

# CASE HISTORIES OF A NOVEL ACID DIVERSION TECHNIQUE, CANTARELL FIELD, MEXICO

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## ABSTRACT

The Cantarell field is the most important complex in Mexico and is the second-largest producing field in the world. The producing formations consist of highly fractured, vuggy carbonate from Jurassic, Cretaceous and Lower Paleocene geological ages. Matrix acidizing has always been the main stimulation process used to improve production from these carbonate reservoirs and this is especially the case now that this mature complex has reached its production peak.

A critical factor for success of the treatments is distribution of the acid between all productive zones. Since most producing wells are not homogeneous and contain layers of varying permeability, even distribution of the acid is a difficult task. In addition, the water saturation of the various zones has a major effect on the acid distribution. Since acid is an aqueous fluid, it will tend to predominantly enter the zones with the highest water saturation, in many cases resulting in increased water production. This brings with it the multitude of problems associated with high water production.

The results of approximately 57 high permeability wells ranging from 1,000 to 6,000 md, which have been acidized using a novel acid diverter based on associative polymer technology (APT), will be presented in this paper. This polymer inherently reduces the formation permeability to water with little or no effect on the permeability to hydrocarbon. Data from production logs from several of the treated wells will be presented, which show excellent oil production distribution along the perforated intervals. In addition, production logs will also be shown for wells acidized with other diverters, such as foams and in-situ crosslinked acid, which showed poorer results.

## INTRODUCTION

### Cantarell Field

The Cantarell field is located 47 miles northeast of Ciudad del Carmen, Campeche. The main productive zones in Cantarell are highly fractured carbonate formations from the Jurassic, Cretaceous and Lower Paleocene geological ages (Figure 1). Production started in 1979 and reached a peak of 1.1 million B/D in 1981 from 40 oil wells. By 1994 the production was down to 890,000 B/D. One year later it was producing 1 million B/D due to the addition of new platforms and wells and a nitrogen injection program. This program was capable of injecting a billion ft<sup>3</sup>/day of nitrogen to maintain reservoir pressure. By 1996 the field was producing 2.1 million B/D.

### Acid Diversion

In most oil wells the producing intervals are nonhomogeneous, containing sections of varying permeability and pressure. Acid treatments tend to predominantly enter the highest permeability zones, thus bypassing the lower permeability, or most damaged layers. In some cases, these high-permeability layers are also predominantly water-bearing, thus the acid also mainly enters those zones because of the relative permeability effect. In other cases, the acid may break into a nearby water-bearing zone. In all of these cases, an acid treatment may result in significant increases in water production after the treatment.

Many placement techniques have been utilized in the past in attempts to achieve uniform placement of acid across all layers. The most reliable method is the use of mechanical isolation devices such as straddle packers that allow injection into individual zones, one by one, until an entire interval has been treated. However, this technique is often not practical, cost-effective, or feasible. Without a packer, some type of diverting agent must be used.

Non-mechanical diverting agents that have been used include ball sealers, degradable particulates, viscous fluids, and foams. Although each of these has been used successfully, each also has potential drawbacks. In addition, none of these techniques addresses the problem of increased water production that often follows an acid treatment.

reason, a material that could inherently decrease the formation permeability to water and also provide diversion is desirable.

Dilute polymer solutions have been shown to decrease the effective permeability to water more than to oil. These types of treatments have been referred to as relative permeability modifiers (RPM), disproportionate permeability modifiers, or simply bullhead treatments. That is, these treatments can be simply bullheaded into the formation without zonal isolation. These systems are thought to perform by adsorption onto the pore walls of the formation flow paths. A large number of such polymer systems have been promoted through the years, and a large volume of literature has been devoted to this topic.<sup>1-3</sup>

A previous paper from this laboratory described an RPM based on a hydrophobically modified water-soluble polymer<sup>4</sup> (here referred to as APT). Because this polymer reduces water permeability with little damage to oil permeability, it was recognized as a potential acid diverter. Another paper from this laboratory has described the laboratory study of this polymer for use as an acid diverter.<sup>5</sup>

### Associative Polymers

The solution properties (such as rheology and viscosity) of both ionic and nonionic, water-soluble polymers are uniquely modified when hydrophobic groups are introduced into the polymer chains.<sup>6,7</sup> In addition, the adsorption behavior of hydrophilic water-soluble polymers can also be modified in a unique manner by the introduction of hydrophobic groups. Rather than reaching a plateau adsorption, as is common for hydrophilic polymers, hydrophobic modification appears to produce a continued growth in adsorption with increased polymer concentration. This behavior is attributed to associative adsorption of polymer chains on previously adsorbed layers of polymers.<sup>8</sup>

The associative polymer (AP) utilized in the current work has previously been shown to exhibit a unique shear thickening phenomena. However, the solutions used in diversion operations show very low viscosity (<2 cp) at surface conditions.<sup>5</sup> Viscosified or foamed fluids commonly used for acid diversion can result in high friction pressure and require special manifolding and/or pumping equipment. The low viscosity of the AP diverting system results in ease of mixing, low friction pressures, no special manifolding or pump requirements, etc. The diversion of aqueous fluids occurs only after the material enters the porous media, whether it is naturally fractured carbonate/dolomitic rock or sandstone matrix. It is theorized that the increased shear encountered upon entering the rock matrix, coupled with polymer adsorption, results in an apparent “viscosity” increase that may be responsible for the pressure increases usually seen during the treatment.

## EXPERIMENTAL PROCEDURES

### Single Core Flow and Acid Diversion Tests

The experimental procedures for single core flow tests have been published previously.<sup>4</sup> Acid diversion tests were run using standard Hassler sleeves. For each test, one core each was taken to residual oil saturation (water core) or residual water saturation (oil core) and initial permeabilities were measured as described in previous papers.<sup>4</sup> The cores were then connected so that the treatment sequence could be bullheaded, allowing the treatment to flow through either core. An ammonium chloride spacer was pumped between the APT treatment and the acid. For the APT treatment and ammonium chloride spacer, a limit of 500 mL or 500-psi differential pressure was used, and in all tests, the 500-psi limit was reached before pumping 500 mL. For the acid stage (5% HCl), the limit was 200 mL or 500 psi, and in each case, 200 mL was pumped without reaching the 500-psi limit. In the final stage, the cores were disconnected and final permeabilities were measured.

## RESULTS AND DISCUSSION

### Core Flow Tests

Prior work<sup>4</sup> has demonstrated the ability of APT to reduce water permeability with little effect on hydrocarbon permeability. Fig. 2 illustrates two single core flow tests on sandstone cores. This is for two separate tests, with one core at residual oil saturation and one core at residual water saturation. The core at residual oil saturation showed a 98% reduction in permeability while the core at residual water saturation showed only a 5% reduction in permeability. The RPM effect, rapid pressure increase in core tests and rheological shear thickening phenomenon led to the conclusion that APT might function as an acid diverter. Figure 3 illustrates the typical pressure increase seen when pumping the polymer into a carbonate core. In this test, brine and oil had been cycled through the core, ending with brine. The graph shows the final stage of this brine flow and the treatment stage. Note that the brine

flow was at 5 mL/min while the treatment was run at 1 mL/min. Even with this lower flow rate, when the polymer entered the core, the pressure very rapidly increased from 125 to over 490 psi. As will be shown later, this pressure increase is often seen on actual jobs.

### Diversion Tests

Figure 4 shows results from a diversion test using two carbonate cores. This test utilized two carbonate cores cut from the same block, so it is assumed that the permeabilities of the two cores were similar. One core was taken to residual oil saturation and one core was taken to residual water saturation. A control test was run in which acid was bullheaded into the two cores. As shown in the figure, out of 200 mL of acid, 142 mL entered the water-saturated core and 58 mL entered the oil-saturated core. In the second test, using two new cores, APT was bullheaded into the cores, followed by the acid. In this case, out of 200 mL of acid, 25 mL entered the water-saturated core and 175 mL entered the oil-saturated core.

