ORGANICALLY CROSSLINKED POLYMER SYSTEM FOR WATER REDUCTION TREATMENTS IN MEXICO

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ABSTRACT

This paper presents the application of an organically crosslinked polymer (OCP) system, a system widely used in the oil industry for water shutoff applications. The OCP system is based on a copolymer of acrylamide and t-butyl acrylate (PAtBA) crosslinked with polyethyleneimine (PEI). To date, about 100 jobs have been performed with this system in Mexico to address conformance problems such as:

- Water coning/cresting.
- High-permeability streaks.
- Gravel pack isolation.
- Fracture shutoff.
- Casing leak repair.

This paper presents an overview of case histories that used OCP in various regions of Mexico for a wide variety of applications. In particular, a case history of an offshore well treated with the OCP is presented. A direct comparison of the application of the OCP with conventional cement squeeze treatments is presented to illustrate the advantage of having a deep matrix penetration for a more efficient water shutoff. In addition, data presented in this paper indicate the development of a retarder that allows the upper placement temperature of the OCP system to be raised to at least 350ºF. The upper placement temperature of the system originally was ~260ºF.

INTRODUCTION

Excessive water production is a widespread problem that has significant economic impact in the profitability of hydrocarbon producing wells. Water production can cause a decrease in gas and oil production rates, or worse, it can completely block hydrocarbon production. In addition, water production will increase the operating expenditure of the well because of the cost of handling, disposing, and/or reinjecting water, the cost of surface facility construction, and/or efforts to meet environmental laws.[1]

Several techniques for controlling water production have been used by the oil industry. Earlier attempts to reduced water production included mechanical isolation, squeeze cementing, solid slurry (clay) injection, and oil/water emulsions. More successful results have been obtained with in-situ polymerized systems, crosslinked polymeric solutions, and silicate-based gels.[2] Perhaps the most widely used chemical system has been chrome crosslinked polyacrylamide gel. However, it is well known that commonly used chrome crosslinkers tend to undergo hydrolysis and precipitation, especially with increasing pH and temperature.[3,4]

Over the last decade, polymer gel systems have emerged as one of the most powerful tools for shutting off or at least controlling water production.[5] The OCP system presented in this paper has been successfully used in field applications up to 260°F for the last 9 years.

DESCRIPTION OF THE OCP SYSTEM

Development [5-7]

The OCP system was developed to improve the properties of the crosslinked systems available at that time. The following features were identified as the minimum requirements for the system:

- ***Low-viscosity fluid system***: A thin fluid system that can be easily injected deep into the matrix of the formation.
- ***Adequate pumping times***: A fluid system capable of controlling crosslinking time (phase change from liquid to gel state) to obtain adequate placement time for a wide temperature range.
- ***Effective water permeability reduction***: A system that provides sufficient strength for resisting drawdown pressure inside the wellbore and stopping water flow.

- ***Thermal stability***: A system capable of keeping its three-dimensional gel structure for extended periods of time to provide an effective water shutoff at elevated temperatures.

The viscosity of the OCP system is approximately 25 cP at room temperature. Gelation time of the system is controlled by the concentration of the PEI crosslinker. As will be shown in the following discussion, at temperatures higher than 260°F, a recently developed retarder is used to obtain longer gelation times. Sufficient strength and thermal stability are obtainable at least up to 350°F based on laboratory studies. In addition, the OCP system is insensitive to formation fluids, lithology, and/or heavy metals. Another advantage of the OCP system is the predictable viscosity profile that can be used to improve diversion over long treatment intervals. The OCP system meets all the requirements identified during the development stage.

Main Components

The primary components of the OCP system are:

- ***Base polymer***: Copolymer of acrylamide and t-butyl acrylate (PAtBA), a high-activity liquid with enhanced thermal stability.
- ***Crosslinker***: Polyethyleneimine (PEI), a high-activity liquid that forms strong covalent bonds with the base polymer.
- ***Mixing brine***: KCl brine, NaCl brine, or seawater. Typically 7% KCl water is used.
- ***Retarder***: a water-soluble carbonate retarder only used for applications in which the bottomhole injecting temperature exceeds 250°F.

The OCP components are easily diluted in the mixing brine. The crosslinking rate is dependent upon temperature, salinity, pH, and base polymer and crosslinker concentrations.

