

## Effect of Initial Water Saturation on the Performance of Fracturing Fluids with and Without Polyallylamine under Simulated EGS Conditions

Guoqing JIAN<sup>1</sup>, Ramesh S. SARATHI<sup>1</sup>, Carlos A. FERNANDEZ<sup>1\*</sup>, Jeff BURGHARDT<sup>1</sup>, Alain BONNEVILLE<sup>1</sup>

<sup>1</sup>Pacific Northwest National Laboratory, Richland, WA, United States

[carlos.fernandez@pnnl.gov](mailto:carlos.fernandez@pnnl.gov)

**Keywords:** StimuFrac, polyallylamine (PAA), CO<sub>2</sub>-reactive polymer, fracturing, initial water saturation

### ABSTRACT

**Objectives/Scope:** StimuFrac (US Patents 9,873,828 B2 and 9,447,315 B2), a CO<sub>2</sub>-reactive polymer aqueous solution [polyallylamine (PAA) 1wt% in water] combined with CO<sub>2</sub>, can be used as a less water-intensive fracturing fluid for enhanced geothermal systems (EGS). Our previous results show that in hot dry rock (HDR), PAA/CO<sub>2</sub> fracturing fluids outperformed other fluids such as water, CO<sub>2</sub>, and CO<sub>2</sub>/water in generating large fractures with less fluid consumed. The objective of this work is to investigate the effect of initial water saturation on the performance of StimuFrac by conducting hydraulic fracturing tests with ½ foot cubic rock samples held under representative EGS stress/temperature conditions and by using cyclic and constant injection rate injection strategies. The resulting fracture hydraulic conductivities, breakdown pressures, and volumes of fluids required are compared.

**Methods/Procedures/Process:** To simulate geothermal reservoir conditions, in all tests, the rock sample was held under triaxial confinement and at 200 °C, and different volumes of water were initially injected into the rock sample before any fracturing processes were initiated. For the single-cycle PAA alternating CO<sub>2</sub> injection fracturing experiments, one complete cycle consisted of two steps: (1) injecting a PAA slug (or water slug) followed by (2) injecting CO<sub>2</sub> to initiate and propagate the fracture. For experiments involving multiple injection cycles, the CO<sub>2</sub> injection pressure is increased until it peaks and begins to decline (indicating fracture initiation at this moment), and then continued being injected for another 30 seconds to propagate the fracture. Then, these two-step cycles [injection of PAA (or water) followed by CO<sub>2</sub> injection (up to 2-4 mL/min)] are repeated.

**Applications/Significance/Novelty:** The results of this study suggest that water saturation significantly affects the fracturing fluid transmission into the rock pore space, thus affecting the fracture initiation and propagation. In this study, fracturing tests via a single injection cycle or multiple injection cycles were performed. Splitting the rock samples in half after testing reveals that fracture propagation is significantly limited under high water saturation conditions (three-day initial water injection) compared to dry initial conditions. The fractures propagate less than 1/3 of the distance from the wellbore to the outer rock surface, and in some cases, no fracture is generated. This may be caused by leak-off dominating the fracturing process and the fluid injection rate is insufficient to overcome leak-off, even under high injection rate conditions. Additionally, CO<sub>2</sub> could be leaking off into the wellbore annulus and this may be making it more difficult to generate sufficiently high-pressure gradients away from the near-wellbore region. Under low water saturation conditions (dry rock or after 1-day initial water injection), PAA/CO<sub>2</sub> consistently generated significantly larger fractures compared with other fluids. CO<sub>2</sub> generated large fractures only in the dry rock and with high injection rates, but data variability is high.

### 1. INTRODUCTION

StimuFrac<sup>TM</sup>, an aqueous polymer solution of polyallylamine (PAA) combined with CO<sub>2</sub>, has been previously reported by our group as a promising, less water-intensive fracturing fluid for enhanced geothermal systems (EGS). The PAA-CO<sub>2</sub> crosslinking reactions, volume expansion, and viscosity increase at high temperatures (Fernandez et al., 2019; Jung et al., 2015; Shao et al., 2015) enable the generation of large fractures in hot dry rock systems (Jian et al., 2021).

Initial water saturation is an important parameter for fracturing processes. A recent study (Zhuang et al., 2020) shows that fractures tend to propagate in wider areas for highly water-saturated samples. However, the study doesn't report on the hydraulic conductivity differences before and after fracturing in dry and water-saturated rock samples. Our previous results show that in hot dry rock, PAA/CO<sub>2</sub> outperformed other fracturing fluids such as CO<sub>2</sub>, water, or water/CO<sub>2</sub>. However, questions remain regarding how the PAA/CO<sub>2</sub> fracturing fluid system performs within rock systems with different initial water saturation. In this work, the effect of initial water saturation was investigated and found to have a significant and complex impact on the fracturing performance of the different fracturing fluids. Fracturing in high water saturation conditions (samples initially flooded with water for three days) can lead to very low conductivity fractures for all fluids systems tested. Under hot dry rock or intermediate water saturation (samples initially flooded with water for one day) conditions, PAA/CO<sub>2</sub> generates larger fractures than water, CO<sub>2</sub> or water/CO<sub>2</sub>. This is particularly the case for single-cycle WAG injections.

### 2. MATERIALS AND METHODS

#### 2.1 Materials

A borehole is drilled longitudinally through each sample and the granite sample is placed in the heated triaxial load cell as described in the previous publication (Jian et al., 2021). The stress field applied by the loading frame is the same in all tests:  $\sigma_{T-B}/\sigma_{N-S}/\sigma_{W-E}$

=7.58/9.65/9.65 MPa (1,100/1,400/1,400 psi) which means the stress in the direction perpendicular to the top and bottom of the rock sample is the minimum principal stress. This directs the fracture orientation in the lateral direction. All experiments were performed under identical temperature (200 °C) conditions. The mass consumption of aqueous PAA, water, and CO<sub>2</sub> during the fracturing process is calculated beginning from the injection of fracturing fluids until the breakdown pressure is reached (water injected to increase the initial saturation is excluded from the mass calculations).

