SPE 80901

A Successful Methanol Treatment in a Gas-Condensate Reservoir: Field Application

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This paper was prepared for presentation at the SPE Production and Operations Symposium held in Oklahoma City, Oklahoma, U.S.A., 22–25 March 2003.

Abstract

A field test was conducted to investigate the effectiveness of methanol as a solvent for removing condensate banks that form when pressure in the near wellbore region falls below the dewpoint. Core flood experiments on Texas Cream Limestone and Berea cores show that condensate accumulation can cause a severe decline in gas relative permeability, especially in the presence of high water saturation. This can result in well productivity declining by a factor of 3 to 5 as bottom hole pressure declines below the dewpoint. PVT analysis performed on field samples taken from the Hatter's Pond field in Alabama indicate retrograde condensate behavior. These high-temperature deep gas wells show low gas productivity and large skin. A preliminary analysis of the data indicated the possibility of condensate and water blocking due to the loss of water-based drilling fluids. Core samples were used to measure gas relative permeability. Compatibility tests were conducted to ensure that the injection of filtrate and methanol did not cause any damage to the core. Since the formation brine is very saline, tests were conducted to check for salt precipitation during methanol injection. Based on these laboratory results and a single-well numerical simulation, a field test was conducted. The well chosen for treatment was producing 250 MSCFPD with 87 BPD of condensate. A thousand barrels of methanol was pumped down the tubing at a rate of 5 to 8 B/min. Gas production increased by a factor of 3 initially and stabilized at about 500 MSCFPD. Condensate production doubled to 157 BPD. The well shows a skin of –1.9 after methanol treatment. The increase in gas and condensate production was observed to persist more than 10 months after the treatment.

Several possible explanations are provided for the positive results obtained in this test. Some general conclusions are made for the design for future treatments.

Introduction

Gas production from reservoirs having a bottom hole flowing pressure below the dewpoint pressure results in an accumulation of a liquid hydrocarbon near the wells. This condensate accumulation, sometimes called condensate blocking, reduces the gas relative permeability and thus the well's productivity. Condensate saturations near the well can reach as high as 50-60% under pseudo steady-state flow of gas and condensate.[1] Even when the gas is very lean, such as in the Arun field with a maximum liquid drop out of 1.1%, condensate blocking can cause a large decline in well productivity.[2-4] The Cal Canal field in California showed a very poor recovery of 10% of the original gas-in-place because of the dual effect of condensate blocking and high water saturation.[5]

Several methods have been proposed to restore gas production rates after a decline due to condensate and/or water blocking.[6-9] Gas cycling has been used to maintain reservoir pressure above the dewpoint. Injection of dry gas into a retrograde gas-condensate reservoir vaporizes condensate and increases its dewpoint pressure.[8] Injection of propane was experimentally found to decrease the dewpoint and vaporize condensate more efficiently than carbon dioxide.[10] Hydraulic fracturing has been used to enhance gas productivity, but is not always feasible or cost-effective.[5,11] Inducing hydraulic fractures into the formation can increase the bottom hole pressure. Hydraulic fracturing successfully restored the gas productivity of a well that died after the flowing bottom hole pressure dropped below the dewpoint.[12]

Recently, a new strategy of using solvents was developed to increase gas relative permeability reduced by condensate and water blocking.[7,9] Al-Anazi et al.[9] found that methanol was effective in removing both condensate and water and restored gas productivity in both low-permeability limestone cores and high-permeability sandstone cores. Gas productivity decreased about the same extent in both low and high permeability cores due to condensate blocking. After methanol treatment, an enhanced flow period is observed in both low and high permeability cores. Condensate accumulation is delayed for a certain time. During this time, the productivity index is increased an order of magnitude in both low and high permeability cores. The duration of the enhanced flow period is controlled by the volume of methanol injected and its rate of mass transfer into the flowing gas phase after treatment. Methanol treatments remove both water and condensate by a multi-contact miscible displacement if sufficient methanol is injected.

Laboratory Studies

Available core plugs from the Smackover dolomite varied in porosity from 9 to 15% and in air permeability from 0.2 to 5 md. Plugs from the Norphlet sandstone varied in porosity from 7 to 15% and in permeability from 0.2 to 150 md. Corefloods were conducted with plugs from the Norphlet sandstone of the Hatter's Pond field.[13] Fluids used in the corefloods included a water sample from Hatter's Pond field, three synthetic brines, and methanol. Three synthetic brines were prepared. The three brines contained 0 wt%, 12 wt%, and 24 wt% sodium chloride (NaCl) plus 500 ppm Ca^{2+} to prevent clay swelling. Table 1 gives the viscosity of each fluid. The cores included plugs from both the Smackover and the Norphlet formations.

Figure 1 shows a schematic diagram of the coreflood apparatus. A coreholder capable of accommodating 1.0 inch diameter core plugs was used in these corefloods. A pressure transducer and a digital data recorder monitored and recorded the differential pressure. A fraction flow collector captured effluent samples in graduated vials. Fluid properties were also measured during these experiments. A couette viscometer was used to measure the viscosity of the water sample from Hatter's Pond field and a picnometer and electronic balance were used to measure the density.

The experimental steps in these corefloods were physical property measurements, core preparation, and coreflooding. Since the Norphlet sandstone core plugs were less than an inch in length, two plugs with similar porosity and permeability were used in series for the coreflood experiments. Cores #10 and #11 were chosen for coreflooding because of their relatively high, and similar, porosity and permeability. Table 2 gives the properties of cores #10 and #11, including the properties of the combined cores.