Figure 5 shows a second set of carbonate diversion tests. In this case, cores with a wider permeability contrast were used. In a control test, cores with an initial brine permeability contrast of 5/1 were used. The cores were then taken to residual water and residual oil saturation, with the higher permeability core taken to residual water saturation. In this test, 92% of the acid entered the water-saturated core. Similar carbonate cores were used for the diversion test, but the same permeability contrast could not be attained. In this test, the initial brine permeability contrast was 17/1. Again, the cores were taken to residual water and residual oil saturation, with the higher permeability core taken to residual water saturation. Following the APT treatment, 69% of the acid entered the water-saturated core. It would be expected that if the control test had been run on cores with a 17/1 permeability contrast, at least 92% of the acid would have entered the water core (based on the 5/1 test results). Thus, it is assumed that the APT did result in diversion of acid into the oil-saturated core. Other laboratories have run similar diversion tests with APT and have seen similar results.<sup>9</sup>

### Cantarell Field Results

Large amounts of drilling mud are typically lost to the formation in this field. Several measures to minimize the amount of damage caused by the lost mud have been taken, including the use of low density, foamed, and solids-free mud formulations. However, the highly fractured condition of the formations and the depleted scenario of the reservoir still result in massive mud losses. Wells in the Cantarell complex require stimulation to overcome the formation damage caused by this mud loss and also to sustain a commercial level of hydrocarbon production. Bullhead matrix acid stimulation is the main technique used in this field. Acid stimulation through coiled tubing has been employed with good results; however, limitations in the size of coiled tubing available in this area leads to long pumping times, making the bullhead technique the main option. The main acid system used is 15% HCl, which is best suited to the bottomhole temperatures, which average around 220°F. The use of a diverting system also has been a routine procedure in every stimulation where typical perforated intervals range from 30 to 50 meters. The highly fractured nature of these formations and the presence of vugs are also reasons for using a diverting system.

### Foam Examples

The use of continuous foam was one of the first diversion techniques used in the acid stimulation jobs of this field. Using nitrogen as the gaseous phase, with initial qualities of 50% increasing progressively up to 70%, this continuous foam technique was the recommended one for long intervals with high permeabilities, which is very typical in this field.

However, buildup tests and PLTs run after the stimulation treatments often showed skin factor remaining in the formation and heterogeneous production profiles along the perforated interval. Figure 6 is an example of a production profile after an acid treatment where foam was used as the diverter. In this example, the bulk of the oil production is coming from the upper 20 m. The buildup test run after the stimulation showed a skin factor of 14.

Figure 7 shows a production profile from the PLT run after a stimulation job where almost 90% of the oil production is coming from the upper half of the perforated interval. Reservoir data from these wells and some additional ones where PLT logs were not run are shown in Table 1.

### In-situ Crosslinked Acid Examples

The use of in-situ crosslinked acid (ICA) as the diverting agent was later initiated because results from the foam applications were not completely satisfactory according to production logs run immediately after the stimulation

treatments. ICA was developed as a system to prevent fluid loss in fracture acidizing and as a diversion system in matrix acid treatments in carbonates. ICA is a gelled acid with a viscosity of approximately 20 cp which forms a highly viscous, crosslinked gel when the acid spends in the formation and the pH increases to a value of about 2. This system seemed to show a better distribution of the acid as compared to foam.

The profile shown in the last track of the composite log in Figure 8 is an example of a satisfactory production profile along the perforated interval following acid stimulation with ICA. Almost 100% of the perforations are contributing to the oil flow.

In Figure 9, the production profile of Well 17 is shown in the last track of the log. This well was also acid-stimulated with ICA as the diverting agent. It can be seen that over 90% of the production enters in the first 9 meters of the perforated interval. The rest of the oil production apparently is coming from the bottom of the interval.

Figure 10 corresponds to the log of Well 18, showing a contribution of 60% of the total of the production entering the upper section of the perforations. The rest of the interval does not contribute, with exception of the bottom of the perforations where 40% of the contribution is observed. Similar observations are seen in the profile of Well 19 (Figure 11), where almost 90% of the production enters the middle section of the perforated interval, with 10% in the top. No contribution is seen from the entire lower one-half of these perforations.

Figure 12 shows an example of a well with two perforated intervals where an attempt was made to acidize both intervals using the ICA diverter. Unfortunately, the bottom interval showed no production following the acid job, perhaps indicating that no acid was diverted to the lower interval. Thus, while some satisfactory results were seen with the ICA diverter, a more efficient diversion system was desired.

#### APT Examples

Other fields of the offshore area of Mexico had previously utilized APT, where good results were reported even in the presence of water<sup>10</sup> and low permeability formations.<sup>11</sup> These results led PEMEX to consider and evaluate the application of this system in the acid stimulations run in Cantarell field. Note that in these cases, diversion away from predominantly water-bearing zones was not the main focus. This new stimulation campaign using the APT diverter started at the end of 2005 and continued throughout 2007. Some wells were selected to carry out PLTs subsequent to these stimulations to evaluate the acid distribution in the stimulated intervals. The results observed in the profiles of the PLTs for some of these wells showed very good contribution of the producing interval, which demonstrated good performance by the APT. On the basis of these results, during 2006 almost 50 wells were acid stimulated using APT. While results for all jobs cannot be shown here, the overall conclusion is that APT has provided more consistent diversion than either foam or ICA.

Figure 13 shows a production contribution of the entire interval slightly loaded to the first one-half of the perforated interval. The production profile begins at 3,398 meters because there was an obstruction in the well below this point.

In Figure 14 the production profile for Well 2 shows a contribution of the entire perforated interval, with major contributions from the bottom. The same situation is observed in Well 3 (Figure 15), where the entire interval has contributed to the total production. The next example is Well 4 (Figure 16), where 100% contribution of the entire perforated interval is seen in the production profile shown in the last track.

The example shown in Figure 17 is similar to that shown in Figure 13 in that a well with two perforated intervals was acid stimulated. However, in this case the APT apparently was able to divert the acid throughout both intervals. The PLT shows that both perforated intervals are contributing to the production.

#### Pumping Charts

Surface pumping pressures measured during the acid treatments have shown that APT provides a larger and more consistent pressure increase than foam or ICA. A particular well was acid stimulated using ICA as the diverter, and a remaining skin factor was left in the formation. Four months later a second acid treatment was carried out to overcome the damage left from the first treatment as well as to improve productivity, which had decreased in the four months following the first treatment. For this second acid job, APT was used as the diverter. In both cases 15% HCl was used as the main acid treatment. Figure 18 shows the pressure increase achieved when the APT stage arrives at the perforations. This pressure increase was not observed on the first treatment using ICA. While surface

pressure is not a definite indication of acid diversion from a higher to lower permeability zone, it is often the only indicator available.

#### Productivity Index

Productivity index and oil production data for wells acid stimulated using foam, ICA, and APT as the diverter are presented in Fig 19. This data comes from wells where buildup tests were available. From this information, we can clearly state that the average productivity index from those wells acid stimulated with APT is higher from those where foam or ICA was used. The average PI for 22 wells acidized using APT was 351; for 17 wells acidized using ICA it was 219; and for 18 wells acidized using foam it was 178.

#### CONCLUSIONS

- Laboratory tests have shown that the AP diverter can divert acid from predominantly water-saturated zones to predominantly oil-saturated zones in both sandstone and carbonate lithology.
- PLT data from field cases in the Cantarell field show better response from those wells stimulated using APT as the diverter as compared to those using foam or ICA.
- Surface pressure response during acid jobs using APT has shown more consistent indication of diversion as compared to ICA.
- Productivity Index data shows superior results for wells stimulated using APT as the diverter as compared to foam or ICA.
- Results from this field study show that diversion with APT is not limited to wells with high water saturation zones.