**Table 1 Fracturing results in dry and pre-waterflooded rock**

Test	Rock ID	Mode/Rate	Fracturing fluid/Method	Water injected into pre-saturated rock ( $S_{wi}$ )	$P_b$	$C_f$	First fixed PAA (or water) slug injected after $S_{wi}$	Additional PAA (or water) injected	CO <sub>2</sub> usage for fracturing
		(mL/min)		(mL)	(psi)	( $\mu\text{m}^3$ )	(mL)	(mL)	(g)
1	B3*	$C_Q = 2$	Dry-H <sub>2</sub> O	0	1675	0.8	0	0.9	0
2	D4*	$C_Q = 10$	Dry-H <sub>2</sub> O	0	3849	0.4	0	1.3	0
3	D5*	$C_Q = 10$	Dry-H <sub>2</sub> O	0	2925	1.4	0	0.8	0
4	D6*	$C_Q = 10$	Dry-H <sub>2</sub> O	0	3708	1.4	0	1.2	0
5	B8*	$C_Q = 25$	Dry-H <sub>2</sub> O	0	3917	1.0	0	0.6	0
6	E5	$C_Q = 3 \text{ to } 12$	H <sub>2</sub> O(3day)-H <sub>2</sub> O	8242	2131	0.6	0	20.8	0
7	E9	$C_Q = 25$	H <sub>2</sub> O(3day)-H <sub>2</sub> O	7524	3289	1.0	0	1.4	0
8	F7	$C_Q = 25$	H <sub>2</sub> O(3day)-H <sub>2</sub> O	13900	2943	1.0	0	2.5	0
9	B10*	$C_Q = 4$	Dry-CO <sub>2</sub>	0	3183	0.7	0	0	14.5
10	B2*	$C_Q = 10$	Dry-CO <sub>2</sub>	0	3375	160.6	0	0	12.8
11	C1*	$C_Q = 10$	Dry-CO <sub>2</sub>	0	3376	10.8	0	0	8.3
12	C7*	$C_Q = 10$	Dry-CO <sub>2</sub>	0	3645	2.0	0	0	9.5
13	G4	$C_Q = 25$	H <sub>2</sub> O(1day)-CO <sub>2</sub>	871	2660	7.5	0	0	<0.1
14	E7	$C_Q = 4 \text{ to } 20$	H <sub>2</sub> O(3day)-CO <sub>2</sub>	10702	1722	0.7	0	0	31.1
15	F1	$C_Q = 25$	H <sub>2</sub> O(3day)-CO <sub>2</sub>	13770	2423	0.4	0	0	10.9
16	F8	$C_Q = 25$	H <sub>2</sub> O(3day)-CO <sub>2</sub>	9768	2271	0.9	0	0	7.1
17	B1*	$C_Q = 2 \text{ or } 3$	Dry-WAG01	0	N/A	N/A	11.3	0	N/A
18	B1*	$C_Q = 10$	Dry-WAG01	0	3019	19.7	11.3	0	2.5
19	C8*	$C_Q = 10$	Dry-WAG01	0	3174	24.4	11.3	0	2.1
20	C9*	$C_Q = 10$	Dry-WAG01	0	2720	8.2	11.3	0	1.9
21	A10*	$C_Q = 2$	Dry-PAG01	0	3974	65.7	11.3	0	4.9
22	B7*	$C_Q = 10$	Dry-PAG01	0	3308	44.7	11.3	0	2.3
23	D3*	$C_Q = 10$	Dry-PAG01	0	3172	77.7	11.3	0	0.9
24	D7*	$C_Q = 10$	Dry-PAG01	0	3242	22.3	11.3	0	0.9
25	D8*	$C_Q = 10$	Dry-PAG01	0	3412	12.5	11.3	0	2.0
26	G3	$C_Q = 25$	H <sub>2</sub> O(1day)-PAG01	934	3510	90.1	11.3	0	<0.1
27	E8	$C_Q = 4 \text{ to } 18$	H <sub>2</sub> O(3day)-PAG01	9093	1971	0.2	11.3	0	11.5
28	F2	$C_Q = 25$	H <sub>2</sub> O(3day)-PAG01	11044	2738	4.3	11.3	0	1.4
29	F9	$C_Q = 25$	H <sub>2</sub> O(3day)-PAG01	9035	2724	0.6	11.3	0	5.2
30	G1	$C_Q = 25$	H <sub>2</sub> O(3day)-PAG01	11274	2488	1.0	11.3	0	0.7
31	E4	$C_Q = 4$	H <sub>2</sub> O(3day)-WAG09	9415	1537	0.7	11.3	16.2	76.9
32	E2	$C_Q = 0.4 \text{ to } 2$	H <sub>2</sub> O(3hour)-PAG17	85.3	2570	0.08	11.3	4.0	58.4
33	E3	$C_Q = 2$	H <sub>2</sub> O(1day)-PAG25	718	4283	0.18	11.3	8.7	58.5

Notes: Rock ID columns with \* symbols mean the data are cited from our previous published paper (Jian et al., 2021).

## 2.2 Injection strategy

Six injection fluids/strategies were used in this study:

Fluid/Method 1: water injection (tests 1-8),

Fluid/Method 2: CO<sub>2</sub> injection (tests 9-16),

Fluid/Method 3: single cycle (WAG01) water/CO<sub>2</sub> injection (tests 13-20),