The two cores, #10 and #11, were placed in series into the coreholder with a piece of very thin laboratory tissue paper between them for capillary contact. Axial and radial confining pressure were then applied. In order to remove any air (nitrogen) from the core, the core was vacuumed for 1 hour, flushed with carbon dioxide for 10 minutes, vacuumed again, flushed with carbon dioxide, and finally vacuumed overnight. Carbon dioxide is more water soluble than nitrogen, and it was assumed the core would have zero gas saturation when subsequently saturated with brine.

Steady-state corefloods were conducted on the composite Norphlet sandstone core (cores #10 and #11) to observe the effect of methanol injection on the permeability of brine-saturated core. Special attention was given to monitor the injection pressure during coreflooding, in case core damage occurred due to salt precipitation, clay swelling, or fines migration. Effluent was collected in graduated vials to measure flow rate.

The water sample from Hatter's Pond field was used to saturate the composite core. No steady-state permeability was measured for this fluid. During initial injection, it was thought that the water sample might cause clay swelling since it was so fresh. Instead, the water with 500 ppm Ca^{2+} was used. Methanol permeability was subsequently measured. After the core was shut in overnight, the methanol permeability was re-measured. This procedure was repeated for the 12 wt% and 24 wt% NaCl brines except no shut-in was conducted for the latter test. Finally, large quantities of the 500 ppm Ca^{2+} brine were injected to see if any damage from salt precipitation could be removed. The brines and methanol were injected at rates of 0.5 to 2 cc/min. Steady state was obtained for one to three rates and 10 to 40 pore volumes were injected for each permeability measurement.

Salt Solubility data. The salinity of the formation water at Hatter's Pond field is an important parameter when considering methanol injection to treat condensate and/or water blocking. The water sample obtained from Hatter's Pond was initially thought to be very saline since the formation brine is known to be very saline. The viscosity and density of the sample were measured at 20°C and found to be 0.99 cp and 0.9998 g/cc, respectively (nearly identical to pure water at this temperature). The resistivity was measured to be 12.3 Ω-m, which corresponds to 300 ppm of NaCl equivalent. The sample was analyzed for electrolytes (Table 3) and found to have 43 ppm Na^+ and 32 ppm Ca^{2+}. The water sample from Hatter's Pond was apparently fresh.

The above data cast doubt on the assumption that the brine in the near wellbore region is very saline. Texaco has been circulating fresh water into these gas-condensate wells to deliver anti-corrosion agents and remove scale. Also, loss of water based drilling fluids may have influenced the salinity in the near wellbore region. This might account for the low salinity of the water sample compared to several estimates of the formation salinity that are all very high. Indeed, the brine salinity in the near wellbore region is uncertain and probably not uniform.

The salinity of the Hatter's Pond formation water is important since mixtures of methanol and high salinity brine could cause salt precipitation when the methanol is injected.[6] Therefore, several solubility tests were done. The solubility of NaCl in pure water at 78° was measured as 263,000 ppm. The value for pure methanol was measured as 990 ppm. Figure 2 shows the mixing paths during injection of methanol into a formation with two different assumed values of salinity (points 1 and 1' being 120,000 and 240,000 ppm NaCl, respectively). If pure methanol is injected, the concentration at the effluent will follow the mixing line 1-2 or 1'-2, depending on the salinity of the brine. If the salinity is 240,000 ppm, precipitation will occur along most of the mixing path.

Figure 3 shows the temperature dependence of NaCl solubility in methanol-water mixtures. Experimental solubility of NaCl in methanol-water mixtures is given for two temperatures (78 and 175°F) and extrapolated to 315°F, which is the average reservoir temperature at Hatter's Pond field). The estimated maximum brine salinity that can mix with methanol and not cause precipitation is 240,000 ppm at 315°F.

The viscosity of methanol-water mixtures is not a linear function of concentration, but has a maximum at a methanol weight fraction of about 0.4 (Fig. 4). Thus, an increase in differential pressure could occur during methanol injection into a brine-saturated core even if no other process takes place.

Coreflood Data. A summary of the Hatter's Pond coreflood data is given in Table 4. For each permeability measurement, data are given for the fluid viscosity, measured flow rate, differential pressure, and pore volumes injected. During initial injection with the water sample from Hatter's Pond, differential pressure showed an increasing trend. Injection was stopped since there was a concern that the water might not have enough hardness to prevent swelling of clays in the Norphlet sandstone. Subsequently, brines with higher salinity were injected to avoid irreversibly damaging the core due to clay swelling.

Figure 5 shows the measured differential pressure and effluent flow rate during coreflooding with the 500 ppm Ca^{2+} brine. The permeability was 81 md based on a flow rate of 0.94 cc/min and a differential pressure of 2.2 psi.

Figure 6 shows the measured differential pressure and flow rate during the subsequent methanol flood. During this flood, it was not known that the methanol accumulator was leaking. While the measured effluent flow rate and differential pressure remained accurate, it was difficult to obtain steady-state flow due to the leak. However, the flow does approach steady-state for part of the flood (~1.7 cc/min at ~2.5 psi). Using these data, the permeability to methanol was calculated to be 75 md. This was a 7% reduction in permeability from the low salinity brine permeability. The core was then shut-in overnight.