#### ACKNOWLEDGEMENTS

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Table 1  
Reservoir Data from Acid Stimulated Wells

	Well No.	Permeability, m	BHST, °F	Interval, m	BHSP, psi	BHFP, psi	Drawdown, psi
Wells Stimulated with APT Diverter	1	3,310	207	3,375–3,400	1573	1556	379
	2	5,000	215	2,650–2,680	1591	1542	183
	3	—	212	3,100–3,130	1581	1572	770
	4	2,000	221	2,740–2,765	1530	997	4
	5	6,410	216	3,282–3,312	1552	1392	56
	6	106	210	2,585–2,615	1613	1120	5
	7	1,010	212	3,170–3,200	1541	1522	227
	8	203	220	2,635–2,660	1607	1254	14
	9	8,340	222	3,388–3,500	1827	1817	682
	10	N/A	217	2,863–2,885	1296	1238	45
	11	N/A	—	2,720–2,750	1579	1537	169
	12	10,000	216	2,585–2,616	1576	1570	1247
	13	5,000	209	2,815–2,865	1624	1610	738
	14	N/A	220	2,800–2,830	1726	1705	474
	15	24,600	217	3,125–3,250	1697	1686	860
	16	10,700	228	3,385–3,410	1784	1715	107
	17	17,200	215	2,808–2,816, 2,821–2,832	1622	1566	195
	18	13,800	207	2,828–2,895	1667	1615	110
	19	S/D	205	2,665–2,695	1558	1533	371
	20	23,000	215	3,045–3,070	1609	1597	507
	21	S/D	225	3,055–3,080	1745	1727	409
	22	4,840	217	2,800–2,830	1753	1714	166
Wells Stimulated with In Situ Gelled Acid	23	3,970	212	3,078–3,155	1906	1889	478
	24	2,330	222	3,277–3,325	1674	1600	93
	25	2,920	209	2,843–2,893	1826	1763	229
	26	1,620	227	2,970–2,995, 3,050–3,075	1548	1487	145
	27	10,400	217	2,570–2,615	1715	1705	1175
	28	1,030	204	2,680–2,710	1669	1299	25
	29	1,030	206	2,865–2,875, 2,880–2,900	1550	1462	31
	30	674	219	2,875–2,900	1338	1275	55
	31	1,790	219	2,670–2,720	1719	1704	441
	32	1,180	210	2,860–2,890	1741	1440	34
	33	167	222	3,277–3,355	1674	1580	84
	34	22	208	3,105–3,120, 3,145–3,180	1608	1251	19
	35	23,000	218	3,100–3,150	2102	2052	151
	36	1,790	212	2,670–2,720	1719	1705	459
	37	2,610	207	2,650–2,700	1561	1507	157
	38	447	215	2,583–2,628, 2,636–2,660	1264	1163	39
	39	563	219	2,520–2,550	1540	1464	115
Wells Stimulated with Foam	40	17,300	204	2,610–2,660	1664	1573	91
	41	13,600	217	2,655–2,705	1666	1640	26
	42	81	223	2,497–2,503, 2,510–2,540	1657	1539	118
	43	5,660	222	2,885–2,935	1493	1428	65
	44	580	218	2,700–2,750	1802	1613	190
	45	1,790	209	2,600–2,620	1624	1157	468
	46	9,560	0	2,505–2,555	1586	1556	30
	47	2,136	205	3,375–3,425	1830	1552	278
	48	10,766	208	2,640–2,690	1707	1695	12
	49	829	208	2,640–2,690	1820	1788	32
	50	388	208	2,730–2,766, 2,791–2,814	1487	1189	298
	51	10,300	209	2,793–2,945	1730	1682	48
	52	65	209	2,725–2,755	1706	1491	215
	53	100	208	2,497–2,503, 2,510–2,540	1654	1539	115
	54	447	214	2,795–2,870	1810	1605	205
	55	2,310	206	3,165–3,209	1421	1369	52
	56	1,710	217	2,830–2,926	1512	1483	29
	58	2,397	199	2,760–2,780	1187	1062	125

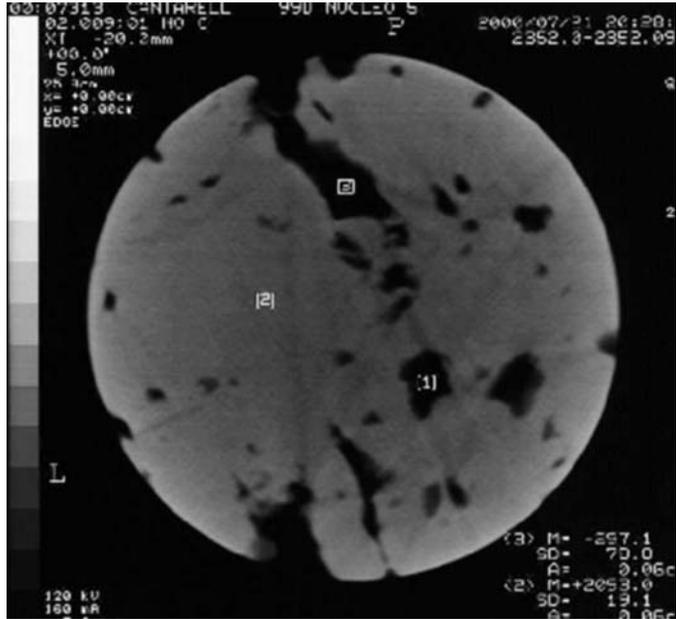


Figure 1 - Core sample showing natural net of fractures and vugs, typical from this formation.

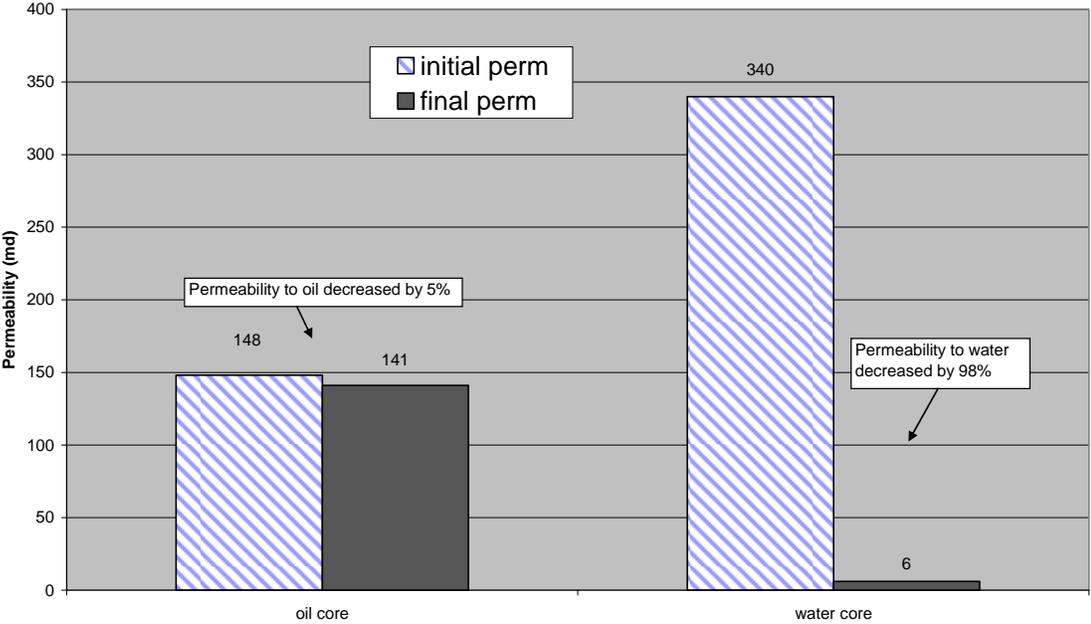


Figure 2 - Single core flow tests on water and oil saturated sandstone cores at 175°F.

