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Improve Low-Permeability Gas Productivity with Unique Flow-Back Chemistry

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Abstract

Gas reservoirs with a permeability of less than about 1 mD are highly sensitive to water saturation. When filtrate or clear brine is lost into these formations, capillary forces pull the fluid into pore spaces and prevent full displacement upon production. This increase in water saturation reduces the relative permeability of the reservoir to gas. Because clear brine completion fluids are generally considered non-formation damaging, this effect is often overlooked as a source of damage to such low-permeability gas productivity.

The authors initiated a study to evaluate chemistries that can be added to completion and workover brines that will effectively reduce capillary forces, recover invaded brine from the formation, and promote optimal productivity of the well. This paper introduces a new and unique flow-back additive that is compatible with all common types of completion and workover brines within a density range of 8.5 to 19.2 lb/gal, is not absorptive to a porous formation matrix, and does not generate stable foam. Simple, low-cost, and innovative methodologies are presented to test capillary pressure reduction and brine recovery in a simulated formation, and that clearly demonstrates this effect in a laboratory setting. The paper illustrates how effective flow-back chemistry reduces water saturation, enhances productivity, and shows the benefit of applying such novel chemistry for low-permeability gas reservoirs.

Introduction

Low-permeability gas reservoirs are usually considered to have a reservoir matrix with an effective *in-situ* permeability to gas of less than 1.0 mD and contain potentially mobile gas saturation. Extensive reserves of natural gas are present on a worldwide basis in both sandstone and carbonate formations that exhibit those properties.[1] For these reservoirs, it has been extensively shown that water-based fluids can significantly reduce reservoir permeability, effective flow area, effective fracture lengths, and impair well productivity.[2,3] This is the result of increasing near wellbore water saturation through the invasion of a water-based fluid into a hydrocarbon-bearing formation. In the case of hydraulic fracturing, the trapped fluid surrounds not only the fracture, but resides within the fracture itself.[4] During the production phase, when oil or gas flows through this low-permeability zone, it may take a considerably long time before the invaded fluid is expelled.[5]

Spontaneous imbibition occurs within low-permeability, under-saturated reservoirs whenever they are exposed to another fluid that has a high invasion potential. Highly invasive fluids typically consist of clear, solids-free brines such as completion fluids.[6] The depth of imbibitions into the rock is determined not only by the permeability and saturation of the reservoir, but also by the chemical affinities between the gas, rock reservoir fluid, and the invading fluids. Chemically driven imbibitions cannot be stopped simply by being under-balanced. On the other hand, to remove the invaded fluids from the formation, the capillary effect (fluid retention force) needs to be overcome.

Both imbibition force and fluid retention force can be quantified by the calculation of capillary pressure. Capillary pressure in porous media is usually simplified in the form of the following equation.

$$P_C = \frac{\gamma \cdot Cos\,\theta}{d}$$

Where:

γ = surface tension (milli-Newton per meter or Dynes/cm); $Cos\ \theta$ = cosine of contact angle between the rock, fluid, and gas; d = diameter of pores in mm. The unit of capillary pressure is Pascal.

For water-wet reservoirs such as sandstone, water spreads on (or wets) the formation surfaces and is spontaneously imbibed into the porous channel. Inside the pore channel, fluid that is in contact with the pore wall moves faster than the fluid in the center of the channel. This creates a water-gas surface in a concave shape as illustrated in **Fig. 1.** This gas-water surface exerts a tension that is tangential to the surface and in the direction illustrated by the arrow labeled **γ**. This surface tension resolves to its component forces perpendicular and parallel to the surface. The parallel force, $\boldsymbol{\gamma_S}$, which equals to $\gamma \cdot Cos\theta$, is the driving force for fluid to propagate further into the porous channel.

Obviously, to “push” the imbibed fluid out of the porous channel, the counter force needs to be higher than the capillary pressure. In other words, the larger the capillary pressure, the more difficult it is for the fluid to vacate the pore space resulting in fluid retention in the formation. The permeability facies in tight reservoirs have an extremely small effective pore throat radii and/or microfracture widths, and therefore, significant capillary pressures must be accounted for.