The following day, methanol was re-injected to see if the core was damaged due to clay swelling. Figure 7 shows the methanol re-injection after the shut-in period. Again the methanol accumulator had been unknowingly leaking. The flow appeared to approach a steady-state for part of the flood (~1.8 cc/min at ~2.7 psi). The methanol permeability remained essentially unchanged at 74 md.

Next, a 12 wt% NaCl brine (with 500 ppm Ca^{2+}) was injected through the core. Differential pressure and effluent rate for this flood can be seen in Fig. 8 and are plotted in terms of pore volumes injected. Steady state is reached quickly without a large spike in pressure (i.e., no indication of salt precipitation). However, small amounts of the effluent at the beginning of the injection were cloudy, but became clear with time. The permeability of the 12 wt% NaCl brine was calculated to be 67 md for a flow rate of 0.91 cc/min and a differential pressure of 3.3 psi. This was an 11% reduction in permeability from the methanol permeability.

Figure 9 shows the subsequent injection of methanol into the core, which was saturated with the 12 wt% NaCl brine. The permeability to methanol was 43 md at a flow rate of 0.94 cc/min and a differential pressure of 2.4 psi. A small volume of the effluent at the beginning of the injection was cloudy, but became clear with time.

The core was shut-in overnight and methanol was injected the next day, as illustrated in Fig. 10. The same methanol flow rate as the day before gave about 1 psi higher differential pressure reading. The permeability was calculated to be 31 md. The reduction from 67 to 31 md was a 54% decrease in permeability from the methanol permeability before the 12 wt% NaCl brine injection. The reduction in brine permeability was probably due to NaCl precipitation, as the mixing path for this flood is very close to the solubility limit.

The 24 wt% NaCl was then injected, as shown in Fig. 11. Upon injection of this very saline brine, the differential pressure spiked at a flow rate of 1 cc/min, which was not seen in the previous cases. The differential pressure was monitored and the flow rate was decreased to 0.5 cc/min to allow the differential pressure to stay in range of the pressure transducer (10 psi). This increase in resistance was due to NaCl precipitation plugging pore throats of the core, as almost the entire mixing path is in the precipitation range. The first vial of effluent collected in this flood (about one pore volume) contained about 0.1 cc of precipitate at the bottom of the vial. The permeability of core was 28 md using the measured flow rate of 0.48 cc/min and a differential pressure of 5.8 psi. There is a gradual increase then decrease in differential pressure during the later stages of the flood, and this could be due to precipitation/dissolution or viscosity effects.

Next, methanol was injected as shown in Fig. 12. No large pressure spike was observed, so the flow rate was increased to a value of 1 cc/min. The differential pressure during the methanol flood shows a steadily increasing trend. The first vial of effluent collected in this flood (about two pore volumes) contained about 0.1 cc of precipitate at the bottom of the vial. The permeability was 18 md (a 36% reduction) using the measured flow rate of 0.94 cc/min and a differential pressure of 5.8 psi (the flow was not steady-state).

Next, the 500 ppm Ca^{2+} brine was injected to determine if the permeability could be restored by dissolving salt in the core. More than 300 pore volumes were injected. The injection was carried out at a nominal flow rate of 4 cc/min (with the pressure transducer closed off from flow) at a differential pressure estimated to be 20 psi. The permeability of the core was 33 md using a flow rate of 0.67 cc/min and a differential pressure of 3.95 psi. Some permeability restoration was achieved (83% increase from the final methanol permeability, 18 md).

These corefloods reinforce phase behavior data indicating what brine salinities would cause core plugging. Surprisingly, even though the core was exposed to methanol-brine mixing paths almost entirely in the precipitation range, the core did not suffer a full order of magnitude reduction in permeability from its original value of 81 md. At reservoir temperature in Hatter's Pond field, brine salinities as high as 240,000 ppm could be encountered without plugging of the formation.

It would have been instructive to re-measure the brine permeability after each methanol injection before proceeding to the next salinity. This would have shown how methanol injection affected the brine permeability for each salinity examined. Also, finer increments in salinity would have given a more detailed understanding of methanol-brine interaction in core.

Field Application

Field History. Hatter's Pond field, located in southwestern Alabama, was discovered in 1974. The field produces from two formations, the Smackover, a shallow marine dolomite and the Norphlet, aeolian sandstone. The formations have permeability in the range of 2 to6 md and porosities in the range of 12 to 15%. The combined pay of the Smackover and Norphlet formations averages 200 to 300 feet at subsea depths ranging from approximately 18,000 ft to 18,300 ft.[15] During the first phase of field development (1974-1985), a total of 40 wells were drilled. 25 of these wells were plugged and abandoned leaving only 15 wells as producers. In the second phase of development (1985-present), 11 wells were drilled (7 new producers, 3 replacements, and 1 gas injector) and 2 sidetracks (1 producer and 1 gas injector). On January 2002, the field was producing 4,700 BPD of condensate (API~50°), 2,200 BPD NGL, and 33 MMSCF/D of gas.

With an average reservoir temperature of 315°F, this is a relatively deep and hot formation with connate water that is very saline. The salinity of the formation water ranges from 164,000 to 206,000 mg/l. The predominant ions are Na^+, Ca^{2+}, K^+, and Cl^-.

