CARBONATED WATER FLOOD: WHAT WE OBSERVED IN SAND PACK EXPERIMENTS

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ABSTRACT

Carbonated water flooding (CWF hereafter) is to inject CO_2 saturated (or nearly saturated) water into reservoirs as the displacing fluid. CO_2 migrates into the oil without forming an separate CO_2 rich phase. The mass transfer of CO_2 from water into oil is substantial because CO_2 has higher solubility in oil than in water at the same pressure and temperature. After CO_2 is dissolved, oil viscosity reduces and oil swells too. Both effects result in improved ultimate recovery over the routine water flood (WF hereafter). CWF does not aim to achieve miscibility so that it has less restrictive requirements of reservoir conditions and oil types. It is also feasible to implement CWF in fields with ongoing WF.

Two CWF field trials were conducted in 1950's. Lab scale experiments were also active between 60's and 80's. But during the past few decades, little work has been done on the topic. Available data in literature are inconsistent in many aspects. To obtain comprehensive understanding of the CWF's displacement mechanism as well as impacts from a number of sensitivity parameters, such as fluid properties and rock fluid interactions, we designed and started the implementation of a multi-year project centered on core/sand pack flooding experiments. This paper summarizes the results from eight sand pack flooding experiments.

INTRODUCTION

WF has been in place for a long time and widely applied worldwide. Besides macroscopic factors, for example channels in the reservoir, WF's performance is heavily affected by the viscosity ratio between oil and water. For instance, in a typical five-spot pattern and with 1 PV (pore volume) injection, WF oil recovery factor (RF hereafter) is about 0.8 when the viscosity ratio is 0.083, but down to 0.25 when the ratio is 754 [5]. In order to improve the WF microscopic displacement efficiency, it is desirable to either reduce the oil viscosity or increase the water viscosity. The way that CWF improves RF is aligned with this principle. During the process, CO_2 diffuses into the oil phase after carbonated water is injected into the formation, which results in oil viscosity reduction. In addition, solution of CO_2 in oil is significant so that the oil volume swells. This leads to

increased oil relative permeability and enhances the oil mobility. It has to be noted that CO_2 solubility in oil is much more substantial than that in water, approximately 3 to 7 times higher under the same conditions [11]. Therefore, oil viscosity reduction and swelling are also significant. Miller and Jones [17] showed that the volume expansion of 17º API oil is up to 20% when fully saturated with CO_2 at 2,000 psia and 140ºF. Moreover, 10º API oil can decrease its viscosity from 7,000 cp down to 100 cp at 140ºF when saturated with CO_2.

In the lab environment, flooding experiments with carbonated water is relatively easier to conduct than adding other aggressive solvents into water, i.e., without substantial changes to materials and seals in pumps, accumulators, tubing, and valves. Surface properties of the core material are not altered under the carbonation level, pressure, and temperature in this study. Therefore cores can be reused. From a field implementation perspective, CWF imposes limited modifications to existing facilities and bear less HSE concerns. At places where there is limited supply of CO_2 and off-shore fields where to build recycling facilities capable of CO_2 or gas injection might be difficult, CWF becomes more suitable if an improved oil recovery method is needed. In general, to use CO_2 as an EOR agent is well aligned with the industry's efforts to reduce green house gas emissions.

Two important features differentiate CWF from miscible or immiscible CO_2 flooding or WAG (water alternating gas). One is that the total volume of CO_2 used in the CWF process is determined by the solubility of CO_2 in water under the targeted reservoir pressure and temperature as well as the salinity level of the injected water, i.e. the amount of CO_2 injected is proportional to the water injection volume (or at least a portion of the injected water if it is decided to chase carbonated water with plain water). The other is that CO_2 stays dissolved either in water or oil and there ought to be a very limited amount of CO_2 rich phase in the reservoir. Miscibility is not sought for in the CWF process. Therefore, CWF has much less restrictive requirements of rock and/or fluid properties than miscible CO_2 flooding.