Numerous tests established a temperature range of approximately 140–260°F for the OCP system. Below 140°F, gel times became excessively long, and 260°F was the maximum temperature at which usable gel times were achieved (~3 hr). However, the gels are stable to at least 350°F if a cooling preflush is used to lower the well temperature to at least 260°F.

Principle of Operation

The principle of operation of this water shutoff technique is to pump the OCP system into the formation around the wellbore and then propagate it through the rock matrix. In-situ gelation is caused by a phase change induced by the well's temperature. The three-dimensional gel structure plugs pore spaces and channels and thereby limits undesired water flow. Then, a permanent barrier strategically placed only in the water zone is formed because the oil-and-gas producing zones can be mechanically isolated.2

Laboratory Testing

During the development of the OCP system, comparisons were made to a chrome-crosslinked polyacrylamide system (the chrome source was chromium propionate). In this study, a stainless steel tube with multiple pressure taps filled with silica or silica/carbonate was used. The pack was taken to residual oil saturation, one pore volume of the gellant was injected into the tube, and it was then shut in for approximately 16 hours (far in excess of the gelation time of the formulations used). The testing temperature was 212°F. After curing, brine was injected to determine the level of permeability reduction inflicted by the treatment, reported as the residual resistance factor (RRF), which is simply the initial permeability to brine before treatment divided by the final permeability to brine after treatment. As shown in Fig. 1, the OCP provided excellent permeability reduction for the entire length of the tube, while the chrome-crosslinked system obviously did not provide an effective water shutoff the full length of the tube. Other tests carried out in this study showed similar results.

Two of the most demanding scenarios for a gel system are stopping gas production and stopping water production through a fracture. Both of these scenarios were tested with the OCP system with outstanding results.

For gas shutoff tests, a stainless steel tube was tightly packed with 100-mesh sand. The pack was saturated under vacuum with degassed API brine. The permeability to brine was 7.4 mD. The pack was then heated to 270°F overnight. Crude oil was injected to bring the pack to residual water saturation. Subsequently, the oil was displaced by nitrogen to bring the pack to residual water and oil saturation. The displacement of oil and water by nitrogen simulated a porous media that produces gas at residual water and oil saturations. The pack was then treated with about 1.5 pore volumes of OCP. The treatment was injected from the opposite direction of the water, oil, and nitrogen injection. After treatment, the pack was shut in overnight to cure the gel completely. The test showed that the gel was able to hold 450 psi for 1 month with no gas flow. After 1 month, the test was stopped. After about 18 days, the pressure drop was increased from an average of 450 psi to about 550 psi. The pressure drop slightly decreased, but no gas flow was observed. No residual permeability determination was performed because the pack was completely shut off to gas.

Fracture testing was carried out using a chalk core with almost immeasurable permeability. An 8.4-cm long core with a diameter of 2.3 cm was sawed in half length-wise. A 0.005-cm spacer was placed between the two halves and the core was glued together with epoxy. The core was then flowed with seawater at 265°F, and the permeability was found to be 302 mD. The temperature was lowered to 200°F, and the core was treated with OCP. The temperature was then raised back to 265°F and the core was shut in overnight. The following day seawater flow was resumed and breakthrough occurred at 196 psi. However, flow was continued, and the permeability reduction was 99.9%.

OCP CASE HISTORIES [8,9]

As of this writing, approximately 275 jobs have been performed worldwide with the OCP system. Most of these jobs have been designed for matrix, natural fractures/voids, and high-permeability streaks shutoff. Some other cases include near-wellbore shutoff, casing leaks, and/or gravel pack isolation. The field application of the OCP system has a high ratio of success, especially when proper diagnostic and analysis techniques are performed to fully understand the problem. Some economic failures of this system are attributable to poor candidate selection and not the fluid system itself.

OVERVIEW OF CASE HISTORIES IN MEXICO

Water management is a challenging problem in Mexico. About 40% of OCP system jobs have been performed in Mexico. In southern Mexico, the main sources of production are natural fractures located along the entire interval. Matrix porosities vary from 2–8%. Some of the mature wells require pressure maintenance by the injection of gas or disposal water. Some of the wells lie within depleted, highly fractured areas and include sandstone and carbonate formations ranging from 168 to 264°F.