Well History. Hatter's Pond Unit Well 3-6 #1 was drilled to 18,550 ft and initially completed in the Norphlet formation in June of 1997. A typical log section of the formations are shown in Fig. 13. The Norplet formation had 126 ft of pay, with k=1.25 md and porosity = 11.7%. The Smackover had 23 ft of pay with k= 0.34 md and porosity = 8.0%. A 5-1/2 inch liner was run and cemented. The 5-1/2" liner was then tied back to the surface. A 2-7/8", packerless tubing string was run inside the 5-1/2" casing. Production flows up the annulus, with the 2-7/8" tubing serving as a treating string (Fig. 14). Fresh water to dissolve salt and corrosion inhibitors are injected in the tubing and chased with sweetened, gaslift gas. The lower Norphlet was perforated at 18,290 to 18,345 ft with 6 spf and acidized with HF mud acid. An initial static BHP was 3230 psi. The lower Norphlet was tested at 2.7 MMCF/D and 348 BPD of condensate. The upper Norphlet was perforated at 18,259 to 18,267 ft, but had no effect on production. Perfs were added to the Smackover formation at 18,228 to 18,253. Again, no significant change in rates were observed.

The productivity of the well gradually decreased with time until it reached 0.25 MMSCF/D and 87 BCPD. The productivity decline may be due to skin induced by loss of water-based mud filtrates and completion fluids, as well as condensate blocking due to production below the dewpoint pressure. Tests conducted on this well showed an average reservoir pressure of 3,519 psi, which is below the dewpoint, a permeability of 0.039 md, and a total skin of 0.68.

Methanol Treatment. In December of 2000, Well #3-6 was treated with 1,000 bbl of methanol. Methanol was bullheaded down the tubing at a rate of 5 to 8 bbl/min. Due to the high injection pressures encountered during the treatment, balls were not used as diverters.

Production from the well, both before and after the treatment are shown in Fig. 15. As seen in the figure the gas production increased from an average of 0.25 MMSCFD to 0.5 MMSCFD, while the condensate production increased from 87 BPD to 157 BPD. Well tests performed on the well before and after the treatment showed a permeability of 0.04 md while the total skin improved from 0.68 to –1.9. This indicates that the methanol treatment effectively removed the condensate/water bank near the wellbore resulting in improvements to both the gas and condensate production. The production remained above the baseline production rate for about 4 months. The longer term stabilized post-treatment rates were also 50% higher than the average production rates for the two months prior to the treatment (Fig. 15).

There are several possible explanations for the sustained increase in gas and condensate production. Removal of condensate and water from the near wellbore region are clearly the primary mechanisms of stimulation. The primary concern with these treatments was their longevity. The removal of water introduced into the formation by drilling, completion and stimulation fluids is a permanent improvement. However, the removal of the condensate bank is only temporary as it is expected to reform. The results from this test indicate that the reformation of a condensate bank does not occur immediately. We can only speculate about the possible reasons for this. A residual phase of methanol will remain in the pore space and can modify the phase behavior of the flowing hydrocarbon phases. The removal of the water from the near wellbore region results in a smaller pressure gradient in the near wellbore region resulting in less condensate dropout.

Production logs indicate that most of the production is coming from about 10 percent of the producing pay. This suggests that the methanol (used without diverting agents) probably went into a small but productive section of the formation. This almost certainly results in a deeper treatment depth than would be expected with uniform placement.

Conclusions

A methanol treatment applied to a gas condensate well in the Hatter's Pond field was found to increase both gas and condensate production by a factor of 2 over the first four months and 50% thereafter. The increased rates were sustained over at least a four-month period. Removal of water and condensate phases from the near wellbore region by the methanol resulted in a reduction in skin from 0.68 to –1.9.

Precautions must be taken to ensure that the methanol injected is compatible with both the reservoir brine and the formation fines. Corefloods were conducted with reservoir cores from the Norphlet sandstone formation in Hatter's Pond field indicated no sensitivity to methanol. The cores were found to be sensitive to fresh water.

Additional work needs to be done to investigate the optimal treatment size and placement method.

Acknowledgments

We would like to thank Bruce Rouse and Jason White for their help with these experiments and would like to thank Glen Baum and Bob Savicki for their help with the experimental apparatus. We would also like to thank the sponsors of this gas-condensate research: ChevronTexaco, Saudi Aramco, Conoco, and JNOC.

Nomenclature

k = Core permeability, md
PI = Productivity index, cc/hr/psi
ppm= part per million
PV = Pore volumes injected, dimensionless
Q = Pump flow rate, cc/hr
ΔP = Differential pressure, psi
μ = Viscosity, cp

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SI Metric Conversion Factors

cp	$\times$ 1.0*	E-03	= Pa.s
ft	$\times$ 3.048*	E-01	= m
°F	(°F-32)/1.8		= °C
bbl	$\times$ 1.589873	E-01	= m^3
in.	$\times$ 2.54*	E+00	= cm
mL	$\times$ 1.0*	E+00	= cm^3
psi	$\times$ 6.894757	E+00	= kPa

*Conversion factor is exact.

Table 1-Calculated[14] or measured viscosity at 20°C.

Fluid	Viscosity, cp
Hatter’s Pond field water sample	0.997*
500 ppm Ca^{2+}	1.02
12wt% NaCl	1.25
24wt% NaCl	1.82
Methanol	0.586

* measured

Table 2-Properties of core plugs from Norphlet sandstone of Hatter’s Pond field.