LITERATURE REVIEW

The first CWF experiment available to us can be traced back to 1940's [12]. Monteclaire Research conducted sand pack studies and showed that tertiary CWF was able to reduce the residual oil saturation up to 15% PV. Earlougher Engineering finished a group of core flooding experiments from 1948 to 1952 using carbonated water. Their results showed that CWF recovered 2% to 26% PV more oil after WF [12].

Martin reported about 12% improvement on oil recovery by using carbonated water [14]. His studies showed that oil recovery enhancement is positively correlated with the

carbonation level and the decrease in oil recovery improvement with respect to reduced carbonation level is more substantial in low API oils.

Holm [10] conducted a number of core flooding experiments using both carbonated water and CO2 slug. He used one foot long, 3.5 inch diameter Berea sandstone cores and West Texas crude (5.1 cp at 70ºF and 2.2 cp at 125ºF). He observed 21% and 19% increase in recovery factor respectively compared to WF on the same cores. With another group of oils, 0.8 cp, 5 cp, and 90 cp at experiment conditions, he obtained 5%, 23%, and 69% improvement in the oil recovery.

Holm also reported results obtained from experiments with CO2 slug as the chasing fluid after the injection of carbonated water [11]. His experiments were conducted at 100ºF and pressures from 600 to 2,600 psig. Displacement rates were from 5 ft/day to 25 ft/day. He observed 30% to 35% improvement on oil recovery compared to plain WF.

In 70's, Institute France du Petrole (IFP) ran core flooding experiments with Bati Raman oil and Dodan gas [13]. Experiment temperature was 149ºF and pressure 406 psig. Both high viscosity oil (290 cp) and medium viscosity oil (42 cp) were used. Experiments consisted of a series of injection cycles with plain water, CO2, and carbonated water with 24 hours shut in period between injectant switch. 14% to 15% improvement in the oil recovery was reported.

Mayers et al. [16] listed two groups of core flooding experiments done in 1981 and 1985. They used core plugs with length between 4.8 inches and 5.7 inches, and diameters between 1.8 inches and 2 inches. Oil viscosities at the experiment temperature (125 ºF) were 475 cp and 406 cp respectively. The initial flooding speed was chosen in such a way that a scaling factor was equal to 1 to reduce the end effect [19]. After water breakthrough, the injection speed was changed to 1 ft/day. Oil recovery improvement was between 13% PV and 24% PV with the average be 17% PV for the 1981 group and 19.4% PV for the 1985 group.

Peres et al. [18] studied carbonated water imbibitions in a fractured reservoir. His carbonation pressures varied from 50 psig to 500 psig. Spontaneous imbibition of plain water and carbonated water into a number of core plugs showed that the latter was able to recover 10% HCPV to 16% HCPV more oil than the former.

Sohrabi et al. [21] used a micro model in their CWF experiments. Conditions were 2,000 psia and 100.4ºF.They used mineral oil (16.5 cp) and n-Decane (0.8 cp). Oil recovery increases were 8.8% HCPV and 23.8% HCPV for two oils respectively.

Shell internal research efforts were also devoted to CWF back in 60's and 80's. Both sand pack flooding experiments [22] and etched-glass model [7] were used. In the flooding study, carbonated water was able to recover 12% PV to 23% PV more oil than WF at 5 PV injections, depending on oil viscosities. While using the etched-glass model, researchers found that oil droplets originally shielded by water swelled after being exposed to carbonated water due to CO_2 diffusing into the oil phase.

Besides lab scale data, two field trials of CWF were also reported in public literature. One is the K&S project in 50's [4][8][9][14]. It was a field located 10-mile north of Bartlesville, OK, with 35 injectors and 24 producers in a regular 10 acre 5-spot pattern. Production of the field started with pressure depletion in 1907 and ended in 1934 due to economy reasons. In 1958, co-injection of CO_2 and water in the same tubing started. Such carbonation process was completed by April 1, 1960. The improved production in the year of 1959 was 123,000 STB more than the total primary oil produced from 1905 to 1934. It was estimated that carbonated water could produce 37% more oil than WF would.