Despite the fact that natural fractures can have a positive effect on oil flow, they can also negatively affect water or gas flow because of coning effects or high-permeability streaks that connect producing zones with other zones above or below. If the contacted zones are water producers, they eventually influence the actual producing zone. This is one reason why fluid flow is difficult to characterize in a uniform pattern.

Table 1 shows production data for 37 wells before and after the treatment, which demonstrates the effectiveness of the OCP system. Most of these wells experienced major improvements in water reduction, and subsequently, oil/gas production. A few of the wells experienced a 100% reduction in water cut. Two of these wells were producing over 80% water before being treated with the OCP system. One of these wells was producing 0 BOPD before the OCP treatment. After being treated, this well began producing 2,000 BOPD.

Case History—Water Coning Shutoff

An offshore well having water coning problems was treated successfully with the OCP system. A squeeze cementing job was performed in an offset well producing from the same formation having water coning problems as well. The results showed the superior capabilities of the OCP system over squeeze cementing in shutting off water caused by deeper penetration inside the matrix of the formation.

Field Background. The Abkatun field is an offshore hydrocarbon producing field located in the southeast part of the Gulf of Mexico, approximately 140 km northeast from Dos Bocas, Tabasco. This mature reservoir is operated by PEMEX and has been in production since 1980. This field is producing from Mesozoic reservoir rocks, more specifically upper Cretaceous-lower Paleocene dolomitic carbonate rocks. The hydrocarbon production comes from coarse-grained carbonated breccias strongly dolomitized and naturally fractured with secondary vuggy porosity caused by diagenetic dissolution processes,[10] having permeabilities from 500–1300 mD and porosity range from 6–14%. This field produces a light oil of approximately 28 API gravity.

This field is currently under secondary recovery (waterflooding) to maintain the pressure of the reservoir and most of the wells are being produced with the aid of artificial lift. Up to date, the average reservoir pressure of the

Abkatun field is approximately 2,900 psi. The average oil production of a well in this field during 2005 was 3,000–5,000 BOPD with a watercut of 50–60%.

Candidate Well Description. The Abkatun-53A well is producing from the BTP-KS formation whose top is around 11,562 ft. It was determined that the excessive water production is a consequence of the combination of water coning and the high-permeability streaks present because of the naturally highly fractured reservoir. It was a standard practice by the operator to abandon (isolate) an interval once the water-oil contact reached the perforations and perforated the same formation a few feet higher up. There were only a few feet left to produce in this interval because the producing layer is almost completely invaded by the coning of water.

According to a log analysis, most of the hydrocarbon production of the Abkatun-53A well came from 11,565 to 11,581 ft measured depth (Fig. 2a). Because of the vertical communication between the interval to be sealed and the future perforated interval, it was necessary to place a barrier between these two intervals to keep the water-oil contact from reaching the new perforations so that the life of this well could be extended. To achieve this objective, it was necessary to completely seal the current producing interval and to obtain a deep penetration into the formation.

Production History. The Abkatun-53A well was initially completed in March of 1992. The original set of perforations was at a depth of 11,598 to 11,696 ft of the BTP-KS formation. The well was stimulated in June 1999 but it was not until February of 2003 that water started to be produced in measurable amounts (7% watercut). The salinity of the water produced was calculated to be about 48,000 ppm. In February 2005, the well was producing around 4,725 BOPD and 2,196 BWPD (watercut of 31.7%) and it was decided to treat it with the OCP system.

Treatment Design. The OCP system was used in combination with a tail-in of standard cement to shutoff 98 ft of perforations (11,598–11,696 ft measured depth). The size of the OCP treatment volume was designed based on 10 ft of radial penetration into the formation. About 315 bbl of treatment were injected at 2 bbl/min. The use of cement as a tail-in is not a standard practice for an OCP application; it was used upon customer request.

The bottomhole injection temperature for this application was approximately 286°F. It is important to mention that by the time this job was performed, the recently developed retarder used for temperature applications higher that 250°F was not available. Then, the formation had to be cooled down with 250 bbl of sea water so that an adequate pumping time could be obtained.