Core #	10	11	Combined
Diameter, cm	2.5	2.5	2.5
Length, cm	1.95	1.83	3.78
Air Permeability, md	121	120	120.5
Porosity. %	13.8	14.4	14.1
Pore Volume, cm^3	1.32	1.29	2.61

Table 3-Chemical analysis of water sample for Hatter’s Pond field.

Ions	Concentration, ppm
Ca^{2+}	32
Mg^{2+}	6
Na^-	43
Cl^-	140

Table 4-Summary of coreflood experiments on Norphlet sandstone cores at 20°C.

Fluid Injected	μ cp	Q cc/min	ΔP psi	PV Injected	k md
Brine #1: 500 ppm Ca^{2+}	1.02	0.94	2.2	19	81
Methanol #1	0.586	1.7	2.5	39	75
Methanol #2	0.586	1.8	2.7	25	74
Brine #2: 12 wt% NaCl	1.25	0.91	3.3	46	67
Methanol #3	0.586	0.94	2.4	54	43
Methanol #4	0.586	0.96	3.4	39	31
Brine #3: 24 wt% NaCl	1.82	0.48	5.8*	10	28
Methanol #5	0.586	0.94	5.8*	13.5	18
Brine #4: 500 ppm Ca^{2+}	1.02	0.67	3.9	>300	33

Table 5-Test results of Well #3-6 before and after methanol treatment.

	Before Methanol Treatment	After Methanol Treatment
P*, psi	3,519	3,413
k, md	0.039	0.04
Total Skin	0.68	-1.9
Gas Rate, MMSCF/D	0.25	0.50
Condensate Rate, BPD	87	157

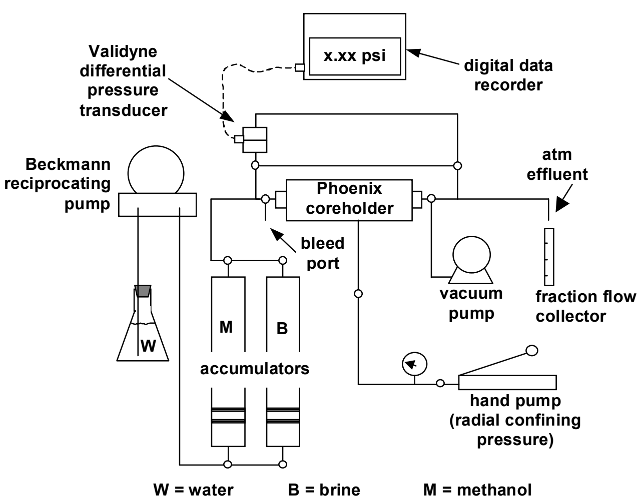

Fig. 1—Schematic diagram of coreflood apparatus.

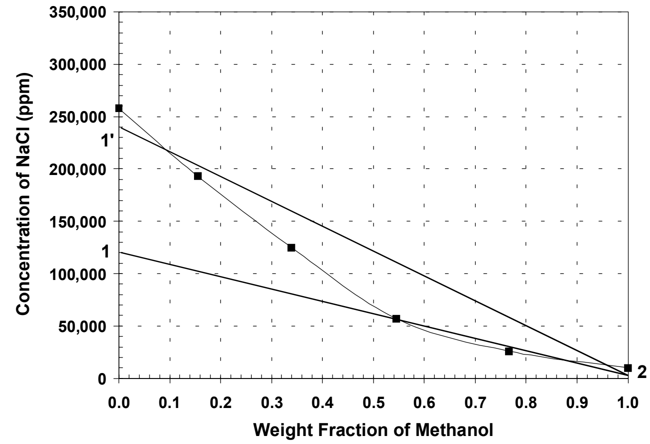

Fig. 2—Solubility of NaCl in methanol-water mixture at 78°F.

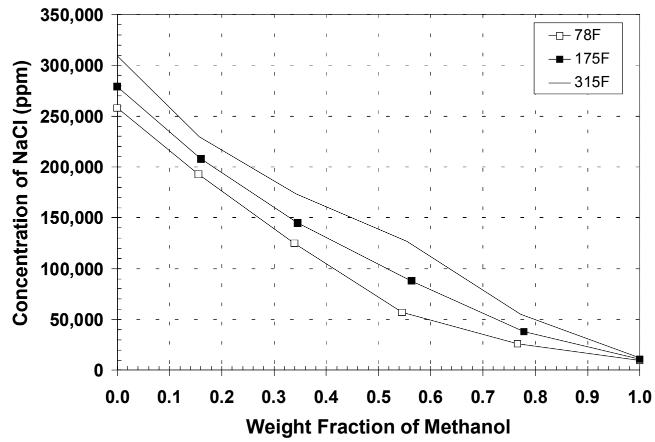

Fig. 3—Solubility of NaCl in methanol-water mixture for various temperatures (extrapolated for 315°F).