The other field program was in Domes Unit in 1965 [20]. The field started production from 1910 and by 1953, 90 wells were drilled and completed. From 1961, the secondary development kicked off. During the process, 13 producers were converted into injectors and three new injectors were also drilled. CO_2 and water injection started in September and October that year. By March 1962, about one third of PV equivalent carbonated water was injected and chased by plain water. It was estimated that the slug injection of carbonated water gave about 9% additional oil recovery.

Overall, CWF used to be an active topic with quite some works done decades ago. But recently, few efforts have been devoted to the area. Literature data are inconclusive in many aspects, such as 1) what is the (reasonable) recovery increase range by applying CWF; 2) what are the sensitivities of CWF recovery with respect to fluid properties, such as oil viscosity, gas oil ratio, and rock fluid interactions, for example wettability; 3) whether the lab scale experiments can be optimized (in terms of the maximized oil recovery improvement) by selecting proper conditions, including pressure, temperature, dip angle, speed, etc.; 4) whether the optimized lab conditions can be scaled up to the field level and if so, how to do that.

In order to obtain answers to the aforementioned questions, we designed a multi-year CWF project with emphasis placed on core/sand pack flooding experiments. Through the project, we intend to achieve a more comprehensive understanding of the CWF displacement mechanism as well as the dependence of its performance on a number of pre-identified sensitivity parameters. This paper is to summarize the Phase I results of

this project, where we focused on the impact of injection speed on oil recovery with other conditions unchanged.

EXPERIMENT SETUP

We will describe in detail regarding 1) how we prepared sand packs; 2) how we mixed CO_2 with DI (deionized) water and measured the gas water ratio (GWR hereafter); 3) how we set up the flooding apparatus and chose experimental conditions.

Sand Pack Preparation

We used a commercial sand to prepare sand packs. This sand has 99% purity and the majority of the sand particles are below ASTM 120 (125 microns). We washed and dried sand before packing in order to get rid of fine particles.

The stainless steel containers together with their clamps and flow lines used in this study were custom made by Swagelok. Figure 1 shows one of these assemblies. The container is 1.35 inch ID with both ends sealed by Viton o-rings. A pair of stainless steel frits is placed on top of o-rings to provide filtration of fine particles so that the risk of clogging equipments downstream can be reduced. 1/8" OD tubing is welded on to end caps.

One challenging problem of packing sand into tubes is how to make sands evenly distributed so that the sand pack is rather homogeneous without spots concentrated with particles of different mesh sizes. Vibration bed did not turn out to be successful in this study although it is a widely applied method to pack sands. Thus, we developed an in-house packing method and proved its effectiveness through multiple rounds of packing and permeability measurements (flow of DI water from both ends). The key to the success of the method is that do not try to shake or consolidate sands while pouring the sand into the container. Instead, consolidate the whole pack while topping the sand. This way, chances for separation of small sands from large sands are significantly reduced. It is also a good practice for us to weigh all parts (see Figure 1) before packing the assembly and after. With the sand density known, it is straightforward to obtain the total sand volume. The average porosity of eight sand packs used in this study is 0.3 with variations less than 3% and sand pack permeabilities vary from 1,700 mD to 3,700 mD (see Table 1).

CO2 Water Mixture

CO_2 is quite soluble in water but salts in water decrease the solubility. As sand pack does not have the clay swelling issue, DI water was used, which helped us to achieve a satisfactory carbonation level without increasing the pressure a lot. Under the desired experimental conditions (600 psig and 104ºF), the maximum amount of CO_2 that can be dissolved into a cc of DI water is 19.2 cc, which is equal to a GWR 108 SCF/STB [2]. It is known that the CO_2 solubility increases with the pressure while decreases with the

temperature when the salinity the same. As mixing CO_2 with water was conducted at the ambient temperature, we had to take into consideration the effect from temperature increase after bringing the CO_2 water mixture bottle into the oven. The bottom line is that we want neither a CO_2 rich phase formed due to the temperature elevation nor very low CO_2 concentration. So what we did was to calculate the CO_2 solubilities at both ambient and experiment temperatures. Obviously, at the same pressure, the former is higher than the latter. Then, we chose the mixing pressure by looking for the ambient temperature solubility that is close to the one at the experiment pressure and temperature. Eventually, we used 300 psig as the mixing pressure because the CO_2 solubility at this pressure is 16.5 cc/cc, which is close to the targeted 19.2 cc but with sufficient buffer to compensate uncertainties from calculations and experiment operations.