Fluid/Method 4: single cycle (PAG01) PAA/CO<sub>2</sub> injection (tests 21-30),

Fluid/Method 5: multiple cycle (WAGn) water/CO<sub>2</sub> injection (test 31),

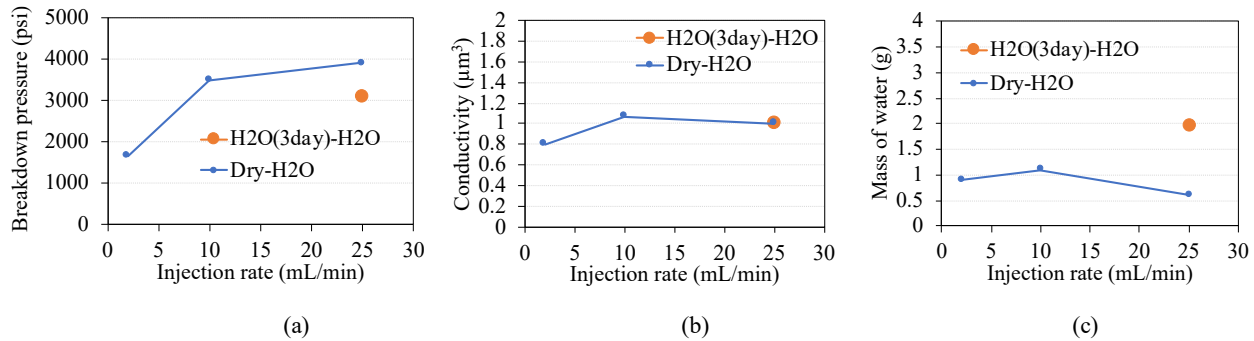
Fluid/Method 6: multiple cycle (PAGn) PAA/CO<sub>2</sub> injection (tests 32 and 33).

The experiments were conducted under three different initial water conditions: dry, 1 day of water injection, and 3 days of water injection. During the initial water injection period, water was injected into the sample at 1,000 psi constant pump pressure (and then water, CO<sub>2</sub>, water/CO<sub>2</sub>, or PAA/CO<sub>2</sub> were used as fracturing fluids). For experiments where water was the sole fracturing fluid, water was injected starting from 1,000 psi at a constant injection rate (tests 1-8 in **Table 1**). For experiments where CO<sub>2</sub> was the sole fracturing fluid, CO<sub>2</sub> was injected starting from 1,300 psi at a constant injection rate (tests 9-16 in **Table 1**). For single-cycle WAG experiments denoted as WAG01 in **Table 1** (WAG refers to water alternating CO<sub>2</sub> injection), water was always injected at 1,000 psi and CO<sub>2</sub> was injected starting from 1,300 psi with a constant injection rate (tests 13-20). For single-cycle PAG experiments denoted in **Table 1** as PAG01 (PAG refers to polymer aqueous solution (1% PAA) alternating CO<sub>2</sub> injection), a fixed volume of 11.3 mL of PAA was injected at 1,000 psi in the first cycle, followed by CO<sub>2</sub> injection at constant injection rate starting from 1,300 psi (tests 21-30). For multiple cycles WAG or PAG (tests 31-33), the procedure was as follows. In the first cycle, a fixed (11.3 mL or 1/3 total pore volume) amount of water (or PAA) was injected followed by injecting CO<sub>2</sub> at a constant injection rate until a pressure peak is observed. Then, we continued injecting CO<sub>2</sub> for an additional 30-seconds. Next, from the second to last cycle, water (or PAA) was injected at constant pressure (1,000 psi) as follows. First, we switched from CO<sub>2</sub> back to water (or PAA) injection at constant pressure (1,000 psi). Since the pressure at the wellbore is originally higher than the pressure at the water (or PAA) pump (i.e., whatever pressure reached after 30 seconds of CO<sub>2</sub> injection in the first cycle), the injection rate measured in the water (or PAA) pump is negative. Therefore, we waited until the injection rate in the water (or PAA) pump switched to positive values, and then from that point on we continued injecting at constant water (or PAA) pressure (1,000 psi) until an injection rate of zero mL/min (PAA) or significantly small values (water) was measured. Simultaneously, the isolated CO<sub>2</sub> pump pressure is set back to 1,300 psi in preparation for the next cycle injection. At this point, we close the valve connecting the water (or PAA) pump to the wellbore and switched back to CO<sub>2</sub> injection by opening the valve connecting the wellbore to the CO<sub>2</sub> pump. Since the pressure at the CO<sub>2</sub> pump is 1,300 psi we waited (in constant pressure mode) for the pressure at the CO<sub>2</sub> pump to equilibrate with the wellbore pressure. Then, we switch the CO<sub>2</sub> pump to constant injection rate mode and inject CO<sub>2</sub> until a new pressure peak is reached followed by another 30 seconds of injection. These cycles of water (or PAA)/CO<sub>2</sub> repeat as shown in **Figure 5** and **Figure 6**.

Following each fracturing test, the fracture conductivity was measured at the same stress and temperature conditions but using oil. Additional information on each test is shown in **Table 1**. The nomenclature used under the column “Fracturing fluid/Method” refers to the rock initial condition, injection fluid, and the number of cycles. For example, test 33 is named H<sub>2</sub>O(1day)-PAG25. This means that there were 25 injection cycles with alternating PAA and CO<sub>2</sub> injection, and the rock was pre-flooded with water for one day. In the column of Mode/Rate, C<sub>Q</sub> means constant injection rate for the fracturing process.  $S_{wi}$  represents the initial water saturation of rock.  $P_b$  means breakdown pressure which is the maximum pressure recorded during the fracturing test and  $C_f$  is fracture conductivity after the fracturing tests are done.

### 3. DISCUSSION

#### *Fluid/Method 1: water injection (tests 1-8)*

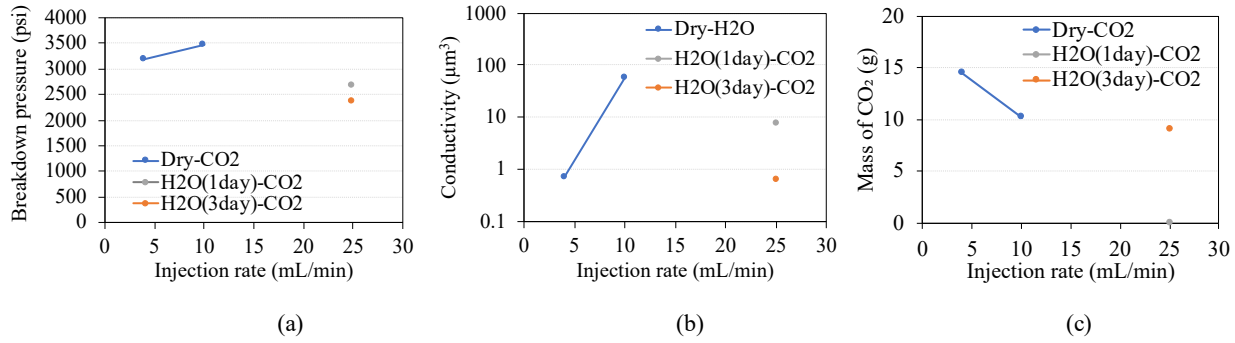


**Figure 1: Average (a) breakdown pressure; (b) conductivity; (c) mass of water consumed for single water injection in dry and water-saturated rocks**