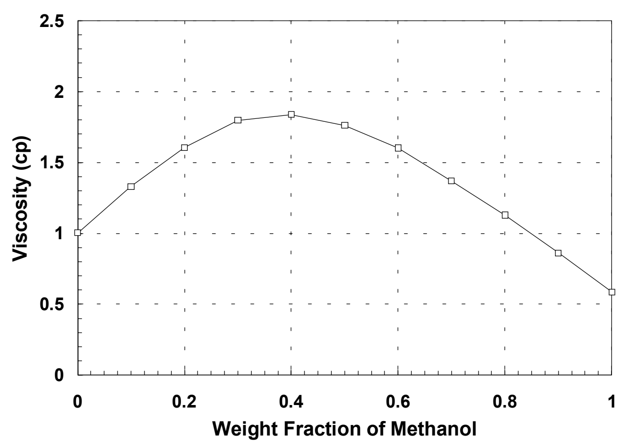

Fig. 4—Viscosity of methanol-water mixtures at 20°C.[14]

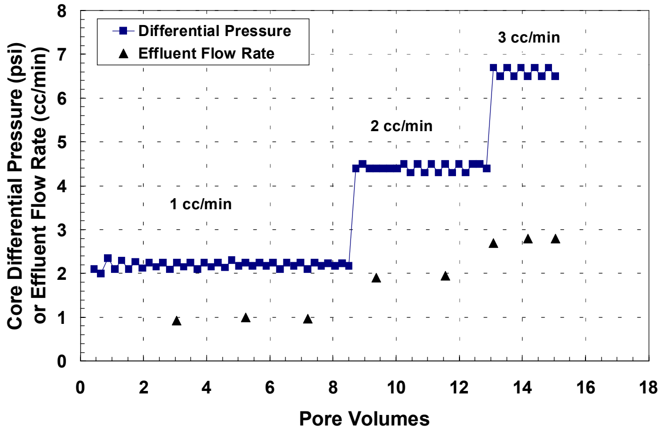

Fig. 5—Differential pressure and measured effluent flow rate during brine flood #1 (500 ppm Ca^{2+}).

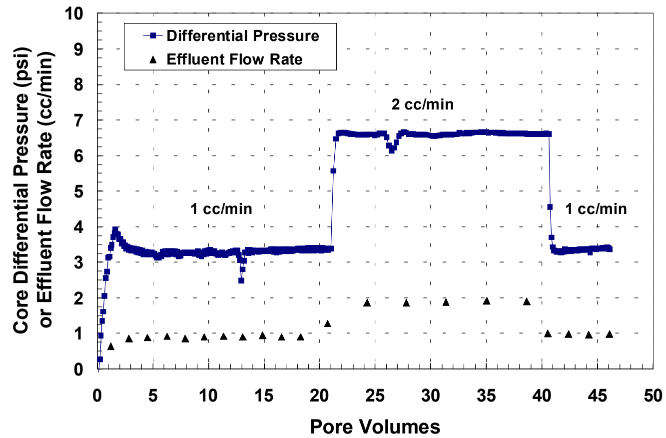

Fig. 8—Differential pressure and measured effluent flow rate during brine flood #2 (12 wt% NaCl).

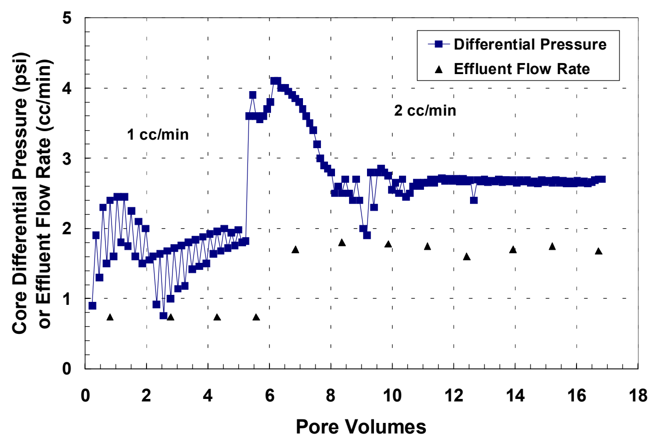

Fig. 6—Differential pressure and measured effluent flow rate during methanol flood #1.

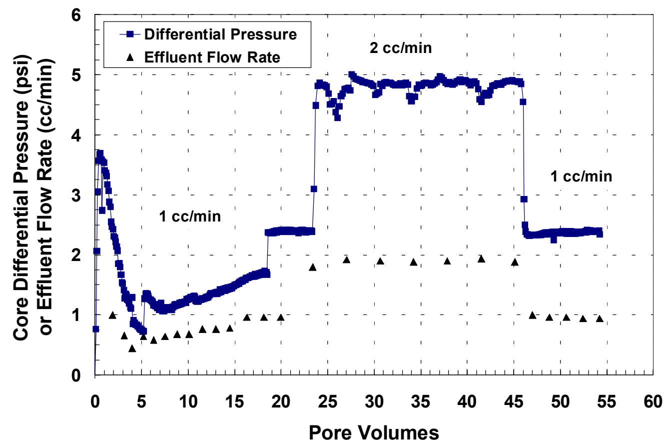

Fig. 9—Differential pressure and measured effluent flow rate during methanol flood #3.

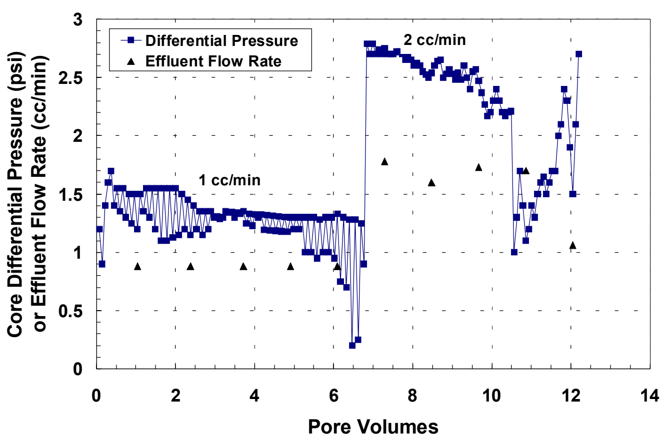

Fig. 7—Differential pressure and measured effluent flow rate during methanol flood #2 (after shut-in).