The mixing process was conducted with a high pressure CO_2 bottle and a syringe pump set at the constant pressure mode. The piston accumulator was filled with DI water first and then connected to the high pressure bottle to let CO_2 come in. The syringe pump was set at 300 psig to provide the pressure support. The accumulator was then placed on a rocker inside a fume hood to equilibrate overnight with the pump connected.

Before moving CO_2 water mixture bottle into the oven for flooding, we measured the CO_2 solubility in water by drawing sub-samples. For each bottle prepared for our experiments, we did three solubility measurements and gauged them against the calculated solubility at 300 psig and ambient temperature. The purpose of doing this exercise was to ensure that the carbonation level met what we desired and there was no CO_2 rich gas phase inside the mixing bottle.

 Solubility measurement device was in-house made and consists of a flask, a high pressure sample pycnometer, and a container (see the high level drawing in Figure 2). Before the solubility measurement, the container was pre-filled with water and the sample pyc was connected to the flask through a 1/8" stainless steel tubing mounted in the stopper so that the released CO_2 won't escape to open air. During the measurement, valve V2 was slowly open to release the CO_2 and the water in the container will be "pushed" out. The total amount of CO_2 was read from the container scale and the total amount of water was obtained by the flask weight difference. Note that the gas displacing water from the container is actually a "diluted" CO_2, i.e. a mixture of CO_2 with air. In addition, release of the CO_2 is fairly rapid (from gas-liquid equilibrium perspective), more like a direct flash from the elevated pressure down to the ambient. Therefore, loss of the CO_2 in the container when gas "bubbling" through the water column and in the residual water inside the flask is insignificant. The impact on the measurement accuracy is thus minimal, although the CO_2 solubility in water at the ambient condition is non-trivial (about 0.8 cc/cc). Our experience shows that the solubility measurement method is

valid and representative. The average solubility of CO_2 in water in all eight runs is 17.6 cc/cc (99 SCF/STB) with variations less than +/- 10%.

Flooding Apparatus and Experiment Conditions

The flooding apparatus used in this study consists of syringe pump(s), a sand pack, a densitometer, a back pressure regulator (BPR hereafter), and multiple piston accumulators holding DI water, CO_2 water, and oil respectively (see Figure 3). Two bypass lines were used between the sand pack in/outlets and the densitometer in/outlets to detour pre-flush fluids before the flooding. The inline densitometer was used to monitor the water breakthrough from the density change. Oil saturation was conducted at the ambient temperature in order to obtain accurate pore volume measurements without effects from thermal expansion. Water and CO_2 water bottles were all equilibrated 24 hours at the experiment temperature before flooding.

The experiment pressure (600 psig) and temperature (104ºF) in this study were taken from an internal work conducted by van Dijk [22]. Crude oil coming from a deep water field in the Gulf of Mexico was used. At the experiment condition, viscosities of the dead oil and DI water are 70.7 cp and 0.65 cp respectively. The viscosity ratio is about 109. The density difference is rather small (0.9368 g/cc vs. 0.9932 g/cc).

Eight sand pack experiments were finished in the Phase I study. They were divided into four groups. Within each group, one sand pack was flooded with the water first and the carbonated water later. The other one was flooded with the carbonated water only. We designed this way to mimic applying CWF in both tertiary and secondary modes. Table 1 shows sand pack indices and their injection rates. As the focus of the Phase I study is to investigate the effects on the CWF oil recovery from the flooding speed, the injection rate was kept the same within a group but varied among groups, with other conditions the same. We started with 15 PV/day used by van Dijk in one of his runs.

RESULTS

Figures 4 to 7 show RF and pressure drop vs. injection PV curves for all eight sand pack experiments. They are ordered in the same sequence as these experiments conducted: 15 PV/day, 1 PV/day, 4 PV/day, and 2 PV/day respectively from top to bottom. In tertiary CWF experiment, red dots/lines denote the CWF phase and blue dots/lines for the WF phase. The improvement of RF over WF ranges from 0.03 PV, when injection speed is 1 PV/day, to 0.35 PV when the speed is 15 PV/day.