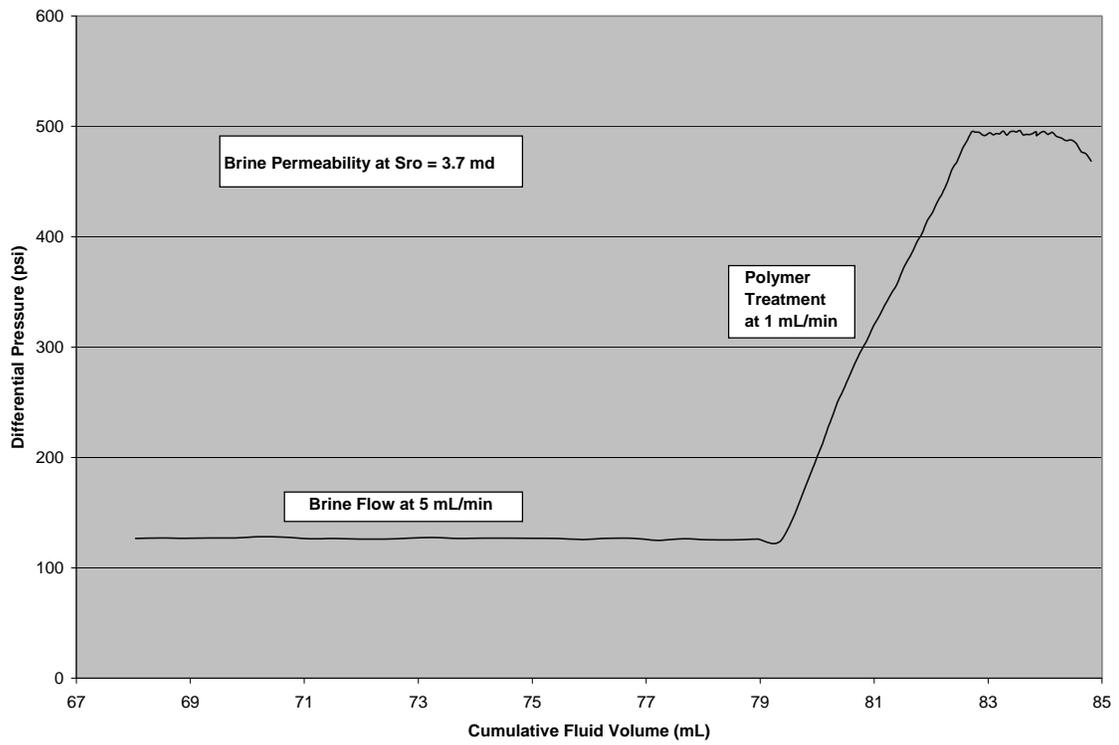


Figure 3 - Pressure buildup during treatment of a carbonate core, 175°F.

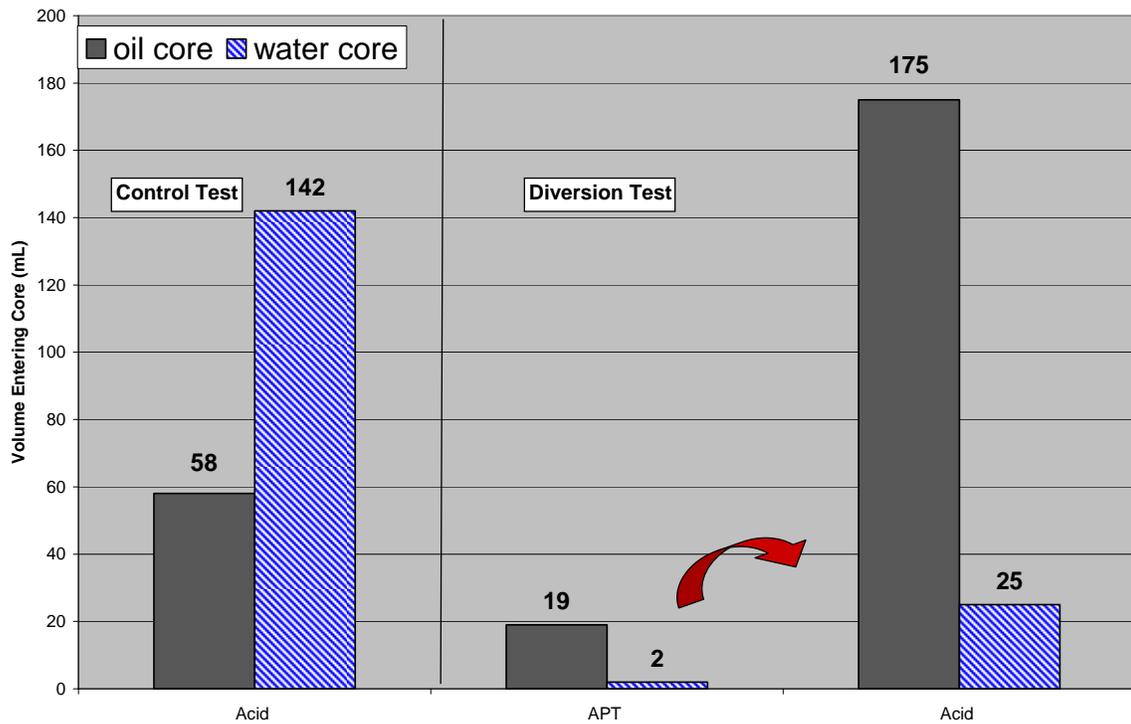


Figure 4 - Diversion test with carbonate cores of similar permeabilities.

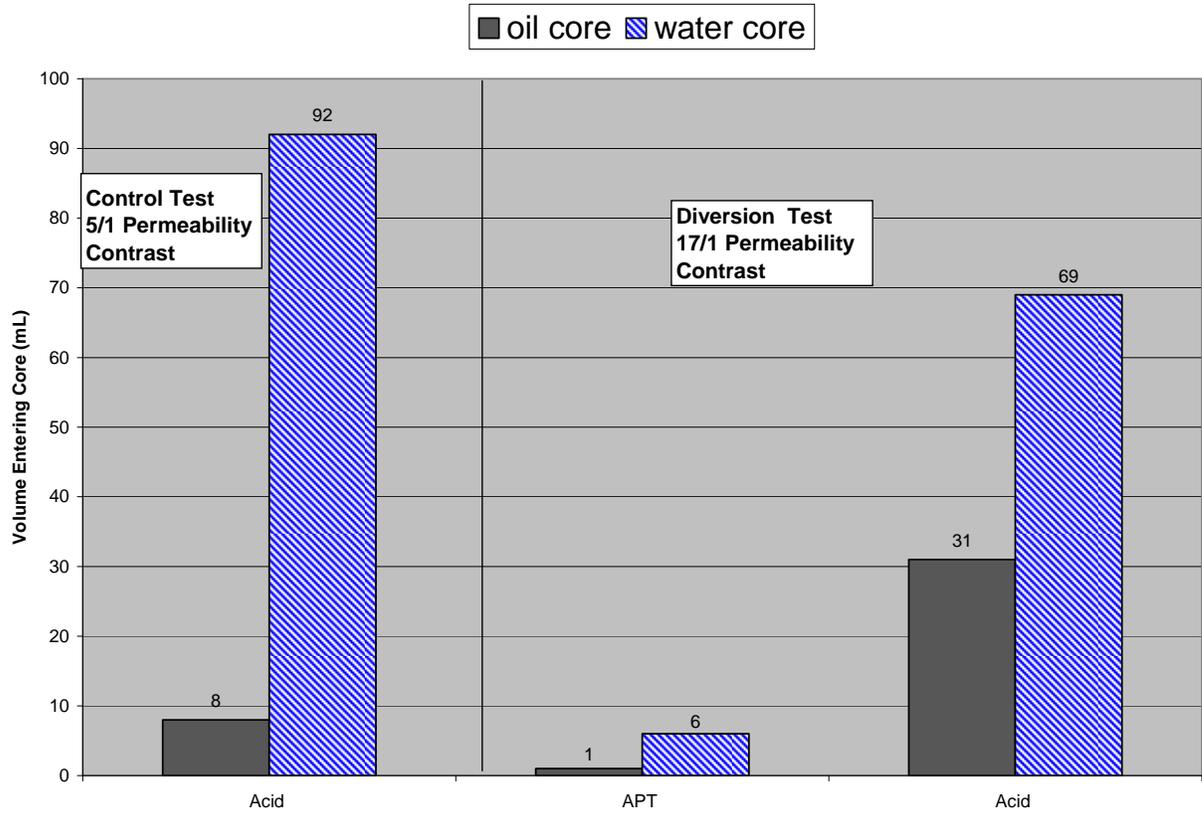


Figure 5 - Diversion test with carbonate cores of different permeabilities.

