related to the temperature-dependent volume expansion of PAA under different CO₂ pressures. In our previous study we have demonstrated that at low temperatures (127 °C), only limited volume expansion (less than 40%) was observed, while at higher temperatures (196-402 °C) volume expansions of up to 2.5 times the original volume was recorded with higher volume expansions at higher temperatures.¹¹ . Nevertheless, the largely decreased effective stress required to create/propagate fracture networks within highly impermeable rock cores at very different P/T conditions suggests the potential of PAA-CO₂ fracturing fluid to reduce energy and cost during reservoir stimulation. Furthermore, the much higher (orders of magnitude) experimental permeabilities measured upon fracturing with this novel fluid as compared to conventional fluids position them as important fracturing fluid candidates to enhance permeability in EGS. For this initial set of experiments where the priority was to demonstrate the efficiency of the PAA-CO₂ fluid in fracturing rocks commonly encountered in geothermal environment, information on the mechanical properties of the rock samples were not available. It is planned in a near future to conduct two new series of experiments: (1) on homogeneous well- characterized natural or synthetic materials with mechanical properties close to crystalline rocks to determine the intimate fracturing mechanism and exact role of the fluid and build a predictive modelling; (2) on real rock samples coming from geothermal fields with known mechanical properties and heterogeneities to validate the proposed model.

3.1.2 Effects of EGS reservoir pH

The formation water chemistry and pH of brine solutions varies from one geothermal site to another one with the majority of geothermal sites in U.S. reporting pH values in the range of 6-

10 (a few sites report pHs as low as 4)²⁰. Then, to evaluate if this newly developed fracturing fluids can perform well at different pH conditions, four experiments (experiments # 10 through- 13) were conducted with rock cores from Coso geothermal field at 300 °C and 333 atm and at solution pH 7 and 10. PAA/CO₂-based and control fracturing fluid experiments (Coso 1-14 and Coso 1-16) were conducted employing a pH=7 buffer (with and without PAA, respectively).

Fig. 5. Representative XMT images of Coso 1-14 (a, b) and Coso 1-16 (c, d) rock cores before and after hydraulic fracturing experiment. The arrows point to the fractures. Note the much larger aperture of the fractures created on Coso 1-14.

The results shows that Coso 1-14 was fractured at an effective stress of 27 atm (Table 1), while the effective stress required to fracture an identical rock core using the conventional fracturing fluid (control experiment, Coso-1-16) was nearly 70% higher. Similarly, the experimental permeability values of Coso-1-14 fractured with PAA-CO₂ fluid system was 2.0 mD, which is nearly four times higher than the experimental permeability obtained when fracturing with a conventional fluid (control experiment, Coso 1-16). XMT analyses also provide evidence that the fractures on Coso 1-14 were larger than Coso 1-16 demonstrating once again the potential of PAA-CO₂ fracturing fluids for creation/propagation of fracture networks in highly impermeable crystalline rock (Fig. 5). Fig. 5 shows that the fractures in rock sample Coso 1-14 were located about 0.5 mm from the top and extended longitudinally~10 mm further down.

Fig. 6. XMT images of rock cores Coso-1-15 (fractured with PAA-CO₂, top) and Coso-1-17 (fractured with DIW-CO₂, bottom) before (left) and after (right) hydraulic fracturing experiment. Note the significant larger aperture on Coso-1-15. The fractures on Coso-1-15 extended ~3 mm above and ~ 6 mm below this transversal section shown in the figure.

Similar experiments were performed in pH=10 buffer solutions and similar results were obtained (see Table 1, experiments #12 and #13). Fig. 6 shows the fractures created/propagated from the center hole to the rock external surface in both samples. Effective stress as low as 24 atm was required to create/propagate fracture networks in Coso 1-15, as compared to a 70 % higher effective stress required to create fracture networks in Coso 1-17 using DIW-CO₂ fracturing fluid system. Furthermore, the experimental permeability resulting from fracturing Coso 1-15 with PAA-CO₂ fluid was an order of magnitude higher than the experimental permeability of the fracture network created when employing DIW-CO₂ control fracturing fluid. The results demonstrate that the novel fracturing fluid PAA-CO₂ can reproducibly generate fracture networks and significantly enhance permeability in highly impermeable rock cores at different reservoir pHs further validating the versatility of PAA-CO₂ fluid systems for potential EGS reservoir stimulation.

3.2 CFD modeling and fracture network description

CFD modeling was conducted for two rock cores, Coso-1-10 and Newberry-04, which represent the two geothermal field sample rock types and the lower and upper EGS pressure and temperature limits. The simulations were used to characterize the spatial distribution and fluid flow characteristics of the post-experiment fractures and permeability distribution within each of the fractures created by the novel PAA fracturing method in two illustrative example experiments.

3.2.1 Coso-1-10

Figure 7 shows velocity vectors for the Coso 1-10. The fractures produced during the fracture experiment were annotated as fracture 1 and 2 as shown in the Fig. 7. Since the volume of the fracture 1 is greater than fracture 2, the volumetric fluid flow in fracture 1 is greater. The higher volumetric flow through fracture 1 can also be attributed to its better connectivity with the central drill hole. The normalized permeability of fracture 1 and 2 computed using Darcy's law were $2.19 \times 10^{-13} \text{ m}^2$ (222 mD) and $6.24 \times 10^{-14} \text{ m}^2$ (63.2 mD), respectively, and the bulk core *model-estimated* permeability was $2.48 \times 10^{-13} \text{ m}^2$ (251 mD).