By just looking at RF curves, the eight plots can be divided into two groups. One group contains 15 PV/day and 4 PV/day results (Figures 4 and 6), where the oil production keeps going on after the water breakthrough, featured as increasing RF curves to rather high recovery. The other group that 1 PV/day and 2 PV/day fall in (Figures 5 and 7), has their RF curves rapidly level off after the water breakthrough, i.e. the oil production decreases fairly fast. There are two reasons for this difference. One is that when flooding

sand packs with high injection speeds, for example, 15 PV/day, the viscous force tends to dominate and results in (artificially) low residual oil saturations. However, the high oil recovery under this condition is not scalable to field applications due to the unfeasible requirement of the injection pressure (if the same speed needs to be maintained). The other reason is that we used 100% oil saturation in sand packs to exclude effects from irreducible water saturation. It has been found that when the core flooding experiment conducted with zero irreducible water saturation, the porous media (even if it is actually water wet) behaves more like oil wet, i.e. substantial amount of oil being produced after the water breakthrough [1][6]. This phenomenon is more pronounced when the flooding speed is high [6].

We also note that water breaks through early (<= 0.2 PV injection) in 15 PV/day and 4 PV/day cases. As the oil water viscous ratio is very unfavorable, we believe that the displacements under the two injection speeds are unstable, i.e. water fingers its way through oil. On the other hand, recovery curves for 1 PV/day and 2 PV/day injections have their water breakthrough time around 0.4 to 0.5 PV. Therefore, the cutoff of injection speed between stable and unstable displacement for the particular rock and fluid pair in this study appears to be bracketed by 2 PV/day and 4 PV/day. Although 1 PV/day also gives stable displacement, low frontal speed makes the flooding more impacted by the capillary force [3][23]. Therefore, in this study, we regard 2 PV/day as the optimal injection rate that is able to provide a representative oil recovery.

Pressure drops are quite similar across the eight experiments except three runs (we will discuss them in detail later on). Different from classic text book cases where pressure drop increases before water breakthrough, reaches the maximum value, and decreases after breakthrough, pressure drops observed in our study start high and keep dropping till water breakthrough. After breakthrough, pressure drops quickly decrease and stabilize on (relatively) smaller values. Behavior like this can be explained by applying the Darcy's law and the total mobility, defined as $k_{rw}/\mu_w + k_{ro}/\mu_o$, where k_r is the relative permeability for oil and water, and μ is the oil and water viscosity. Under a constant injection rate, pressure drop across a core or sand pack is inversely proportional to the total mobility. Whether there is a maximum pressure drop depends on the total mobility curve. If the latter has a minimum point, the former will increase first and then decrease afterwards. If, however, the total mobility curve is monotonic, then pressure drop won't have maximum point. Remember that the total mobility curve is a function of both phases' viscosities and their relative permeability curve. Thus, from one pair of rock and fluid combination to the other, pressure drop behavior can be substantially different.

The three different ones are sand packs J, S, and U (see Figures 5, 6, and 7 respectively). Overall, they share the same aforementioned feature regarding pressure drop vs. water breakthrough. But after breakthrough, they look somewhat different. For sand pack J

(Figure 5), before switching to carbonated water, pressure drop has two up-tipping periods. They are likely caused by localized oil banking because if we look closely at RF curve, we will see that both up-tipping are overlapped with jumps at oil RF, i.e. more oil produced after pressure going up. Sand pack S (Figure 6) has its pressure drop increase steadily before carbonated water kicking in. Different from sand pack J, there is no drop in this case. Considering the fact that sand pack S was unstably displaced under 4 PV/day injection rate, we tend to interpret this as a result of large amount of water and oil simultaneously flowing in the sand pack after breakthrough. The unfavorable viscosity ratio between oil and water is an important factor here, which is why after carbonated water injection starts, pressure drop reduces again. Sand pack U (Figure 7) has its pressure drop increase tremendously, almost double the pre-breakthrough value. The answer to this has nothing to do with technical aspects. Instead, it is caused by a jammed stainless steel frit used to filter our fine particles at the outlet of the sand pack. We did not find this until we dissembled the sand pack and cleaned the setup after flooding done. The clog in the frit might improve to some distance after carbonated water injected as oil viscosity reduced. That's why during the carbonated water flooding period, there is no more pressure increase.