Treatment Results. Water production for this well was decreased substantially following the polymer treatment and the perforation of the new interval (11,562–11,598 ft measured depth, 36 ft of perforations). After perforating the new zone, the customer decided to stimulate the well with an aggressive acid treatment of 190 bbl. Even after the acid job, watercut decreased from 31.7% to 3.7% as Fig. 3 illustrates. This well is currently producing at low watercut one year after the OCP treatment.

As mentioned, an offset well (Abkatun-77A, Fig. 2b) producing from the same formation and having similar water coning problems was treated with a standard squeeze cementing job. As Fig. 4 illustrates, watercut before the treatment was approximately 22% and eventually has increased to 55.4% after the treatment (an average watercut for wells in the Abkatun field). Because the squeeze cementing job did not provide a barrier deep inside the matrix of the formation, the attempt to reduce water production was unsuccessful. Well Abkatun -77A was abandoned 7 months after the squeeze cement job because of excessive water production.

RECENTLY DEVELOPED RETARDER FOR THE OCP SYSTEM

Although the OCP system has been successfully applied in field operations, some features needed improvement for high-temperature applications. As mentioned, the upper temperature limit of the OCP system was ~260°F because placement times were short above this temperature. A recently developed water-soluble carbonate retarder allows adequate gelation times up to 350°F without the need of cooling down the formation to obtain an acceptable gelation time. Fig. 5 shows gelation time vs. concentration of the retarder at various temperatures.

In addition, the thermal stability of the system was evaluated at 350°F in a sandpack flow experiment. The objective of this extended flow test was to evaluate the effectiveness of the OCP system in reducing permeability of water as a function of time. In this test a stainless steel tube was packed with a mixture of sand, silica flour, and bentonite, giving a permeability to API brine of 1069 mD at residual oil conditions. The pack was then treated with 10 pore volumes of the OCP system plus the retarder and shut in overnight. The following day, the pressure on the pack was raised to 100 psi, and no brine flow was observed. This procedure was repeated every 2 days for the following 30 days, and no brine flow was ever observed. Thus it appears that the retarder was able to extend the working temperature range without detrimental effect on the gel strength and ability of the gel to stop fluid flow.

An additional use of the OCP system currently under development is a combination with cement or inert particulates for squeeze applications. Cement squeezes are often used to plug water-producing zones. However, cement may not completely seal the perforations, or may not withstand high drawdown pressures. With OCP as the “mix water,” the filtrate lost into the matrix will gel and form an additional seal capable of withstanding high drawdown pressures. While development remains ongoing, combinations of OCP with cement have been used successfully in field operations.

CONCLUSIONS

- The OCP system has proven to be successful in various applications in Mexico and throughout the world.
- The OCP system is able to address conformance problems such as water coning/cresting, high-permeability streaks, gravel pack isolation, fracture shutoff, and casing leak repair.
- The new retarder allows expanding the temperature range of applicability of the OCP system to 350°F without compromising its thermal stability.
- The OCP system is capable of penetrating deep into the matrix of the formation to provide a more effective seal, particularly for water coning shutoff applications. Conventional squeeze cement techniques do not provide this property.

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NOMENCLATURE

BOPD barrels oil per day
BWPD barrels water per day
MBPD million barrels per day
MD measured depth
OCP organically crosslinked polymer
PAtBA copolymer of acrylamide and t-butyl acrylate
PEI polyethyleneimine
RRF residual resistance factor

Table 1
OCP Treatment Results in Mexico: Water Production Before and After Treatment

Example Well Number	Produced Water, %					
	Before Treatment	30 Days After OCP Treatment	90 Days After OCP Treatment	180 Days after OCP Treatment	270 Days after OCP Treatment	360 Days After OCP Treatment
1	30	0	0	0	0	0
2	74	0	0	0	0	0
3	70	0	0	0	0	0
4	80	0	0	0	0	0
5	69	1	2	9	19	20
6	69	1	2	9	19	20
7	30	3	1	1	1	1
8	80	0	0	0	0	5
9	80	80	—	—	—	—
10	53	42	55	63	—	—
11	84	23	23	40	40	40
12	75	75	—	—	—	—
13	64	64	—	—	—	—
14	98	45	86	78	91	50
15	50	50	—	—	—	—
16	64	64	—	—	—	—
17	45	20	16	16	—	—
18	40	25	35	52	46	46
19	45	20	16	16	—	—
20	25	1	1	1	1	1
21	27	0	0	0	0	0
22	44	44	—	—	—	—
23	43	8	8	28	53	83
24	75	12	12	10	5	—
25	76	4	3	1	—	—
26	46	36	5	43	70	75
27	50	31	31	33	—	—
28	50	3	8	—	—	—
29	93	13	67	74	80	—
30	82	6	7	—	—	—
31	78	16	36	49	87	—
32	50	3	8	—	—	—
33	25	0	2	—	—	—
34	40	36	49	18	—	—
35	80	80	—	—	—	—
36	80	60	—	—	—	—
37	41	1	1	—	—	—