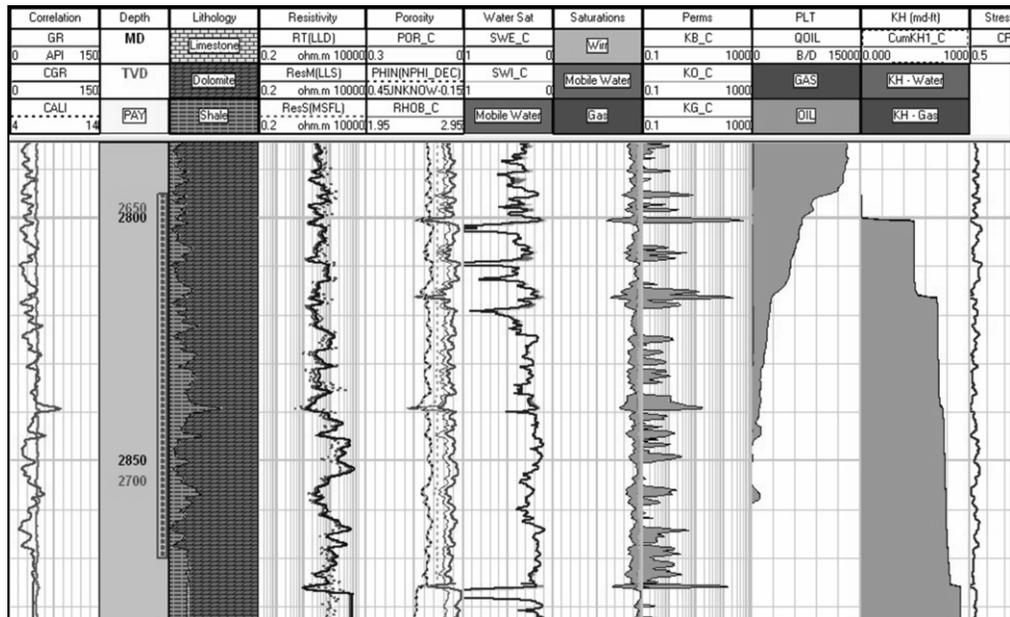


Figure 6 - Composite log from Well 34 acid stimulated using a foam diverter.

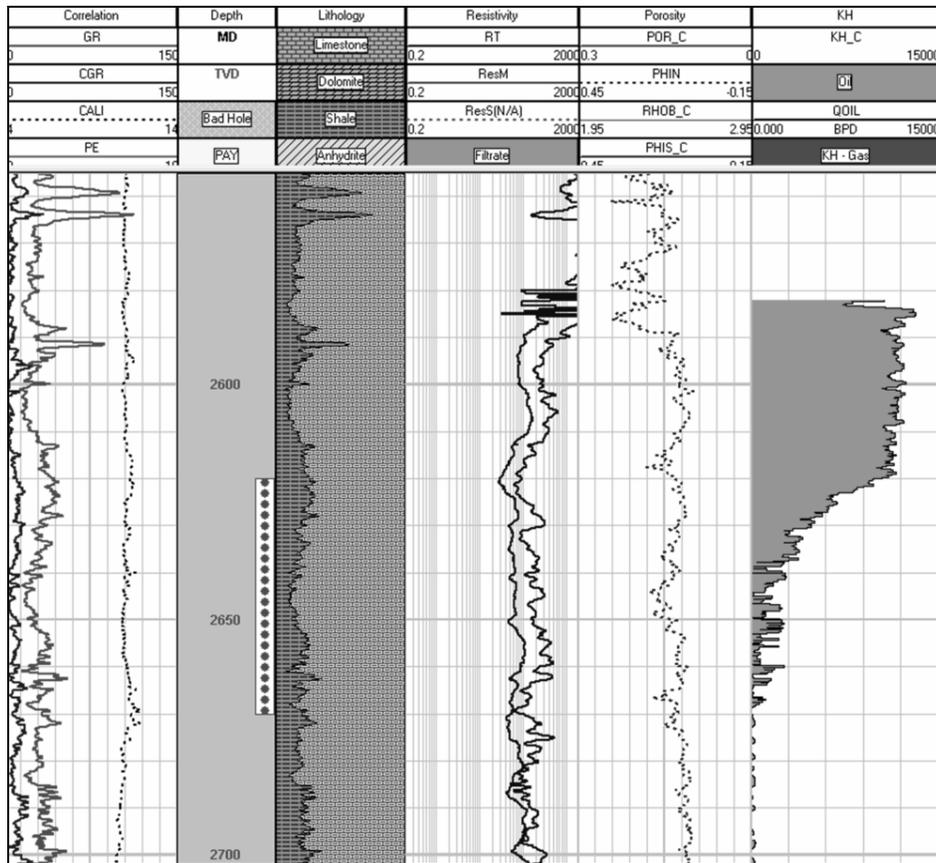


Figure 7 - Composite log from Well 30 acid stimulated using a foam diverter.

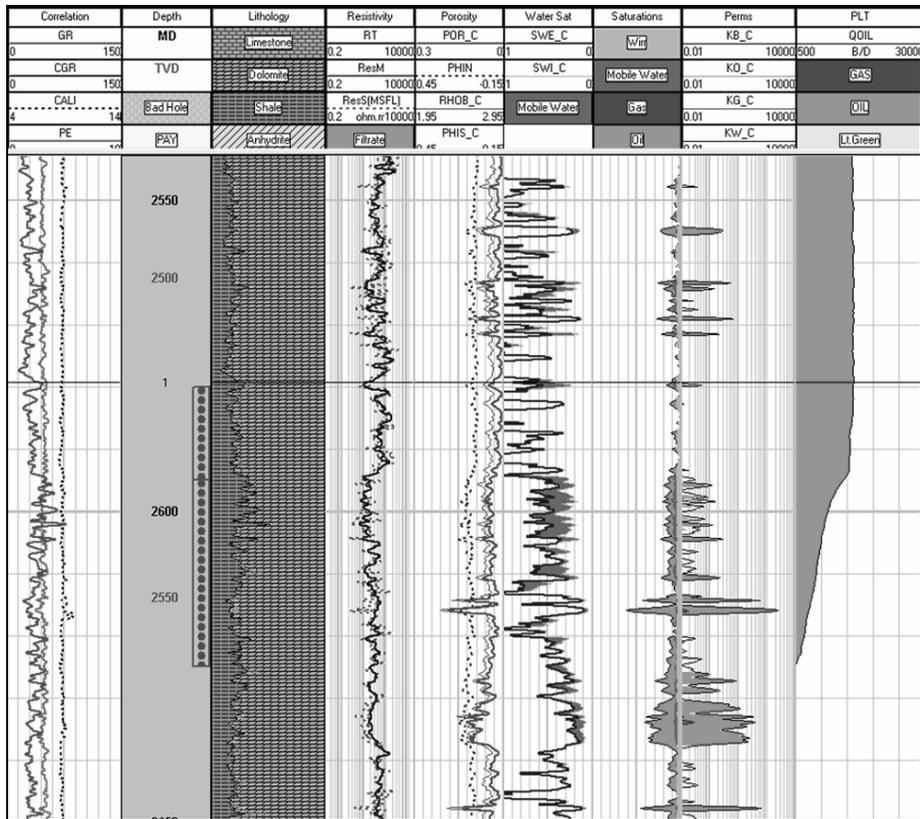


Figure 8 - Composite log with PLT from Well 16 acid stimulated using ICA diverter.