In this work, carbonated water has its viscosity only slightly higher than that of DI water, less than 5% increase at the experiment conditions. As oil viscosity is much larger than either DI water viscosity or carbonated water viscosity, pressure increase due to switching the injectant from DI water to carbonated water is minimal and likely be masked by reading noise in pressure transducers. That's the main reason that no obvious increase in pressure drop is seen when the injection of DI water stops and the carbonated water starts flowing.

CONCLUSIONS

Our main conclusions are

- Carbonated water is able to recovery more oil than the conventional WF in both secondary and tertiary modes.
- 2 PV/day is the optimal injection speed for this setup. Higher flooding rates give more optimal RF but scalability to field applications decreases.

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Table 1: Sand Pack Index, Porosity, Permeability, PV, and Injection Speed

	Sand Pack #	Flooding Type	Average Perm (Darcy)	Porosity	PV (cc)	Injection Speed (PV/day)
Group 1	G	WF + CWF	1.9	0.30	85	15
	I	CWF only	2.8	0.30	86	
Group 2	J	WF + CWF	1.8	0.30	88	1
	K	CWF only	2.5	0.31	89	
Group 3	S	WF + CWF	3.5	0.31	91	4
	T	CWF only	3.7	0.31	90	
Group 4	U	WF + CWF	1.7	0.30	88	2
	V	CWF only	3.2	0.31	88	

Figure 1: Sand Pack Assembly, including a) End Pieces with Valves; b) Viton O-ring; c) Stainless Steel Frit; d) Pipe; e) Clamp; f) Nuts and Bolts
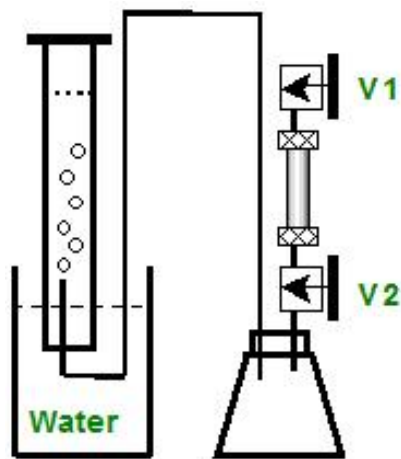
Figure 2: Schematic of CO2 Solubility Measurement Device
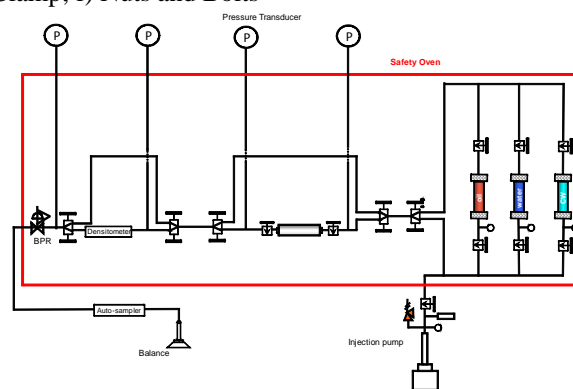
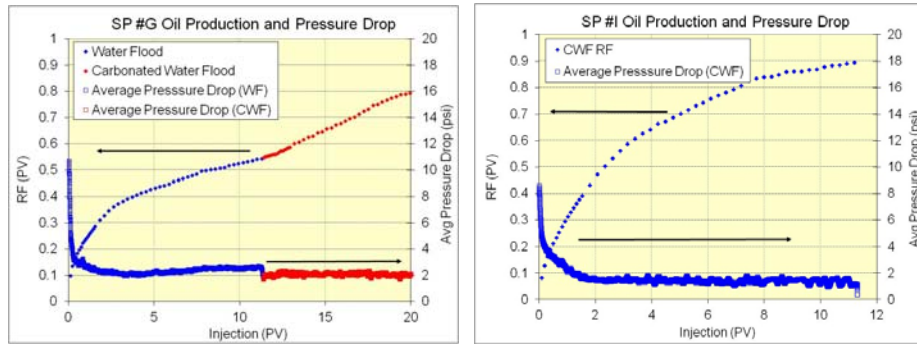Figure 3:   Schematic of Flooding Device Used in This Study