Tests 1 to 8 were conducted using water injection in the dry rock and rock pre-waterflooded for 3 days (as shown in **Table 1**). The average (a) breakdown pressure; (b) fracture conductivity; and (c) mass of water injected are shown in **Figure 1**.

For the average breakdown pressure in dry rock, the average breakdown pressure increases from 1,675 psi to 3,917 psi with the injection rate increasing from 2 mL/min to 25 mL/min as shown in **Figure 1(a)**. The average breakdown pressure in rock pre-water flooded for 3 days is around 3,116 psi, which is lower than that in dry rock.

For the average fracture conductivity, shown in **Figure 1(b)**, both fracturing tests in dry and pre-waterflooded rocks resulted in very low fracture conductivities. The average fracture conductivity is 0.8~1.1 μm³ for dry rock as compared with 1.0 μm³ for 3-day pre-water flooded rock. The average mass consumption of water is shown in **Figure 1(c)**; at 25 mL/min injection rate, the average water consumption is 2.0 g in rock pre-water flooded for 3 days while it is only 0.6 g in dry rock. This indicates that high initial water saturation increases the water usage, likely because of increased water relative permeability and thus greater water leak-off.

*Fluid/Method 2: CO<sub>2</sub> injection (tests 9-16)*

**Figure 2: Average (a) breakdown pressure; (b) conductivity; (c) mass of CO<sub>2</sub> consumed for single CO<sub>2</sub> injection in dry and water-saturated rocks**

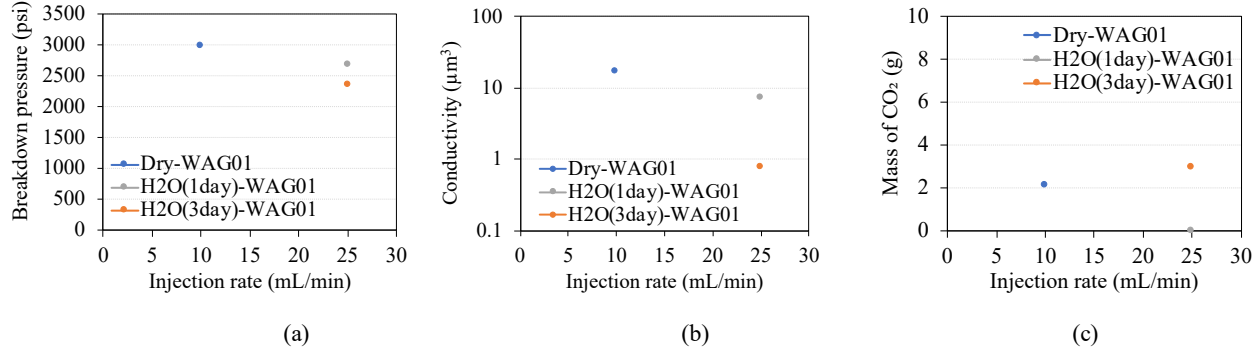
Tests 9 to 16 were conducted using CO<sub>2</sub> injection in dry and pre-waterflooded rock samples (as shown in **Table 1**). The average (a) breakdown pressure; (b) conductivity; (c) mass of CO<sub>2</sub> consumed are shown in **Figure 2**.

The average breakdown pressure (**Figure 2 (a)**) for dry rock changes from 3,183 psi to 3,465 psi when the injection rate changes from 4 mL/min to 10 mL/min. For the breakdown pressure in 1-day and 3-day pre-waterflooded rock, the average breakdown pressure is 2,660 psi and 2,347 psi, which is much lower than in dry rock.

The average fracture conductivity (**Figure 2 (b)**) increases with the injection rate in dry rock. In 1-day and 3-day pre-waterflooded rock, the fracture conductivity is lower than that in dry rocks, though the tests were conducted under higher injection rate conditions. Comparing the average fracture conductivity between 1-day and 3-day pre-waterflooded rock, the conductivity is reduced under higher water saturation conditions.

The average mass consumption of CO<sub>2</sub> (**Figure 2 (c)**) decreases with the injection rate in dry rock. Comparing the results between 1-day and 3-day pre-waterflooded rock, the mass-consumed increases with higher water saturation conditions.

It is important to note that the above-described results could be also affected by the fact that a larger injection rate was used for tests in water-flooded rock (25 mL/min vs 4 mL/min to 10 mL/min) since no fracturing was observed at low injection rates.

*Fluid/Method 3: single cycle (WAG01) water/CO<sub>2</sub> injection (tests 13-20)*

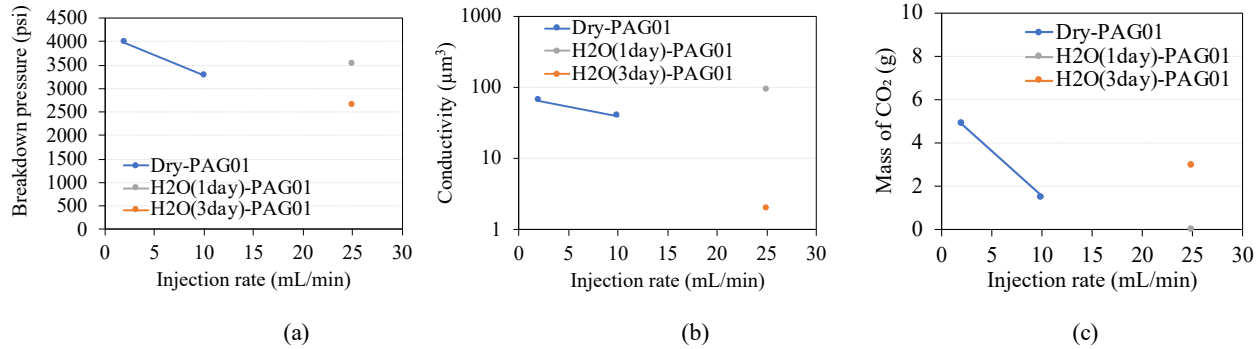
**Figure 3: Average (a) breakdown pressure; (b) conductivity; (c) mass of CO<sub>2</sub> consumed for single cycle (WAG01) in dry and water-saturated rocks**