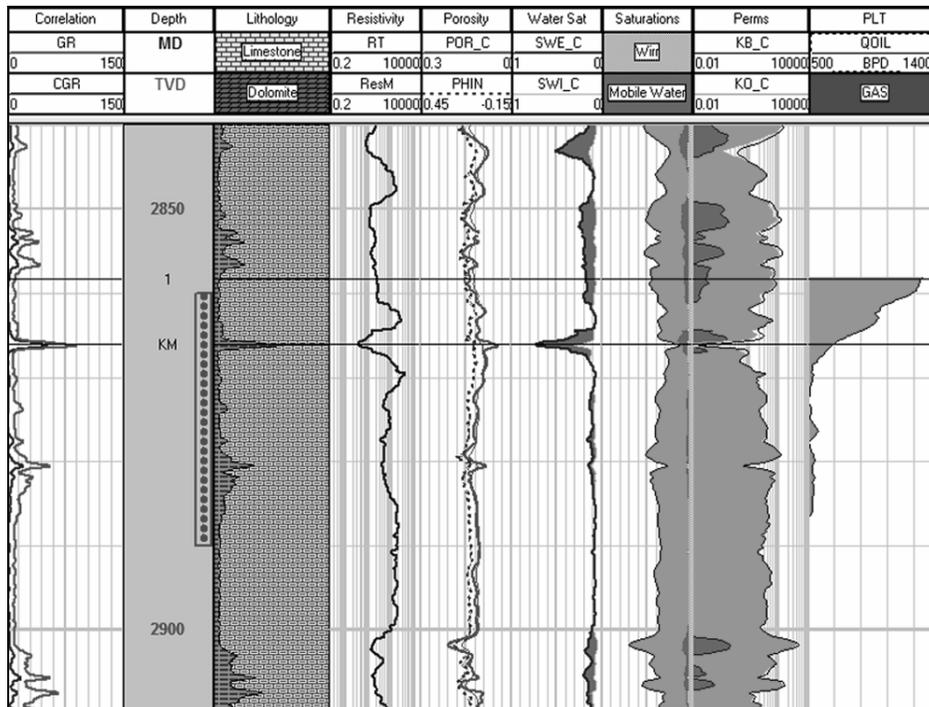


Figure 9 - Composite log with PLT from Well 17 acid stimulated using ICA diverter.

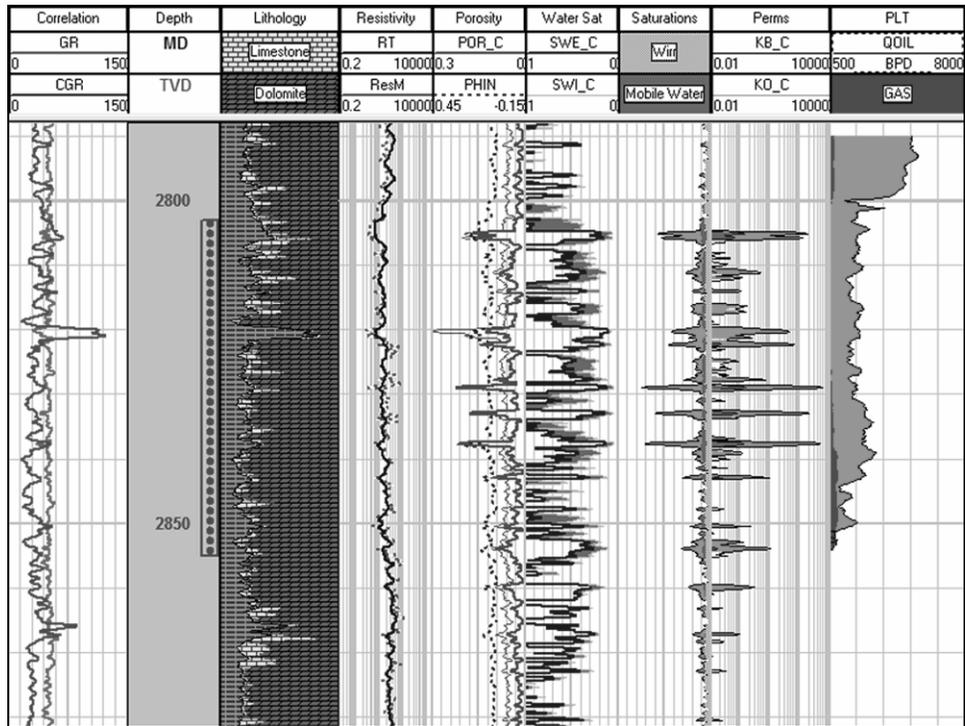


Figure 10 - Composite log with PLT from Well 18 acid stimulated using ICA diverter.

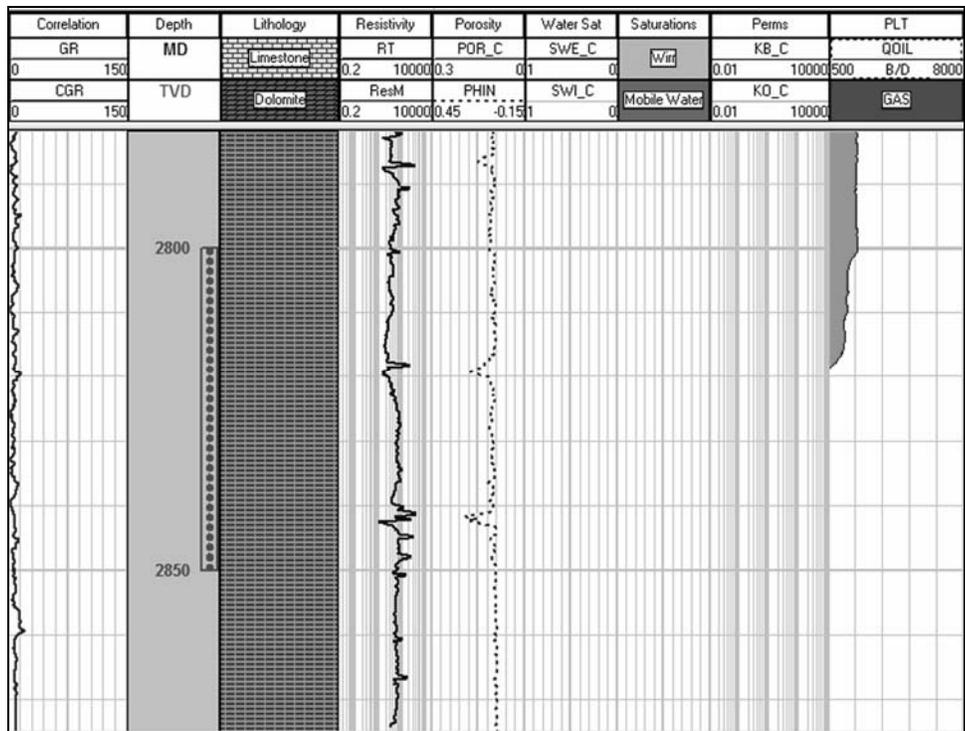


Figure 11 - Composite log with PLT from Well 19 acid stimulated using ICA diverter.

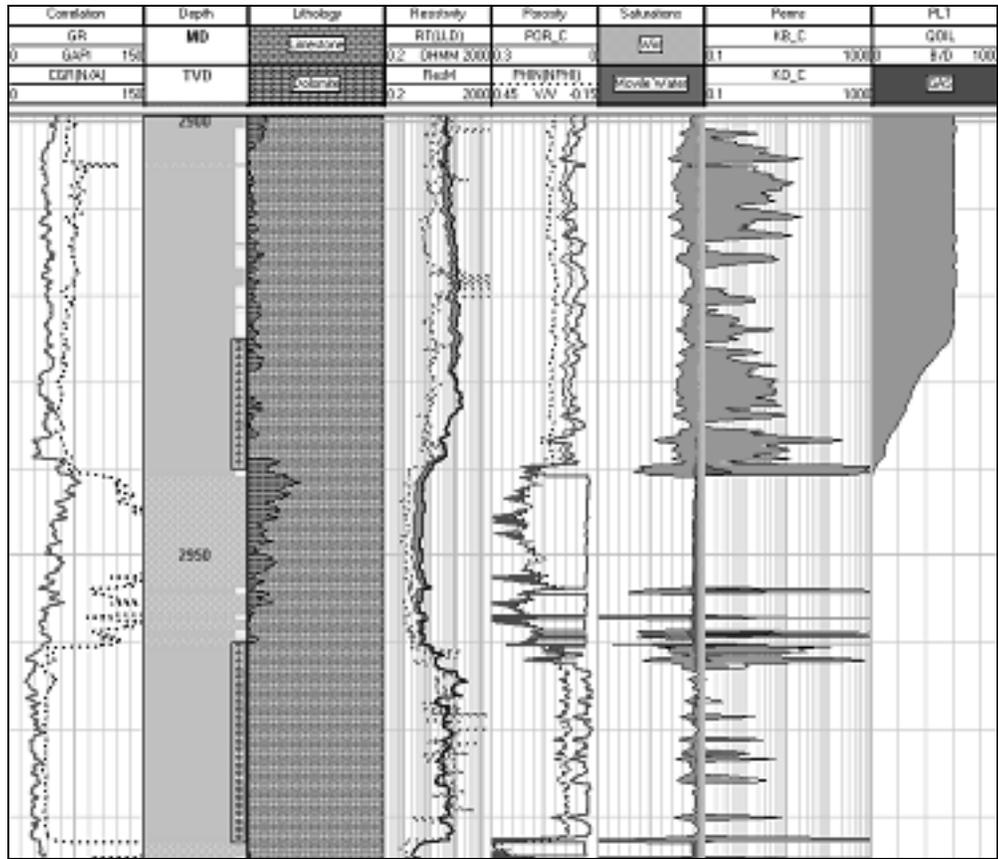


Figure 12 - Composite log with PLT from a well acid stimulated using ICA diverter.