If the surface of the porous channel is oil-wet, (i.e., water - based fluids do not spread or wet the surface), the fluid cannot then spontaneously imbibe into the pores. In an overbalanced situation, fluid will be forced into the porous channel, but the water-gas surface would be in a convex shape as illustrated in **Fig. 2**. As the fluid attempts to recede from the surface, fluid in the center of the porous channel moves faster than the fluid on the surface. Therefore, the surface tension is reverse and tangential to the water-gas surface, as indicated by the arrow labeled **γ**. Thus, water-based fluid retention is less of a concern in oil-wet reservoirs.

One can see that capillary pressure can be reduced by either reducing surface tension or increasing the contact angle. Surface-active materials have been studied and applied, attempting to achieve such purposes. While most effort has been allocated towards fracturing fluids, where water or light density brines are often applied, little effort has been devoted to clear brine completion fluids or drill-in fluids to manage the issues of high salinity, high pH, and high solids content.

Therefore, this paper initiated a study to evaluate chemistries that can be added to clear brines within a density range of 8.5 to 19.2 lb/gal. These chemistries must effectively reduce capillary forces, recover invaded brine from the formation, and promote optimal productivity of the well. This paper introduces a new and unique flow-back additive that is compatible with all common types of completion and workover brines, is not absorptive to a porous formation matrix, and does not generate stable foam.

This paper also presents a series of low-cost and innovative methodologies to test capillary pressure reduction and brine recovery in a simulated formation, as it has always been a challenge to establish simple, straight-forward testing methods to demonstrate the capillary effect, and to evaluate different chemicals in a consistent manner.

Experimental

Additive Compatibility with Brine

Compatibility testing between brine and flow-back additives was conducted. The additives were blended with all common types of brines (KCl, NaCl, $CaCl_2$, $CaBr_2$, $ZnBr_2$, and formates) at 0.5 ~ 1.0 vol% and static aged for several days at both room temperature and 150°F (65.5°C). Visual observations were performed to detect any incompatibilities (such as cloudiness, precipitates, and phase separation) between the additive and the brine.

Formation Adsorption

Surface-tension measurements were made with a DuNouy ring tensiometer (CSC Scientific, model 70545) at room temperature and atmospheric pressure. To determine formation adsorption tendency of the flow-back additives, the surface tension of the treated brine was measured before and after intimate contact with synthetic formation material. The synthetic formation is comprised of 70 wt% of natural sand (50/70 mesh), 10 wt% of fine calcium carbonate, 10 wt% of silica flour, and 10 wt% clay.

These tests were conducted per the following procedure:

1) Transfer 50 mL of brine to a glass jar

2) Add 15 g of synthetic formation material to the brine

2) Dynamically age the glass jar at 104°F (40°C) for 15 hr

3) After aging, filter out the brine portion through 1.2-µm filter paper

4) Measure the surface tension

Foam Control

Foam testing was conducted by hand shaking the solution to generate foam and then monitor the foam volume versus time. Details are as follow:

1) Prepare the brine with flow-back additives

2) Transfer 100 mL of fluid into a 250-mL graduated cylinder

3) Vigorously shake the cylinder for 10 s to generate foam

3) Start timer and record foam volume versus time

Tests were also conducted to determine foaming characteristics when a significant amount of air is entrapped in the brine, such as when it is in turbulent flow. To simulate a large amount of air-trapping during turbulent flow, foam was generated by shearing 500 mL of the fluid on a high speed mixer (Silverson) set at 6,000 rpm and the rate of total volume expansion was monitored. If the total volume continuously increased as the fluid was sheared, the product failed the foam-control test. On the other hand, if the entrapped air collapsed fast enough so that the total volume maintained the same level during the shearing, foam control was considered successful. When the total volume reached 1,000 mL, the mixer was stopped and the foam dissipation rate was recorded. If the foam totally disappeared within one minute the test was successful.

Brine Imbibition Test

Brine imbibitions were tested with 2-in. long by 2-in. diameter dry sandstone cores. Twenty milliliters of brine was placed in a pint-sized jar lid. A 100-mD sandstone core was positioned in the lid, the timer was started, and the propagation of brine upward along the core was recorded.

The sandstone core was periodically removed from the brine, at preset time intervals, and weighed on a balance. The increase in core weight indicates the amount of brine spontaneously imbibed into the core under capillary pressure.