Tests 13 to 20 were conducted using single cycle (WAG01) water/CO<sub>2</sub> injection in dry and pre-waterflooded rock samples (as shown in **Table 1**). It should be noted that test 13, which is H<sub>2</sub>O(1day)-CO<sub>2</sub>, is equivalent to H<sub>2</sub>O(1day)-WAG01 and that tests 14-16, which are H<sub>2</sub>O(3day)-CO<sub>2</sub>, are equivalent to H<sub>2</sub>O(3day)-WAG01. The reason is that the last 11.3 mL injection of water during the pre-flooding corresponds to the water injection in a single cycle of WAG. Therefore, tests 13-16 are used as H<sub>2</sub>O(1day)-WAG01 and H<sub>2</sub>O(3day)-WAG01 for comparison with Dry-WAG01 (which is one cycle WAG in dry rock). The average (a) breakdown pressure; (b) conductivity; (c) mass of CO<sub>2</sub> for single cycle WAG injection in dry and water-saturated rock are shown in **Figure 3**.

The average breakdown pressure (**Figure 3(a)**) for dry rock is 2,971 psi when the CO<sub>2</sub> injection rate is 10 mL/min. In rock pre-waterflooded for 1 day and 3 days, the average breakdown pressure is 2,660 psi and 2,347 psi though the CO<sub>2</sub> injection rate is 25 mL/min.

The average fracture conductivity (**Figure 3(b)**) for dry rock averages  $17.4 \mu\text{m}^3$  while in 1-day and 3-days pre-waterflooded rock, the fracture conductivity is between  $0.8\text{--}7.5 \mu\text{m}^3$ . This indicates that the resulting average fracture conductivity is reduced under higher water saturation conditions. The average mass consumption of  $\text{CO}_2$  (**Figure 3(c)**) in dry rock is less than that in 3 days pre-waterflooded rock. The  $\text{CO}_2$  mass-consumed for the 1-day pre-waterflooded rock was negligible or close to the uncertainty of the pump.

*Fluid/Method 4: single cycle (PAG01) PAA/ $\text{CO}_2$  injection (tests 21-30)*



**Figure 4: Average (a) breakdown pressure; (b) conductivity; (c) mass of  $\text{CO}_2$  for single cycle (PAG01) in dry and water-saturated rocks**

Tests 21 to 30 were conducted using single cycle (PAG01) PAA/ $\text{CO}_2$  injection in dry and pre-waterflooded rock samples (as shown in **Table 1**). The average (a) breakdown pressure; (b) conductivity; (c) mass of  $\text{CO}_2$  consumed for single cycle (PAG01) PAA/ $\text{CO}_2$  injection in dry and water-saturated rock are shown in **Figure 4**.

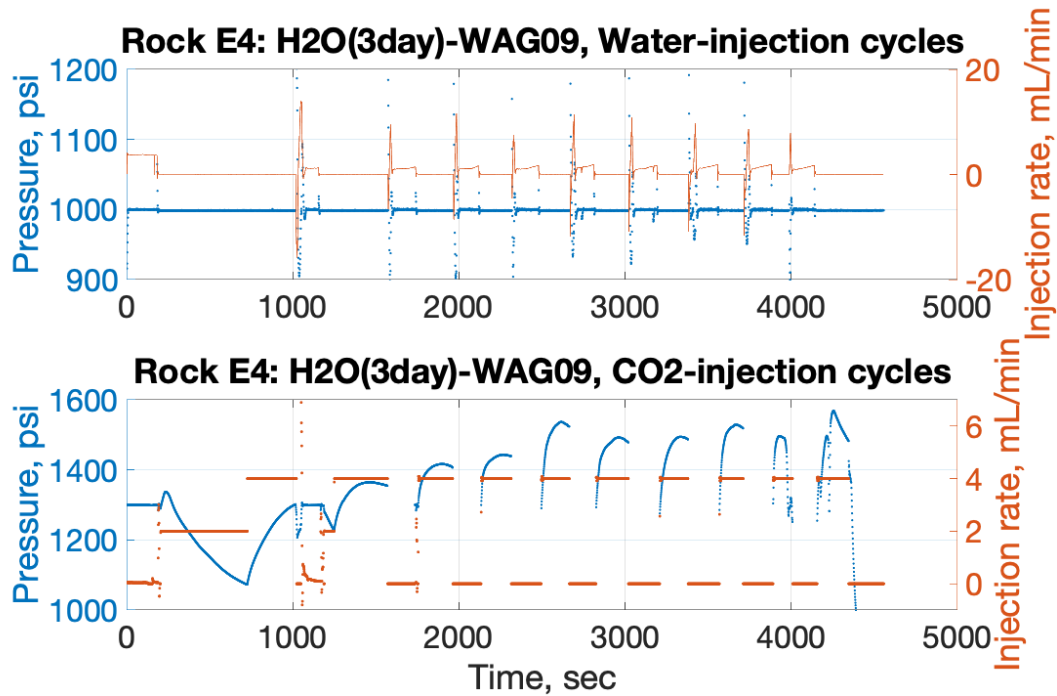
The breakdown pressure (**Figure 4(a)**) for dry rock averages 3,974 psi when the injection rate is 2 mL/min and 3,284 psi when the injection rate is 10 mL/min. For the breakdown pressure in 1-day and 3-day pre-waterflooded rock, the average breakdown pressure is 3,510 psi and 2,650 psi. This indicates that high water saturation may reduce the breakdown pressure when fracturing with PAG injection.