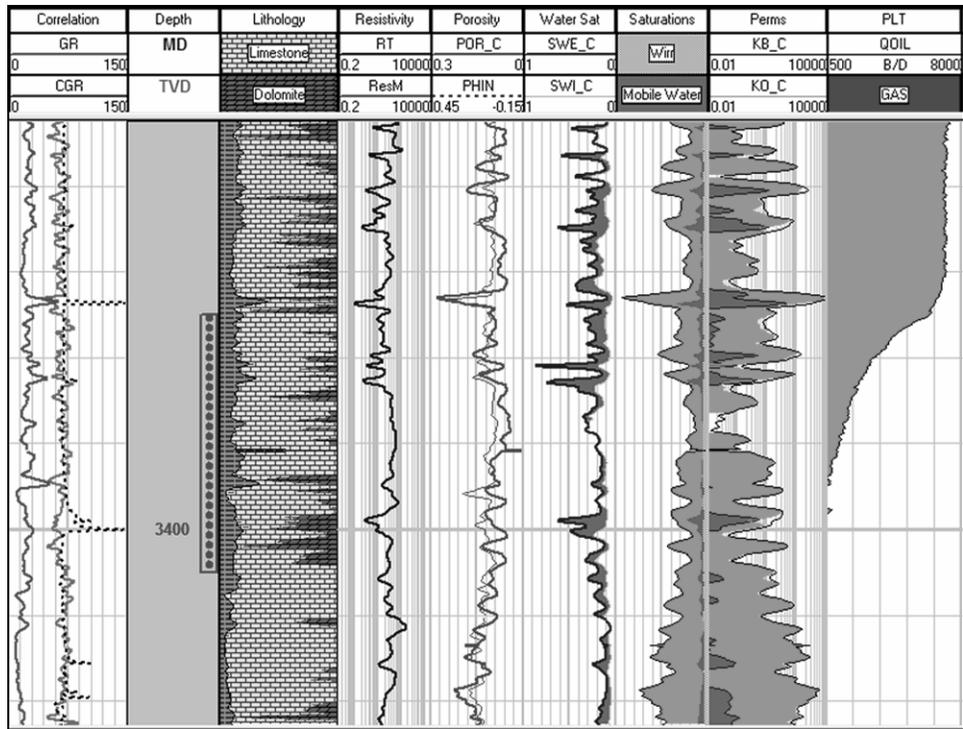


Figure 13 - Composite log with PLT from Well 1 acid stimulated with APT diverter.

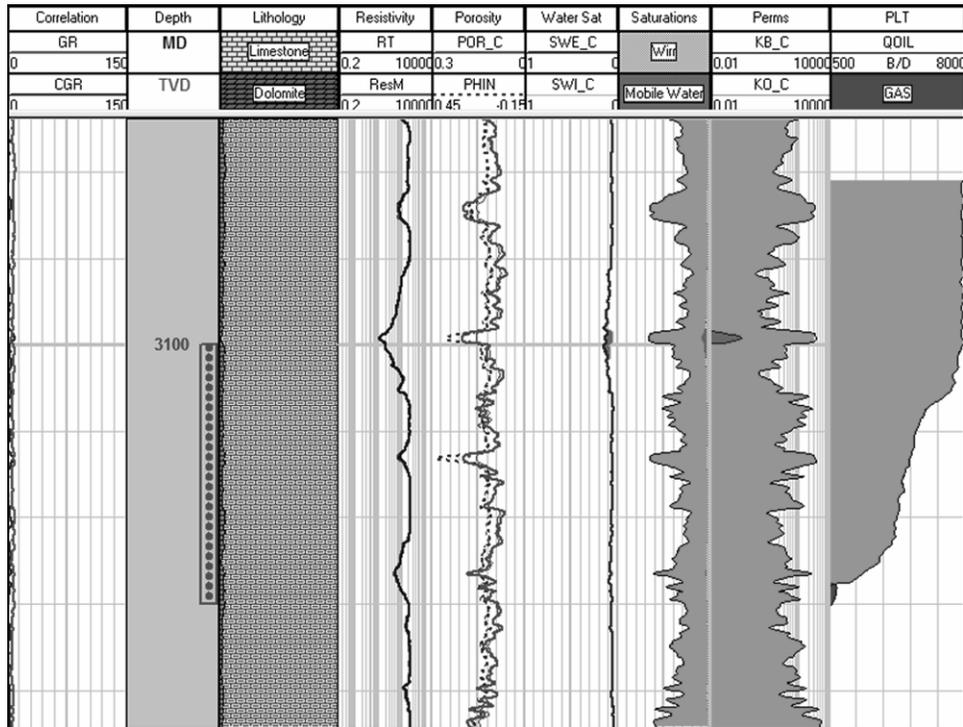


Figure 14 - Composite log with PLT from Well 2 acid stimulated with APT diverter.

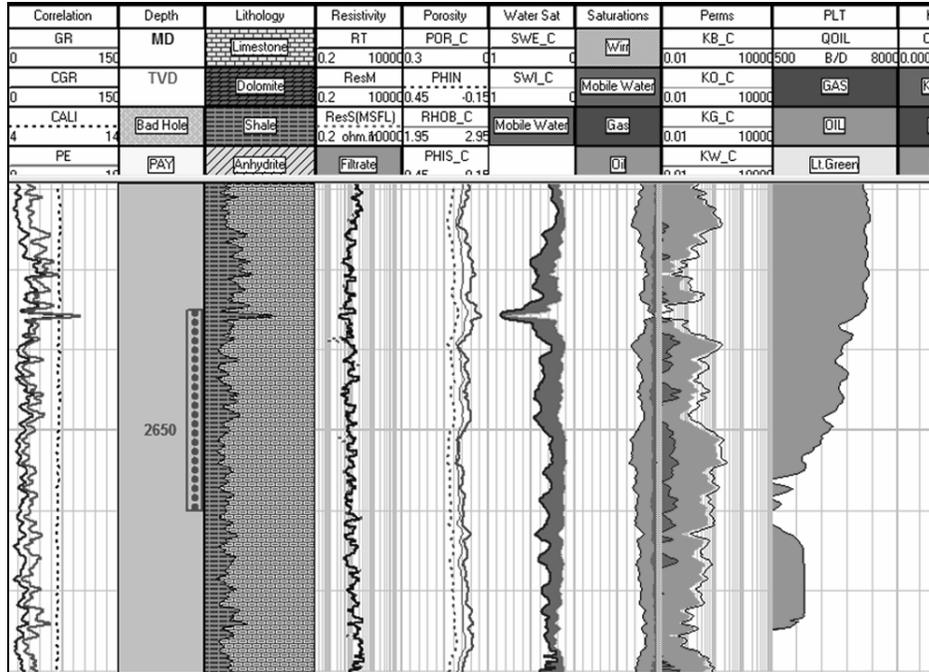


Figure 15 - Composite log with PLT from Well 3 acid stimulated with APT diverter.