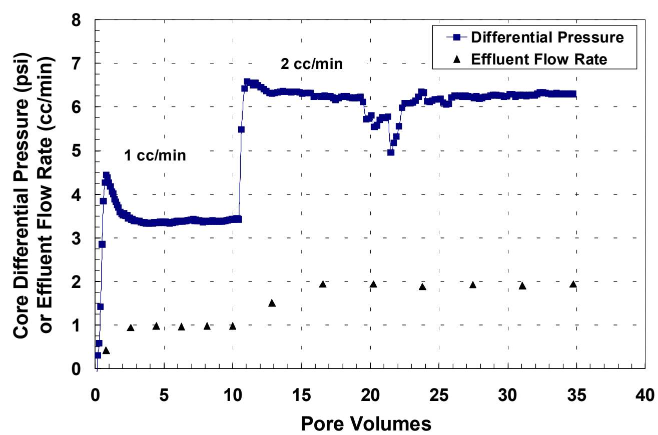

Fig. 10—Differential pressure and measured effluent flow rate during methanol flood #4 (after shut-in).

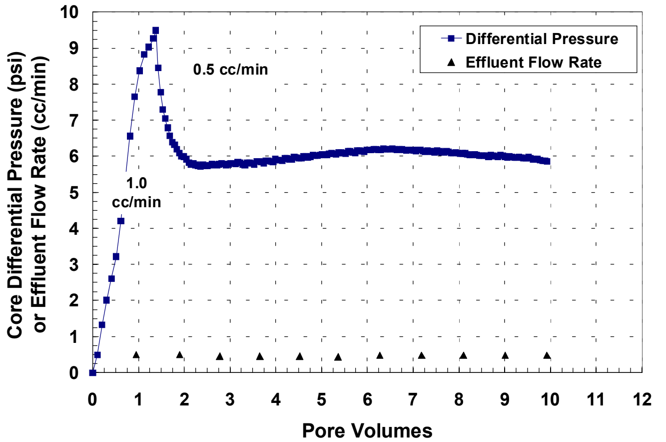

Fig. 11—Differential pressure and measured effluent flow rate during brine flood #3 (24 wt% NaCl).

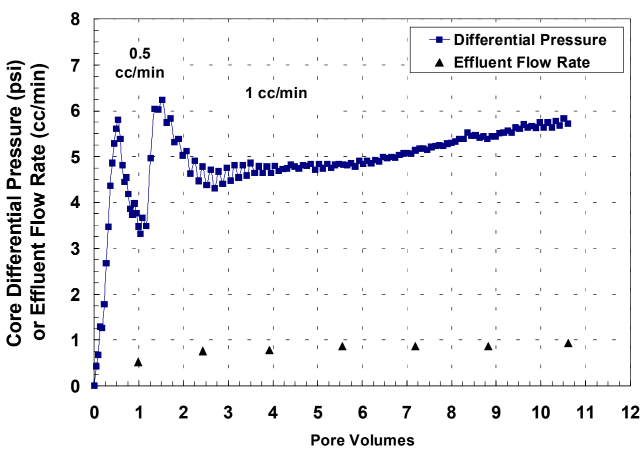

Fig. 12—Differential pressure and measured effluent flow rate during methanol flood #5.

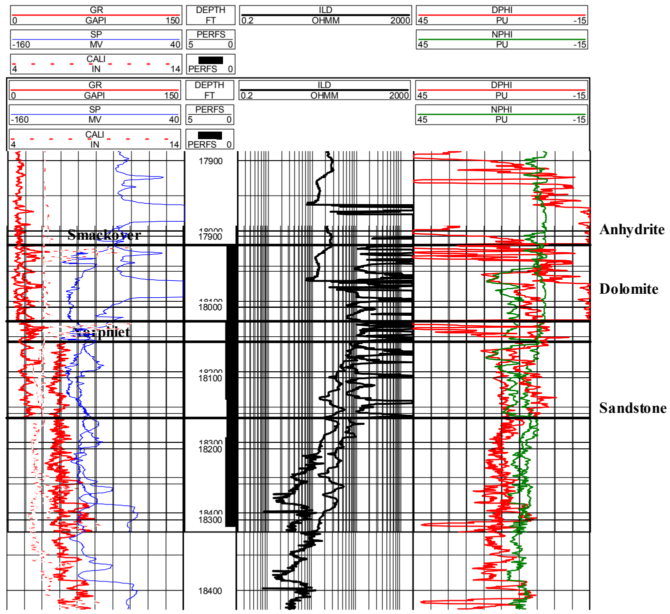

Fig. 13—Hatter's Pond type log.