Figure 4: RF and Pressure Drop vs. Injection PV for Sand Packs #G (WF + CWF) and #I (CWF Only) with 15 PV/day Speed
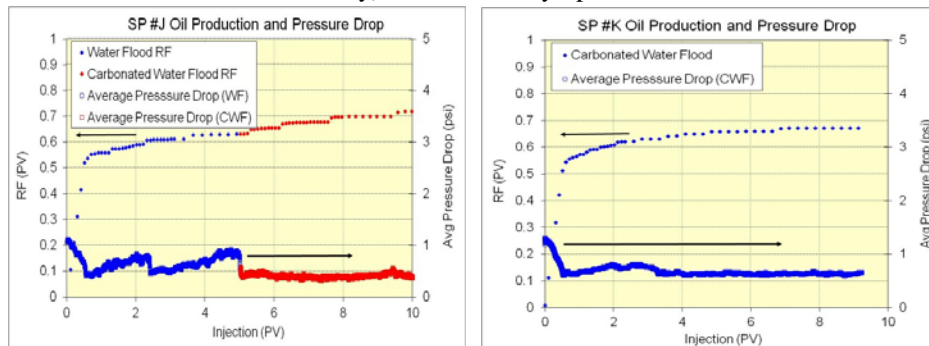

Figure 5: RF and Pressure Drop vs. Injection PV for Sand Packs #J (WF + CWF) and #K (CWF Only) with 1 PV/day Speed
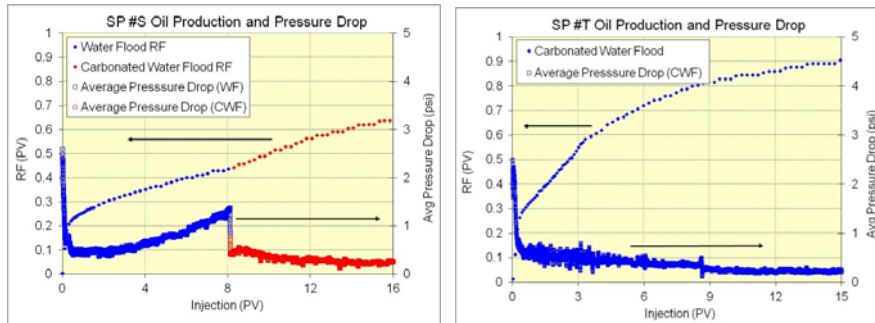

Figure 6: RF and Pressure Drop vs. Injection PV for Sand Packs #S (WF + CWF) and #T (CWF Only) with 4 PV/day Speed
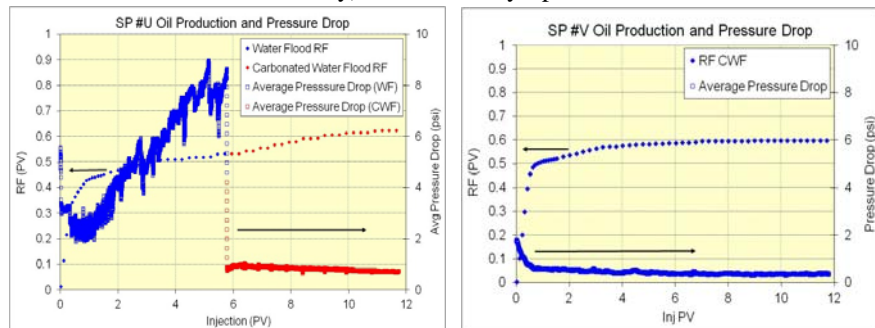

Figure 7: RF and Pressure Drop vs. Injection PV for Sand Packs #U (WF + CWF) and #V (CWF Only) with 2 PV/day Speed