Brine Recovery Test

Experiments of brine recovery (or drainage) were designed to assess the ability of the non-treated brine or additive solutions to unload from porous media. A detailed procedure is listed below:

1) Fix an aloxite disk to the 250-mL HTHP cell (Fig.3-1)

2) Fill the cell with 170 g of 100-mesh sand to represent a coarse, non-swelling formation or 130-g synthetic formation material to represent a tight, swelling formation (Fig.3-2a and Fig. 3-2b)

3) Transfer 50 mL of brine into the cell for a non-swelling formation or 35 mL of brine for synthetic formation pack. (this amount of brine will fill the pores in the sand pack without leaving an excess brine phase on top)

4) Put on the top end cap and connect the cell with the air

pressure charger (Fig.3-3)

5) Adjust air pressure to 0.5 psi and open the bottom stem of the cell to collect fluid. Maintain the pressure for 10 minutes. Record the volume of fluid collected during the 10 minutes.

6) Increase air pressure to 1.0 psi and maintain the pressure for 10 minutes. Record the accumulative volume of fluid collected at the end of the 10 minutes.

7) Follow the same procedure to test air pressure at higher psi. Run the test for 10 minutes at each pressure.

8) Calculate percentage of brine recovery by dividing the accumulative brine volume collected at each air pressure by the initial total brine volume (**Table 1**)

9) Plot percent brine recovered versus air pressure (Fig. 3-4).

Results

Additive Compatibility with Brine

Full compatibility between the additive and the base brine ensures that the additive's molecules are uniformly distributed in the brine. This is important so that the additives can be delivered to wherever the brine goes. In addition, full compatibility leads to stable fluids that will not phase separate or precipitate during aging or as temperature changes. Incompatibility can lead to additive failure or even cause formation damage. Furthermore, the benefit of developing a single product compatible in the complete range of brines greatly facilitates future logistical and inventory issues. Both commercial and proprietary products were investigated for compatibility in commonly used brines ranging in densities from 8.5 to 19.2 lb/gal. Incompatibility is often observed with certain types of brines or at elevated temperature, as shown in **Table 2**. **Table 3**, on the other hand, shows example products that are compatible with all the brines in the matrix. When a product demonstrates compatibility in all brines, it qualified for additional testing.

Formation Adsorption

The interaction between flow back additives and formation media was characterized by measuring the change in surface tension before and after contacting simulated formation material containing sand, clay, silica flour and carbonate. The preferred product should show little to no adsorption tendencies onto the formation. This is validated by measuring the surface tension before and after exposure to the simulated formation, that is, a low surface tension is maintained after exposure to the formation. The criteria are set so to avoid having a product that is depleted from the solution.

A strongly adsorbing additive will alter the contact angle in the near wellbore or fracture region, but may leave the resulting leak-off fluid farther in the reservoir, with a high surface tension, and thus a high capillary force. Furthermore, this same application extends to reservoir drill-in fluids to lower the capillary force of filtrate. For this to occur, the surfactant molecule must not be retained and/or adsorbed on the solids present in the formulation (drill solids, clays, calcium carbonate or barium sulfate, etc.), so that the molecule can easily pass through the external and internal filter cake.

Three types of performance were observed for the formation adsorption tests. Some products can initially reduce the surface tensions of brines effectively, but when exposed to the simulated formation, surface tensions return to approximately 50 to 70 dyne/cm, as shown in **Table 4** with product Nonq-1. Some products, when applied with low density brines (such as 3 wt% KCl), can maintain a low surface tension after contacting the simulated formation, but cannot maintain low surface tension when applied in higher density brines such as 10.6 lb/gal NaCl/Br. An example of this type is given in **Table 4** as product Nonq-2. The third type of product is shown in **Table 4** as Qual; where low surface tension was maintained for both light and heavy brines. Therefore, Qual is preferred over Nonq-1 and Nonq-2.

Foam Control

It is well known that surface tension reducers promote and stabilize foams. Foam may cause circulation problems, (such as low efficiency pumping), storage problems (such as overflow), and a reduction in density. Therefore, it is very important to ensure that the brines treated with flow back additives possess no foaming issues during mixing, transferring, and pumping. Highly effective antifoaming and/or defoaming agents were rigidly evaluated and included as part of the formula.

Foam stability was first tested by shaking the solution containing the flow back additive to generate foam. One of the criteria for qualifying foam control is that the foam generated by shaking should disappear within a few seconds. The foam was then tested in a more stringent manner: fluids with flow-back additives were sheared on a high-speed mixer set and the rate of total volume expansion was monitored. If the total volume continuously increased as the fluid was sheared, the product failed the foam-control test. On the other hand, if the entrapped air collapsed fast enough so that the total volume maintained the same level during the shearing, foam control was considered successful. When shearing was stopped, foam should totally disappear within one minute. Many commercial and proprietary antifoaming/defoaming materials were evaluated, but very few met the stringent requirements. Some can effectively control the foam, but will push the flow-back additive, or partial gradients of it, out of solution, rendering it unusable.