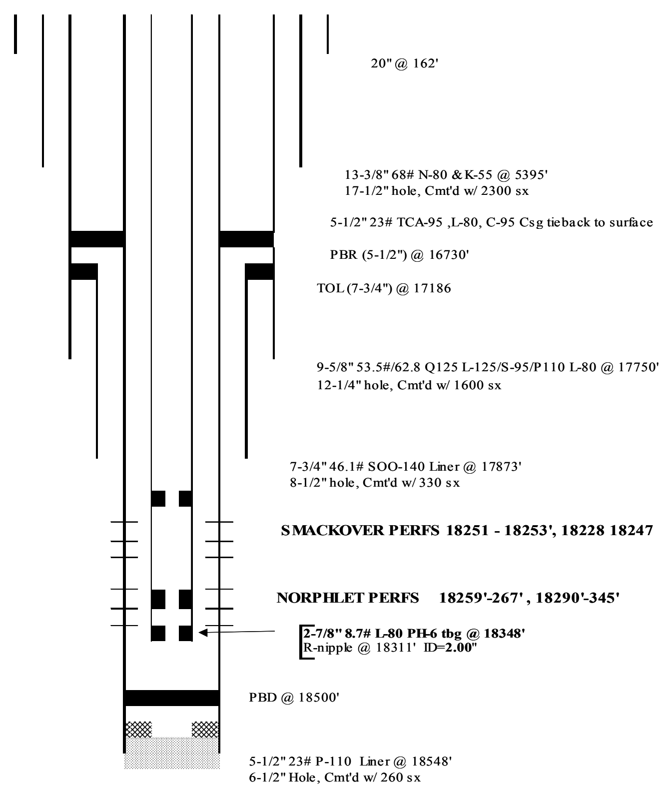

Fig. 14—Wellbore sketch for Hatter's Pond Unit 3-6 #1, Hatter's Pond Field, Mobile Co., AL.

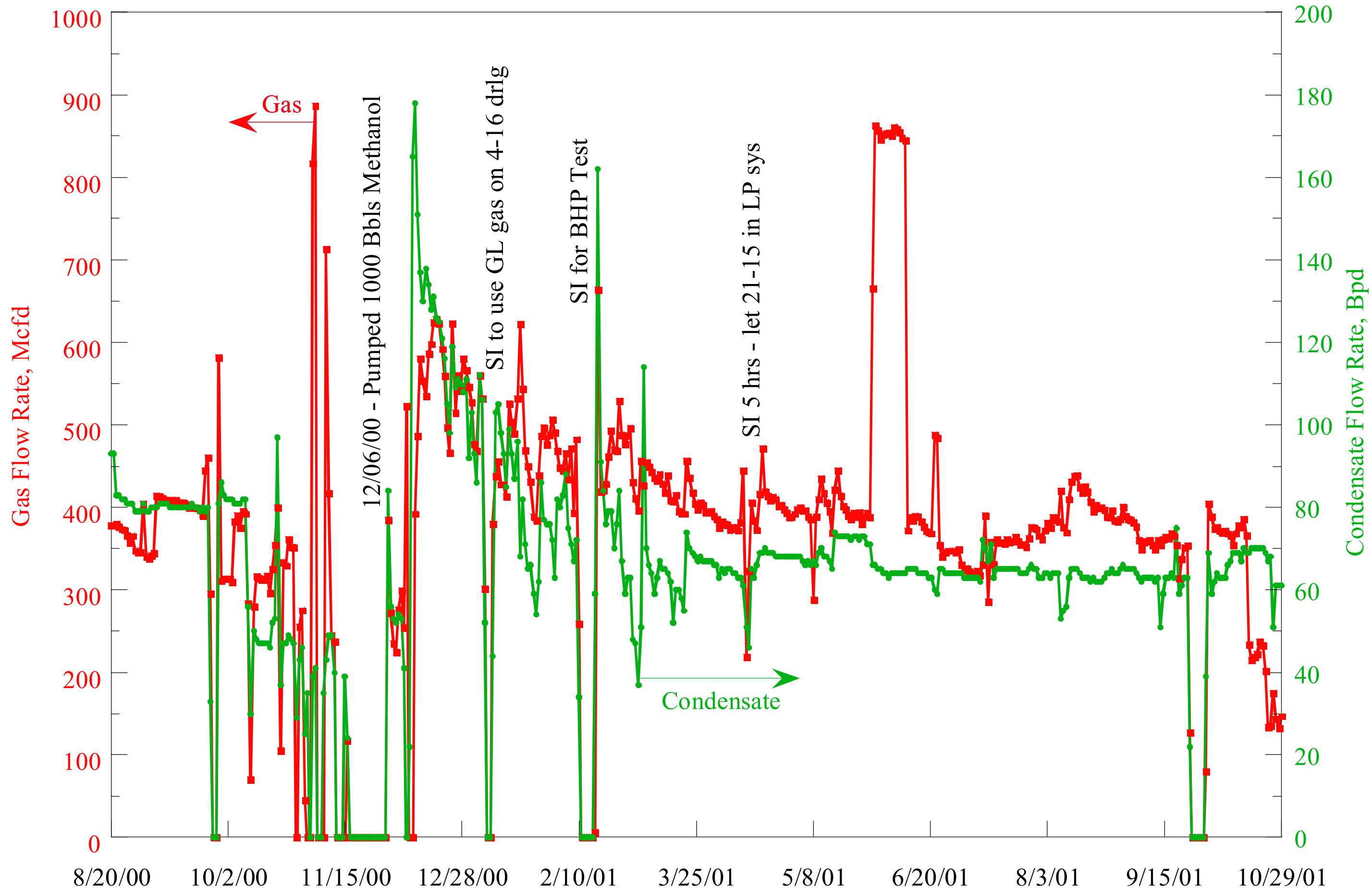

Fig. 15—Gas and condensate production rates for Hatter's Pond Unit 3-6 #1 before and after methanol treatment.