The average fracture conductivity (**Figure 4(b)**) in dry rock is  $65.7 \mu\text{m}^3$  at 2 mL/min  $\text{CO}_2$  injection rate and  $39.3 \mu\text{m}^3$  at 10 mL/min  $\text{CO}_2$  injection rate. In 1-day pre-waterflooded rock, the fracture conductivity is  $90.1 \mu\text{m}^3$ , while in 3-day pre-waterflooded rock it is only  $2.0 \mu\text{m}^3$ . Comparing these average fracture conductivity values to the values attained for  $\text{H}_2\text{O}/\text{CO}_2$  at 25 mL/min injection rate, the PAA/ $\text{CO}_2$  test provides significantly higher fracture conductivity than the  $\text{H}_2\text{O}/\text{CO}_2$  test for the 1-day pre-waterflooded rock samples, though only one test was conducted for each case (**Figure 3(b)** and **Figure 4(b)**). The fracture conductivity results for the  $\text{H}_2\text{O}/\text{CO}_2$  tests and PAA/ $\text{CO}_2$  tests in 3-day pre-waterflooded rock samples were within the same order of magnitude.

The average mass consumption of  $\text{CO}_2$  (**Figure 4(c)**), is similar in tests with dry rock and 3-day pre-waterflooded rock. However, the  $\text{CO}_2$  mass-consumed for the 1-day pre-waterflooded rock was negligible or close to the uncertainty of the pump. Follow-on work will focus on performing more PAG01 tests in 1-day pre-waterflooded rock to better understand if this is the case and why.

*Fluid/Method 5&6: multiple cycle WAG (test 22) and multiple cycle PAG injections (tests 31-33)*

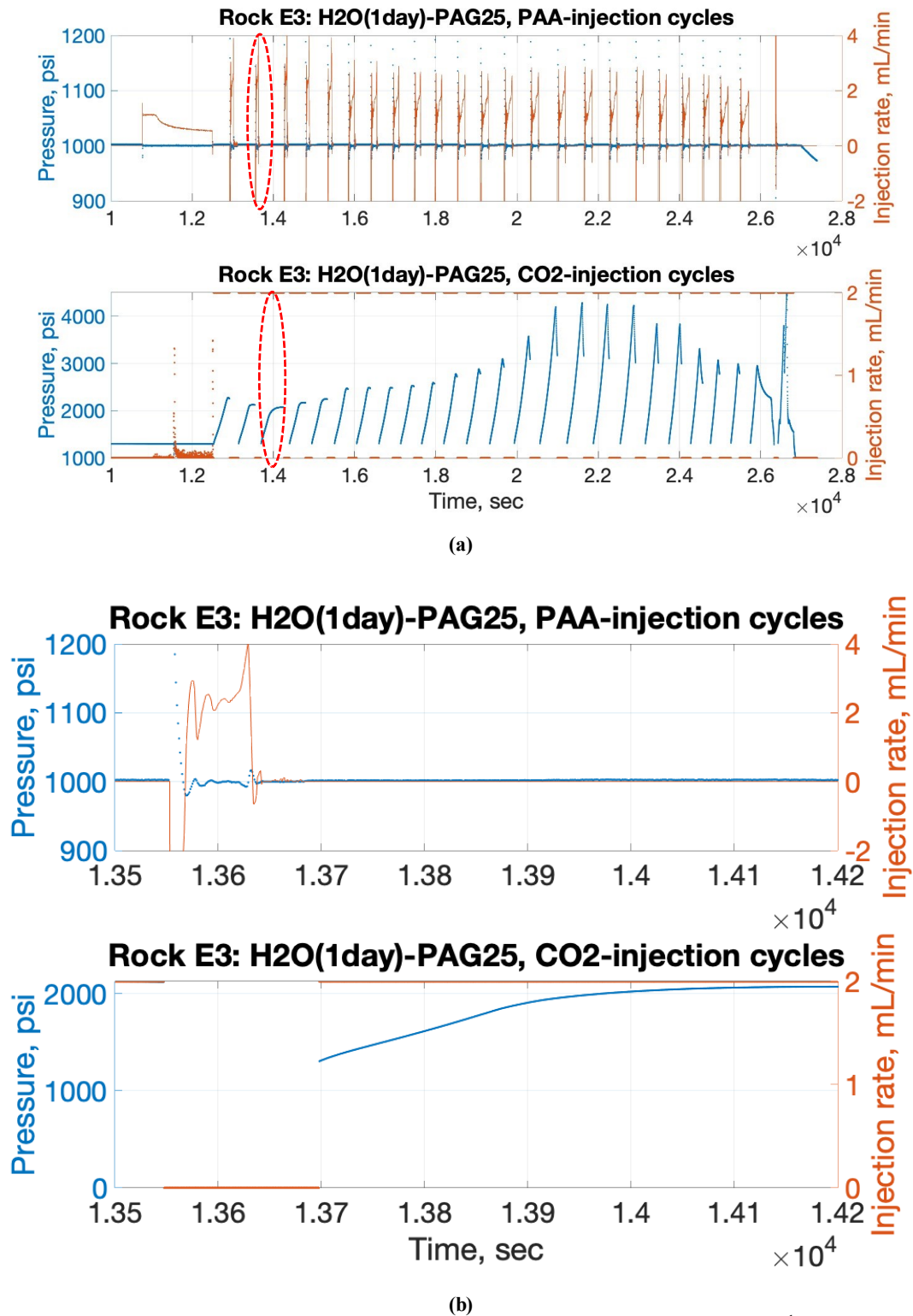
**Figure 5** shows the continuous pump pressure and pump injection rate information for the multiple cycle WAG case (WAG09). The top and bottom plots are complementary to each other: the top figure shows the water injection information while the bottom figure shows the  $\text{CO}_2$  injection information. The pre-waterflooding period is not shown here. For the fracturing process illustrated in **Figure 5**, water was injected at a constant pressure of 1,000 psi. Then,  $\text{CO}_2$  was initially injected at 2 mL/min, during which the pressure increased by several psi and then decreased significantly to around 1,100 psi. In the following cycles,  $\text{CO}_2$  was injected at 4 mL/min, and it seemed that a no fracture was formed since during each cycle the leak-off rate of water was decreasing to values significantly lower than the water leak-off rate values (3.5 mL/min) observed during the end of the 3-days water saturation process. In addition, if a fracture is initiated and propagated from the wellbore to the rock external walls, the water injection rate (constant pressure conditions) should increase steadily. This was not observed in all the cycles. Nevertheless, **Figure 5** plots correspond to those of a typical WAG injection, where  $\text{CO}_2$  injection pressure steadily increases due to the reduced total mobility associated to phase interference and  $\text{CO}_2$  trapping. The final measured average rock conductivity is  $0.7 \mu\text{m}^3$ , which is very low and indicates that there is no large effective fracture formed in this test.