Brine Imbibition

The magnitude of capillary pressure can be compared through the measurement of completion brine imbibed into a core plug. The photo sequence shown in **Fig. 4** demonstrates the capillary pressure lowering effect of a flow-back enhancer in 11.6-lb/gal $CaCl_2$ brine with a synthetic sandstone core. A 100-mD synthetic sandstone core was positioned in the lid, the timer started, and propagation of brine upward along the core was recorded. The treated brine propagated slower than the untreated brine giving a clear indication of reduced capillary pressure.

Other than visually capturing the difference a flow-back additive makes in spontaneous imbibitions, this effect can also be easily measured numerically by weighting the amount of brine adsorbed with and without the flow-back additive. **Table 5** shows the results of one such comparison test with 20 grams of 5 wt% KCl. The cores were periodically removed from the brine and weighed on a balance. The increase in weight indicates the amount of brine spontaneously imbibed into the core. One can see that the untreated brine moved inside the core faster than the treated brine, demonstrating that the treatment with the flow-back enhancer decreased capillary pressure.

Brine Recovery Test

The brine recovery or drainage test was designed to demonstrate that by reducing capillary pressure, fluid would easily flow back out of a formation, thereby reducing fluid retention in porous media. These tests were conducted to recover brine from a sand pack (or a simulated formation pack) using gas (air).

Fig. 5 shows the recovery (or drainage) of untreated and treated 5 wt% KCl from the sand pack. The sand pack was chosen to represent a coarse and non-swelling formation. One can see that the treatment with the flow-back enhancer significantly improved brine drainage. At the lowest tested pressure of 0.5 psi, the untreated brine had 52% recovery, while the treated brine had 65% recovery.

Fig. 6 shows the drainage of the same brines from a simulated formation pack. This formation contains sand, clay, silica flour, and carbonate to represent a tight and swelling formation. Again, results show that the treatment with the flow-back enhancer (Qual) improved brine drainage by about 50%.

The synthetic formation material used in the brine recovery test is the same composition as the formation adsorption test. Additives that passed the adsorption test and qualified as non-adsorptive were able to improve brine recovery from the synthetic formation pack. Consistently, the additives that did not pass the adsorption test, that is, adsorbed to the simulated formation and were not able to maintain a low surface tension, did not improve the recovery of the brine either. As shown in **Fig. 7**, (the result of the recovery of 11.6-lb/gal $CaCl_2$ brine from the synthetic formation pack), the non-adsorptive flow-back enhancer (Qual) was able to improve the recovery of brine by 3 to 5 times more than the untreated brine. The other two products, Nonq-1 and Nonq-2, which did not pass the adsorption test, were not able to improve brine drainage at all.

Conclusions

- This paper initiated a study to evaluate chemistries that can be added to completion and workover brines to effectively reduce capillary forces, recover the invaded brine from the formation, and promote optimal productivity of the well.
- The authors created a testing matrix in which a sizeable quantity of flow-back additives can be evaluated and compared in a fast, simple, and yet comprehensive, controlled manner;
- This paper introduces a new and unique flow-back additive that is compatible with all common types of completion and workover brines within a density range of 8.5 to 19.2 lb/gal, is not adsorptive to a porous formation matrix, and does not generate stable foam.
- Simple, low-cost, and innovative methodologies are presented to test capillary pressure reduction and brine recovery in a simulated formation, and that clearly demonstrates this effect in a laboratory setting.

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Table 1: Brine Recovery from a Sand Pack (vol%)

Air Pressure	3% KCl	10.6-lb/gal NaCl/NaBr	11.6-lb/gal $CaCl_2$
1 psi	50.2	51.7	18.8
2 psi	58.5	57.4	40.4
3 psi	66.0	59.0	49.7
4 psi	70.2	68.2	54.5
5 psi	76.6	71.6	60.0

* Percent brine recovered is calculated by dividing the accumulative brine collected at each air pressure by the initial total brine volume.