Fig. 7. CFD model of Coso 1-10 showing: left: isosurface of fractures 1 and 2 for Coso 1-10 with XMT data (left). The inlet was extruded during volume meshing to improve solution convergence. Middle: CFD model of Coso 1-10 showing velocity vectors colored by absolute velocity. The flow rate and velocity of the flow in fracture 1 is higher than fracture 2 due to smaller cross-sectional area but higher fracture volume. Right: contours of static pressure showing gradient along the fracture wall.

3.2.2 Newberry-04

Similar to Coso 1-10, the fracture experiment resulted in two fractures named 1 and 2, (see Fig. 8) but these fractures merge together in the distal portion of the sample (lower end of the drill hole). From the plot of velocity vector colored by absolute velocity, we can notice fluid velocity in fractures 1 and 2 to be similar in magnitude. The volumetric flows in both fractures are also similar. This could be attributed to the fact that both fractures have similar aperture sizes and also fracture volumes. In the distal portion of the sample, a slightly higher fluid velocity region can be noticed due to narrowing of the fracture aperture. Since fracture permeability depends on fluid flow characteristics, the similarity between fractures 1 and 2 results in similar

permeabilities. The (rock) volume-normalized permeability of fracture 1 and 2 were $1.83 \times 10^{-13} \text{ m}^2$ (185 mD) and $1.94 \times 10^{-13} \text{ m}^2$ (196 mD), respectively, and the bulk core *model-estimated* permeability was $3.78 \times 10^{-13} \text{ m}^2$ (383 mD). The similarity in flow characteristics and permeability between fractures 1 and 2 suggest isotropic behavior of the fracture network.

Fig. 8. CFD model of Newberry-04 showing: Left: a slice of XMT data with isosurface generated using segmented data for Newberry 4 sample. The interface between the rock and the rock core cradle was assumed as the outlet for the CFD model. Middle: CFD model of Newberry-04 showing velocity vectors colored by absolute velocity. Volumetric flow and fluid velocity in both fracture 1 and 2 are similar since the volumes and apertures of fractures 1 and 2 are comparable. Right: contours of static pressure.

It is important to mention the apparent discrepancy between the model-estimated fractures network permeabilities and the experimental permeability values measured. These differences in permeability could be attributed to the following reasons. 1) Fluid flow was modeled at steady state, hence, energy loss due to acceleration of fluid was not accounted. On the other hand, the experimental setup accounted for inertial losses due to fluid acceleration while increasing the pressure gradient; 2) using the computational model, individual permeabilities were computed for the two fractures for both Newberry 4 and Coso 1-10 where the experimental procedure measured only the permeability of one fracture or the fracture where the colored solution was first seen; 3) the length of the fracture used for the experimental determination was assumed to be the diameter of the sample less the central void which is a simplification; 4) time for the color solution to traverse the fracture was timed using a chronometer, which was prone to human errors.

4. Conclusions

Energy consumption continues to escalate and outpace population growth, and hydrocarbon extraction rates are only expected to increase despite concerns over CO₂ emissions and potential climate change impacts. Geothermal energy represents one of the most promising renewable sources of energy within the US and worldwide. Current locations viable for geothermal production are limited by formation permeability, and enhancing formation permeability, as in Enhanced Geothermal Systems (EGS), is required to expand geothermal energy production. The primary limitation that makes commercial EGS infeasible is our current inability to cost-effectively create high-permeability reservoirs from impermeable, igneous rock within the 1-4 km depth range. Fracturing for oil and gas is now standard practice, but the applicability of the conventional fracturing methods and chemicals at elevated EGS temperatures and pressures is uncertain. In addition, there is a widespread concern about the synthetic and highly-proprietary chemicals employed in conventional fracturing and the resulting potential contamination of shallow drinking water aquifers. This work evaluates at the laboratory scale the EGS applicability of a novel, environmentally-friendly and potentially recyclable hydraulic fracturing fluid that undergoes a controlled and large-volume expansion with a simultaneous increase in viscosity triggered by CO₂ at temperatures relevant for reservoir stimulation in EGS. The results illustrate the versatility of this novel fracturing fluid for EGS applications. The phase-switchable fluid fractures impermeable igneous rocks at lower effective stresses, and increases permeability to a significantly (several orders of magnitude) larger level, compared to conventional hydraulic fracturing methods. This is confirmed for two rock types from geothermal fields, over the entire range of EGS pressures and temperatures, and over a wide range of formation pH values, which confirms the feasibility of this novel method for formation

stimulation and potential development of EGS at various locations world-wide. With softer rocks and lower pressure formations, this novel fracturing fluid would be viable for enhancing hydrocarbon production, as well. The efficiency and effectiveness of the permeability enhancement combined with the potential extractability of the switchable fluid make this novel fracturing method more cost-effective and environmentally cleaner than current approaches.

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Supporting Information

Schematic diagram and photos of rock core cradle setup, photos of gas leakage test, and XMT images of rock cores before and after hydraulic fracturing experiments are included in the supporting information.

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541 **TOC/Abstract Art**

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8