**Figure 5:** Nine cycles WAG fracturing with H<sub>2</sub>O-CO<sub>2</sub> in 3-day pre-waterflooded rock

**Figure 6** shows the continuous pump pressure and pump injection rate information for the multiple cycle PAA-CO<sub>2</sub> test case PAG25. Only the fracturing period is shown and the 1-day pre-waterflooding period is not shown. In the first injection cycle, 11.3 mL of PAA was injected at 1,000 psi, then CO<sub>2</sub> was injected at 2 mL/min until the pressure peaked (and began to decline, again indicating either breakthrough/leak-off or fracture initiation). The CO<sub>2</sub> injection continued then for 30 more seconds. Subsequent cycles followed, with injection of PAA at constant pressure (1,000 psi) until PAA injection rate is reduced to around 0 mL/min [this is shown in each cycle in the top plot of **Figure 6(a)** and (b)]. The bottom figure in **Figure 6(a)** shows that the CO<sub>2</sub>-pressure peaks and this maximum steadily increases during cycles 1-15. Then, this maximum plateaus and decreases. The detailed pressure behavior of PAA can be read from the zoomed-in cycle 3 for PAA and CO<sub>2</sub> injection, which is shown in **Figure 6(b)**. At the beginning of each cycle, there is a negative injection rate of PAA since the pressure at the wellbore is high due to the high-pressure CO<sub>2</sub> that remains from the previous cycle. After a few seconds, the PAA injection rate becomes positive and is followed by a sharp reduction to 0 mL/min as shown in the top plot of **Figure 6(b)**. The net injection volume of PAA is positive and is quantified in each cycle. We hypothesize that at the end of each PAA/CO<sub>2</sub> cycle, fresh PAA becomes in contact and reacts with CO<sub>2</sub>. As a result, the CO<sub>2</sub>-crosslinked polymer product reduced the relative permeability of PAA and the injection rate of PAA reduced to 0 mL/min. Since multiple processes are taking place over each cycle, including 1) PAA-CO<sub>2</sub> reaction, 2) saturation changes of PAA and CO<sub>2</sub>, and 3) pore pressure changes, it is difficult to infer whether a fracture is generated and propagated from simply measuring the injection rates and pump pressures. The average conductivity of the post-test sample is only 0.13  $\mu\text{m}^3$ , which indicates that for cyclic injection at these injection rates, PAA/CO<sub>2</sub> is not efficient in generating highly conductive fractures, unlike in the case of higher injection rates previously discussed in single-cycle PAG.



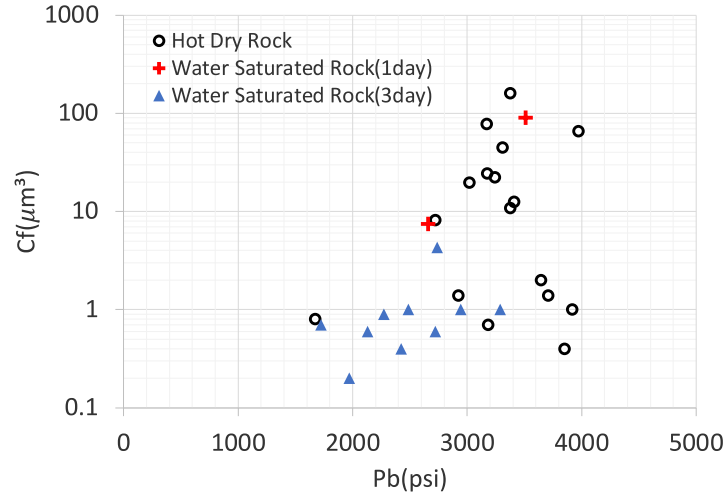


**Figure 6:** (a) 25 cycles PAG fracturing with PAA-CO<sub>2</sub> in 1-day pre-waterflooded rock; (b) zoomed-in 3<sup>rd</sup> cycle for PAA and CO<sub>2</sub> injection

Multiple cycles WAG and PAG were limited to low injection rates to avoid propagating the fracture too quickly due to the small size of the rock (3" from center to rock walls). However, these less than realistic injection rates attained fractures with very low conductivities independently of the fracturing fluid used (or the initial water saturation of the rock). In view of this, we opted for one WAG (or PAG) cycle at high (more realistic) injection rates. The results show that PAA/CO<sub>2</sub> outperforms water/CO<sub>2</sub> in terms of fracturing efficiency under dry and 1-day water flooded rock conditions. We hypothesize that multiple injection cycles at low injection rates (2 mL/min) may generate fractures with smoother surfaces and/or no fracture wall displacement. On the other hand, a single fracturing event at high

injection rates (1-cycle WAG) may produce a rougher fracture surface and/or a small displacement needed for the fracture to self-prop. This is evidenced when comparing the test in Rock E3 with the test in Rock G3 where, under similar pre-water flooding initial conditions, one PAA/CO<sub>2</sub> cycle with CO<sub>2</sub> injected at 25 mL/min attains a fracture 2-3 orders of magnitude more conductive than when injecting PAA/CO<sub>2</sub> over multiple cycles at low injection rates (2mL/min CO<sub>2</sub>).