Table 2: Test Result Example of Disqualifying Product for Compatibility Test of Brine and Flow-Back Additive

Brine	Observation with 0.5 to 1.0 vol% Additive	
	Room temp	150°F
Seawater	clear	cloudy
3 wt% KCl	clear	cloudy
9.5-lb/gal KCl	clear	cloudy
9.2-lb/gal NaCl	clear	cloudy
10.6-lb/gal NaCl/Br	turbid	cloudy
11.6-lb/gal $CaCl_2$	clear	clear
10.6-lb/gal NaBr	clear	cloudy
12.5-lb/gal NaBr	turbid	cloudy
12.5-lb/gal $CaBr_2$	clear	clear
14.2-lb/gal $CaBr_2$	turbid	phase separation
13.1-.lb/gal $KCHO_2$	not dispersible	clear
19.2-lba/gal $Zn/CaBr_2$	cloudy	Phase separation

Table 3: Test Result Example of Qualifying Products for Compatability Test of Brine and Flow-Back Additive

Brine	Observation with 0.5 to 1.0 vol% Additive	
	Room temp	150˚F
Seawater	clear	clear
3 wt% KCl	clear	clear
9.5-lb/gal KCl	clear	clear
10.6-lb/gal NaCl/Br	clear	clear
11.6-lb/gal $CaCl_2$	clear	clear
12.5-lb/gal NaBr	clear	clear
14.2-lb/gal $CaBr_2$	clear	clear
10.0-lb/gal $NaCHO_2$	clear	clear
13.1-lb/gal $KCHO_2$	clear	clear
19.2-lb/gal $Zn/CaBr_2$	clear	clear

Table 4: Surface Tension of Brines Treated with 0.5 vol% Additive - Before and After Contacting the Simulated Formation Material

Surface Tension (dyne/cm)	Nonq-1		Nonq-2		Qual	
	Before	After	Before	After	Before	After
5 wt% KCl	33.8	53.7	32.1	34.3	31.4	35.3
10.6-lb/gal NaCl-NaBr	33.7	70.0	31.5	63.9	34.6	34.5

Table 5: Imbibition Effect of Flow-Back Additive on Sandstone Core in Contact with 5 wt% KCl Brine

Time (min)	Weight of Brine Spontaneously Imbibed into the Core (g)		
	5 wt% KCl Blank	with 0.5 vol% Qual	Difference Δg
Initial	0.0	0.0	
5	7.5	6.1	1.4
15	12.6	11.0	1.6
20	14.3	12.5	1.8
25	15.7	13.7	2.0
Surface Tension (mN/m)	75	27.7	

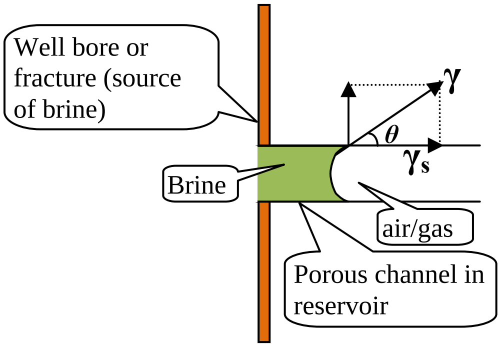

Fig. 1: Illustration of brine-gas surface in water-wet formation

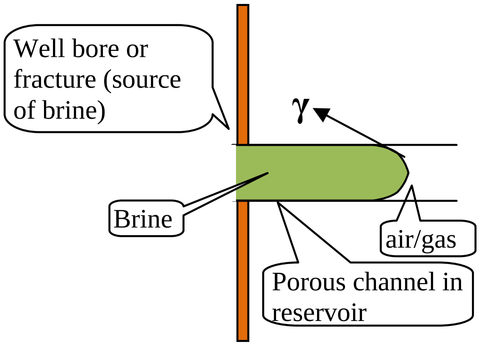

Fig. 2: Illustration of brine-gas surface in oil-wet formation

Fig. 3-1: Fann HTHP cell with FA0-00 disk.

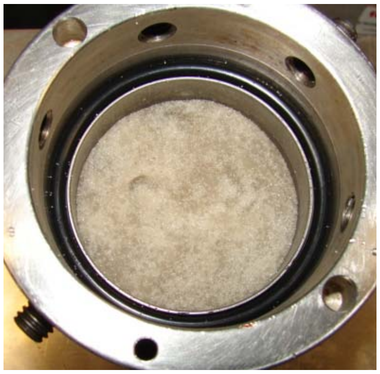

Fig. 3-2a: Fann cell loaded with sand and brine.