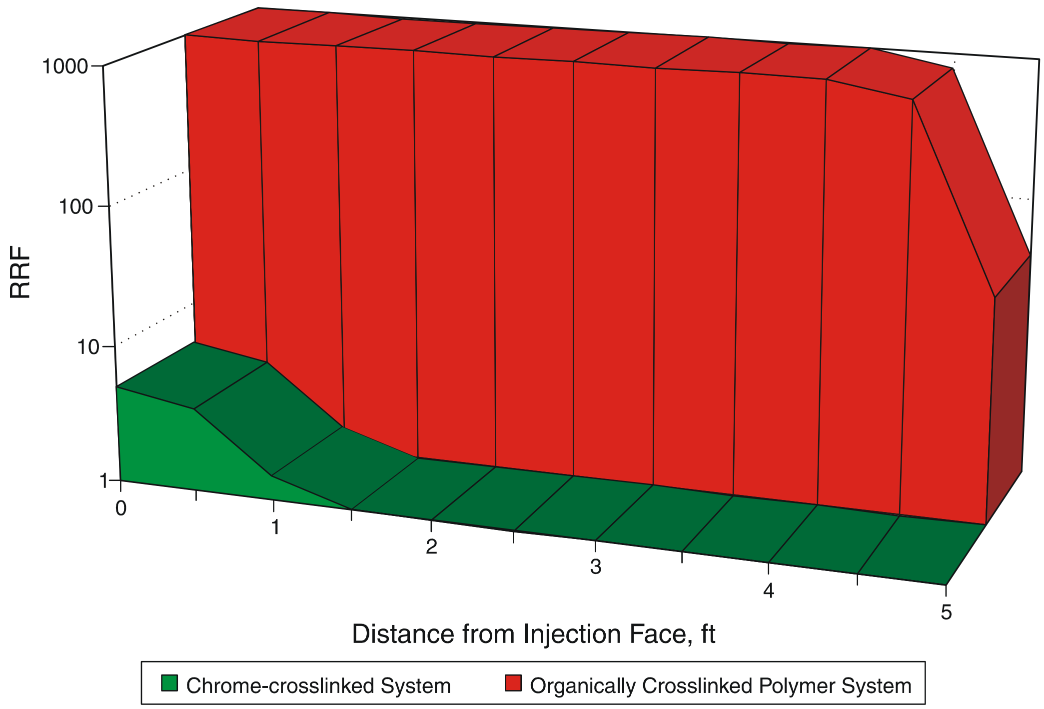

Figure 1—Comparison of RRF values of OCP and chrome-crosslinked system treated sandpacks (injection temperature = 212°F; packing material 80% silica, 20% calcium carbonate).