As a side note, the reader could ask why the fracturing experiments in hot dry rock were performed at 10 mL/min while the experiments on rock samples pre-flooded (1-day or 3-days) with water were performed at 25 mL/min. The reason lies in that the test in rock E7 (test 14), which is the test using CO<sub>2</sub> as a sole fracturing fluid injected in 3-days water-saturated rock, we found that even at a high (20 mL/min) injection rate, the rock conductivity after fracturing was very low. Therefore, higher injection rates were adopted for these water-flooded rock samples.



**Figure 7: Results of conductivity Vs. breakdown pressure with different injection strategies in different water-saturated rocks**

The fracturing results in the hot dry rock and 1-day or 3-days pre-waterflooded rock specimens are shown in **Figure 7**. The black circles are experimental results in hot dry rock. The red cross symbols are the data with 1-day pre-waterflooded rock. And the blue triangle data shows the data of fracturing in 3-days pre-waterflooded rock. Multicycle WAG and PAG data are not plotted in this figure since the fracture conductivity is low and there is no apparent fracture breakthrough to the rock surface after multiple cycles.

From **Figure 7**, it is evident that for most of the tests in 3-days pre-waterflooded rock samples, the conductivity of the rock after fracturing is below 1  $\mu\text{m}^3$  except for one PAA/CO<sub>2</sub> test where CO<sub>2</sub> is injected at 25 mL/min.

When performing fracturing experiments in 1-day pre-waterflooded rock, the conductivity after fracturing was as large as 90.1  $\mu\text{m}^3$  only when PAA was used. Without the presence of PAA, the conductivity of the rock after fracturing using 25 mL/min CO<sub>2</sub> was an order of magnitude lower (7.5  $\mu\text{m}^3$ ). And this fracture conductivity is larger than all the conductivity values attained in 3-days pre-waterflooded rock samples. Since only one 1-day pre-waterflooded test was conducted (for each fluid), so additional tests are required to better quantify potential data variability. Nevertheless, the low conductivity fractures obtained in all tests performed in 3-days pre-waterflooding rock as compared against the hot dry rock results, indicate that water saturation has a significant impact on fracturing efficiency independently of the fracturing fluid used. In hot dry rock or pre-waterflooded rock, the PAA/CO<sub>2</sub> system was demonstrated to outperform other fracturing fluid systems in terms of hydraulic conductivity enhancement.

#### 4. CONCLUSIONS

Higher breakdown pressures are typically observed in this study when higher injection rates are used for fracturing with water or CO<sub>2</sub>. When fracturing with water, CO<sub>2</sub>, or single cycle WAG, breakdown pressure is lower in 1-day or 3-days waterflooded rock specimens. Single-cycle PAG fracturing show complex breakdown pressure changes under different water saturating conditions. The breakdown pressure of single-cycle PAG fracturing is higher in 1-day water-saturated rock than in 3-days water-saturated rock.

The initial water saturation condition has a significant impact on the fracture conductivity for the stimulation tests. In hot dry rock or 1-day pre-waterflooded rock, the fracture conductivity is the highest when using PAA/CO<sub>2</sub> fracturing system. In the case of 3-days pre-waterflooded rock samples, the post-test conductivity is low independently of the fracturing fluid/method used. One PAA/CO<sub>2</sub> cycle with CO<sub>2</sub> injected at 25 mL/min generates a fracture 2-3 orders of magnitude more conductive than when injecting PAA/CO<sub>2</sub> over multiple cycles at low injection rates (2mL/min CO<sub>2</sub>). In addition, PAA/CO<sub>2</sub> fracturing fluid consumes the least mass of CO<sub>2</sub> in the stimulation test in 1-day pre-waterflooded rock as compared to dry rock and 3-days pre-waterflooded rock.



## REFERENCES

- Fernandez, C.A., Gupta, V., Dai, G.L., Kuprat, A.P., Bonneville, A., Appriou, D., Horner, J.A., Martin, P.F., Burghardt, J.A., 2019. Insights into a Greener Stimuli-Responsive Fracturing Fluid for Geothermal Energy Recovery. *ACS Sustainable Chem. Eng.* 7, 19660–19668. <https://doi.org/10.1021/acssuschemeng.9b04802>
- Jian, G., Sarathi, R.S., Burghardt, J., Bonneville, A., Gupta, V., Fernandez, C.A., Garrison, G., 2021. Evaluation of a Greener Fracturing Fluid for Geothermal Energy Recovery: An Experimental and Simulation Study. *Geothermics* 97, 102266. <https://doi.org/10.1016/j.geothermics.2021.102266>
- Jung, H.B., Carroll, K.C., Kabilan, S., Heldebrant, D.J., Hoyt, D., Zhong, L., Varga, T., Stephens, S., Adams, L., Bonneville, A., Kuprat, A., Fernandez, C.A., 2015. Stimuli-responsive/rheoreversible hydraulic fracturing fluids as a greener alternative to support geothermal and fossil energy production. *Green Chem.* 17, 2799–2812. <https://doi.org/10.1039/C4GC01917B>
- Shao, H., Kabilan, S., Stephens, S., Suresh, N., Beck, A.N., Varga, T., Martin, P.F., Kuprat, A., Jung, H.B., Um, W., Bonneville, A., Heldebrant, D.J., Carroll, K.C., Moore, J., Fernandez, C.A., 2015. Environmentally friendly, rheoreversible, hydraulic-fracturing fluids for enhanced geothermal systems. *Geothermics* 58, 22–31. <https://doi.org/10.1016/j.geothermics.2015.07.010>
- Zhuang, L., Kim, K.Y., Diaz, M., Yeom, S., 2020. Evaluation of water saturation effect on mechanical properties and hydraulic fracturing behavior of granite. *International Journal of Rock Mechanics and Mining Sciences* 130, 104321. <https://doi.org/10.1016/j.ijrmms.2020.104321>