Fig. 3-2b: Fann cell loaded with synthetic formation and brine.

Fig. 3-3: Fann cell connected to air pressure charger.

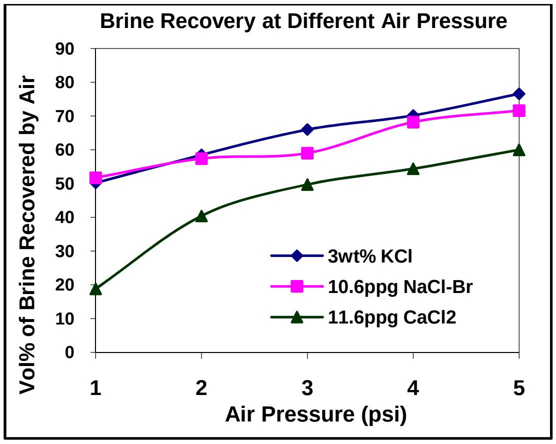

Fig. 3-4: Brine recovery chart (based on data in Table 1).

Fig. 4: Imbibition of brine into dry sandstone cores. Both cores are resting in 11.6-lb/gal $CaCl_2$ brine. The core on the left is untreated and the core on the right is treated with flow-back enhancer. Note imbibition of brine as time increases from top to bottom of photo sequence.

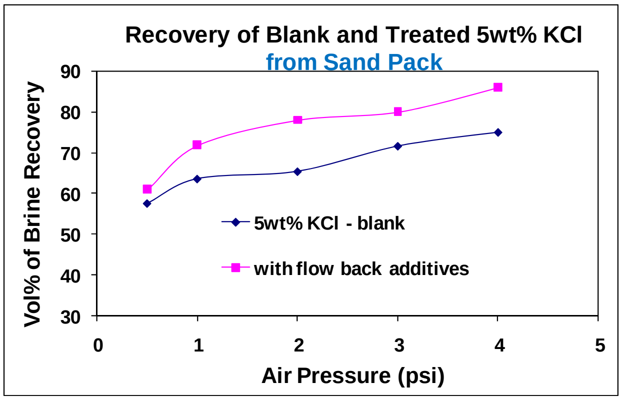

Fig. 5: Recovery of 5 wt% KCl brine from sand pack.

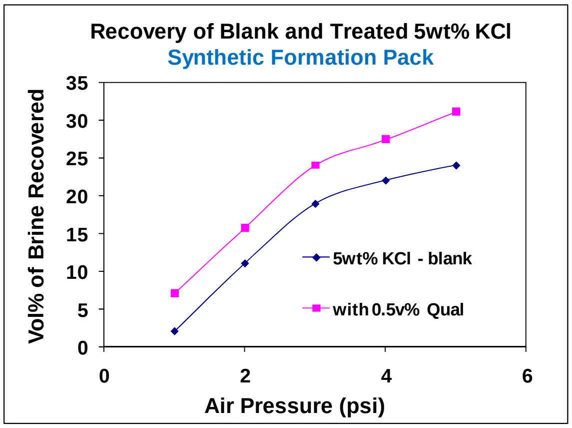

Fig. 6: Recovery of 5 wt% KCl brine from simulated formation pack.

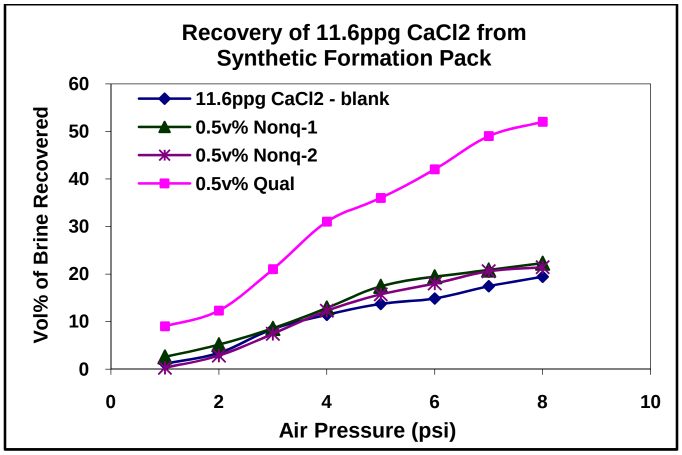

Fig. 7: Recovery of 11.6-lb/gal $CaCl_2$ brine from simulated formation pack.