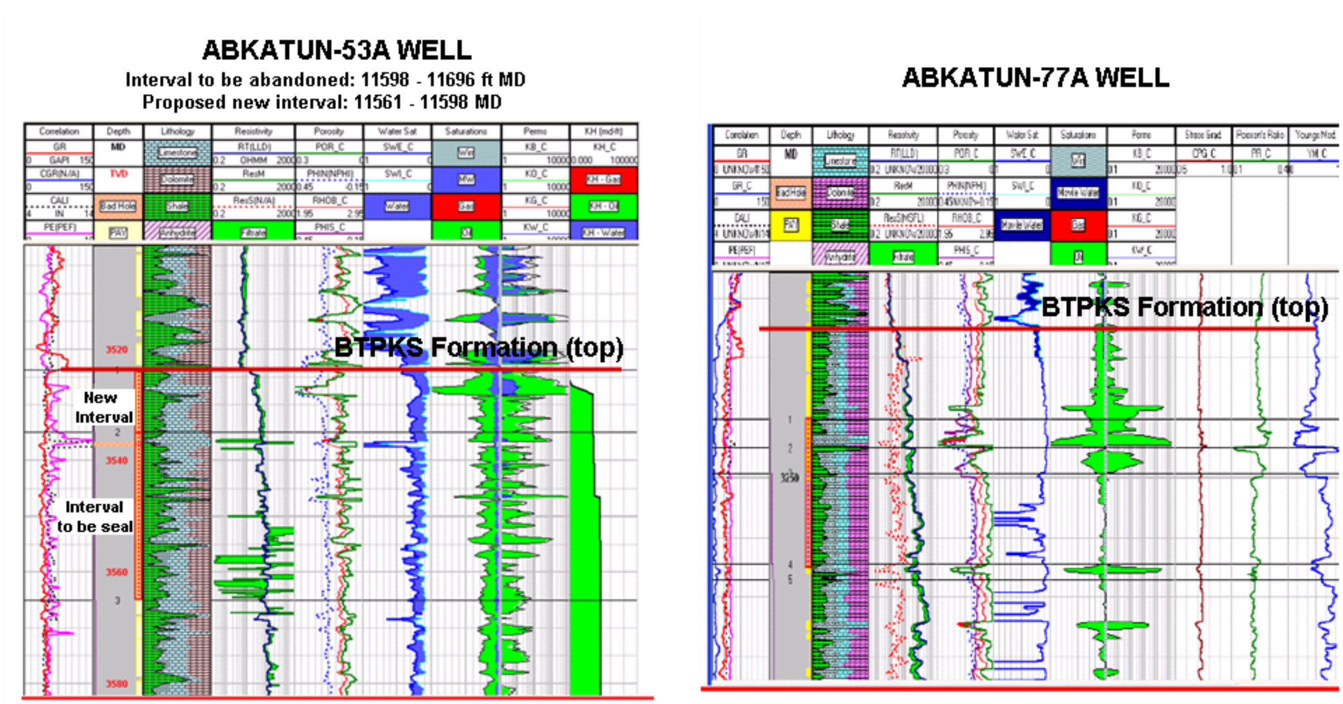

Figure 2—Openhole logs for: (left) Well Abkatun-53A (treated with the OCP system), and (right) Well Abkatun-77A (treated with a standard squeeze cement job).

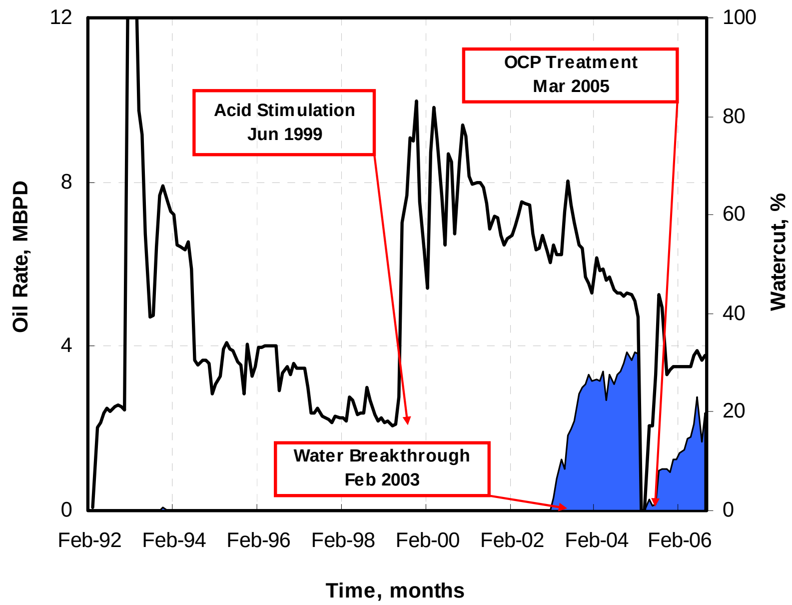

Figure 3—Production history of Abkatun-53A well before and after the OCP system treatment.