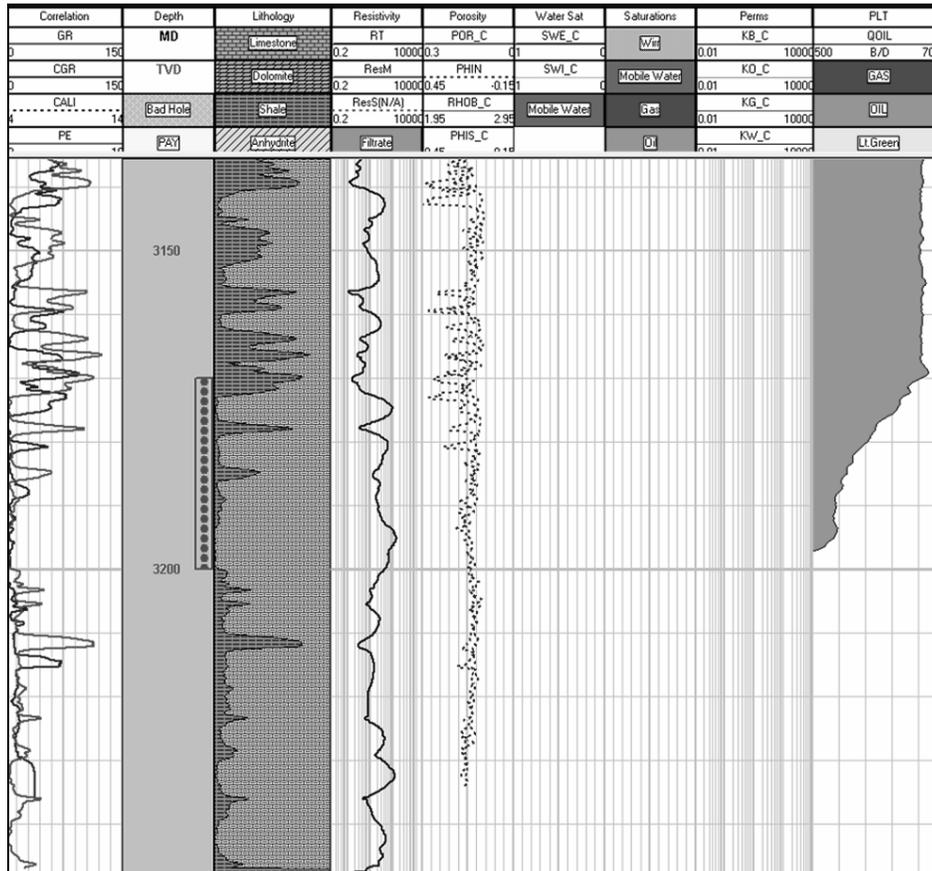


Figure 16 - Composite log with PLT from Well 4 acid stimulated with APT diverter.

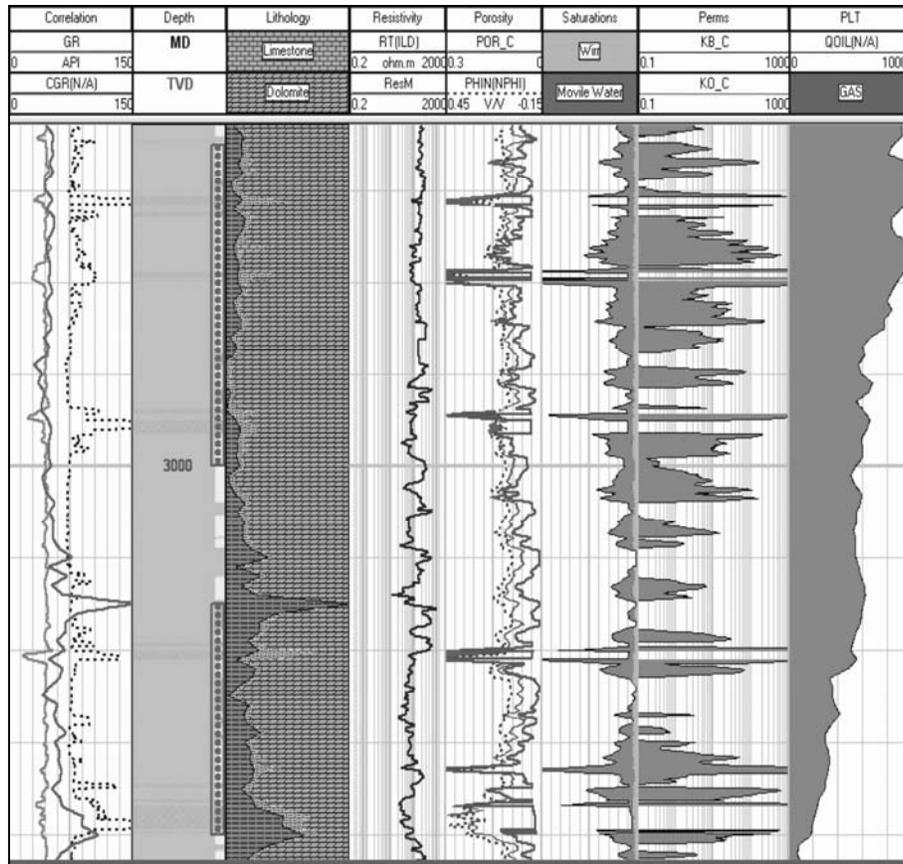


Figure 17 - Composite log with PLT from a well acid stimulated with APT diverter.

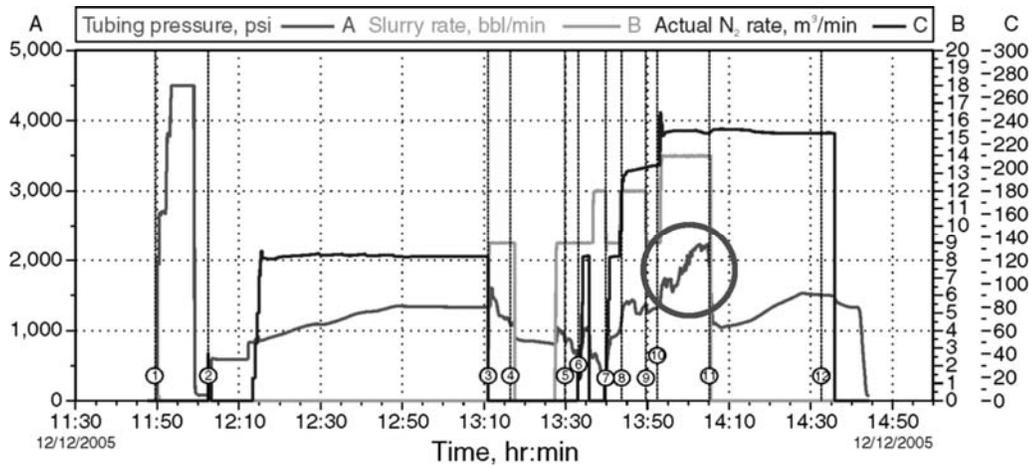


Figure 18 - Job chart from a well acid stimulated with APT diverter.

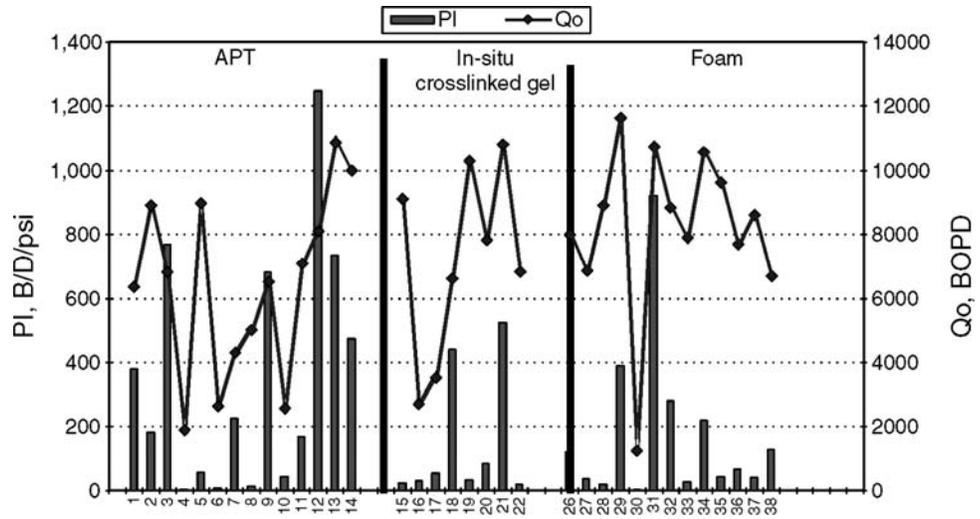


Figure 19 - Productivity index data.