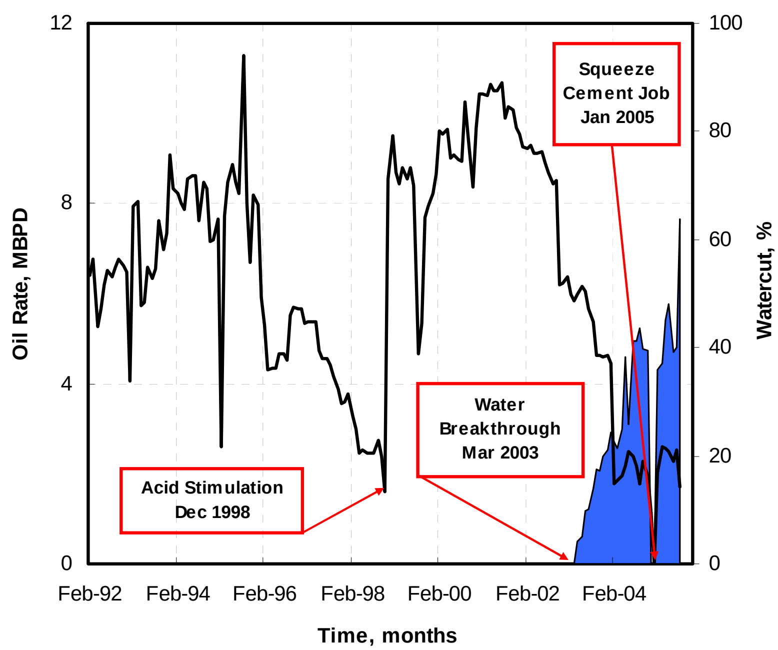

Figure 4—Production history of Abkatun-77A well before and after the OCP system treatment.

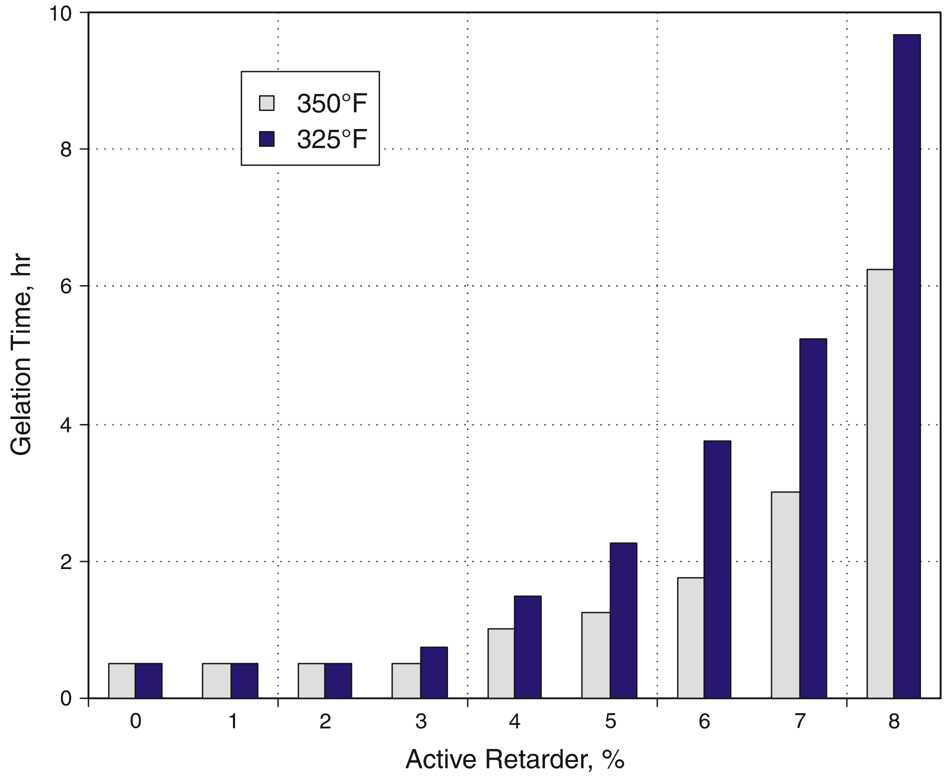

Figure 5—Gelation times of OCP system vs. concentration of the carbonate retarder at various temperatures (7% active PAtBA, 2% active PEI, in 2% KCl).