# ACETIC ACID SUCCESSFULLY STIMULATES SAN ANDRES

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## ABSTRACT

Carbonate formations are predominate in the Permian Basin and as such are commonly stimulated with acids. Success of an acid treatment is dependent on knowledge of the reservoir, design techniques, execution and emphasis on obtaining good zone coverage. In addition, effectiveness is very dependent on how many times a well has been acidized and with what kind of acid.

Case histories of acid stimulation, with production results, are presented on a new technique for stimulating the San Andres dolomite. Treatments were all low rate matrix treatments designed to minimize the increase in water production. Discussed are conditions to overcome in order to get effective acid penetration and thus stimulation. The case histories presented are on San Andres wells that have been acidized several times in the past. Where this new technique has been used to provided an improved response over a longer period of time following the treatment.

## BACKGROUND

It has been previously reported that dilution of weak acids facilitates increased dissolution of carbonates.[1,2] The reaction of acetic acid and other "weak" acids on calcite have been studied by many.[2-7] Principle equations of this reaction are:

$$\mathbf{H^{+} + CaCO_3 \Leftrightarrow Ca^{2+} + HCO_3^{-}} \text{ …………………. } \mathbf{(1)}$$

$$\mathbf{H^{2}CO_3 + CaCO_3 \Leftrightarrow Ca^{2+} + 2HCO_3^{-}} \text{ ....……….. } \mathbf{(2)}$$

$$\mathbf{H_2O + CaCO_3 \Leftrightarrow Ca^{2+} + HCO_3^{-} + OH^{-}} \text{ ………} \mathbf{(3)}$$

$$\mathbf{HAc \Leftrightarrow H^{+} + Ac^{-}} \text{ ......................................……….. } \mathbf{(4)}$$

It has been found that when the partial pressure of $CO_2$ is low and the pH is low equation (1) is dominant and when the pH is high equation (3). $CO_2$ partial pressure greater than 0.1 atmospheres and pH greater than 5 equation (2) dominates the dissolution of calcite.[4] Investigation into reaction kinetics of acetic acid on calcite using rotating disks determined that over the pH range 2.3 to 2.9 dissolution was mass transfer limited.[5] However, the dissolution rates were lower than expected based on reactant diffusion coefficients. It was decided that the diffusion of the reactants to the surface and the products away from the surface interacted to reduce the dissolution. It was also found that above pH 3.7 the surface reaction rate has a major effect on the dissolution. Chatelain, et al. (1975)[6], determined that influence by the products transport away from the surface was the primary reason for the difference in dissolution. Fredd, et al. (1998)[5], determined the transition region to be at a pH less than 3.7. Several researchers have put together models for the dealing with kinetic expressions governing weak acid reactivity and the associated equilibrium constants.[5,7]

The possibility of treating carbonate producing and injection wells with acid to a deeper penetration appeared to be feasible. This patented process[2] incorporates the lead acid reaching equilibrium some distance into the carbonate formation and remaining at equilibrium as long as it is under pressure. Once recovery begins and pressure is released the equilibrium will have to shift do to a loss of carbon dioxide gas from the fluid. This shift in equilibrium will mean the dissolution of more rock. At the acid and overflush water interface, dilution of the acid forces the continued change in equilibrium. This continuous shift in equilibrium results in further dissolution of rock.

The San Andres (~4,700 to 5,700 feet) is a dolomitic formation with solution gas drive in combination with gas cap expansion.[9-10] Average permeability is over 9 md with an average porosity greater than 13%. Acid solubility varies from 78% to 92% in 15% hydrochloric acid. The main components of the lithology are dolomite (77% to 92%) and Anhydrite (3% to 20%). Typical values are illustrated in **Figure 1,** which is based on core work from Gaines County, Texas. Bottomhole temperature is typically 100° to 125°F. The keys to getting a successful stimulation treatment are deep penetration, staying out of water, and keep costs down. To keep the water production from getting higher, the wells must be treated at low rates. The low rate means that acid is the best way to go for an attempt at stimulation. However, there are several problems with this technique. First, since these wells have been acidized several times the effectiveness of subsequent acid treatments depends on making changes to either rate, volume or type of acid system used. Each subsequent acid treatment in the same wellbore will see more surface area for it to react with and therefore will spend a shorter distance from the wellbore (**Figure 2**). Overcoming this can be accomplished by pumping more acid or a different type of acid

## FIRST STUDY AREA

In the first area of interest (**Figure 3**), three wells in the San Andres were treated. The characteristics of the wells and the treatment volumes are listed in **Table 1**. All of these wells had been acidized several times over their producing lives (over 15 years) and therefore, as stated above, have experienced the increased surface area around the near wellbore area which can limit the effectiveness of each subsequent treatment. The application of this method of pumping a concentrated Acetic Acid solution appeared to be in accordance with what is understood as a means of going beyond this increased surface area into the reservoir and therefore effecting stimulation. A summary of the different treatment schedules pumped on the four wells are listed in **Table 2**. Hydrochloric acid was used ahead of each treatement in order to insure good fluid entry into the perforated intervals. An example of the rate and pressures observed on the treatment of Well #3 is illustrated in **Figure 4**. As stated above the wells must be treated at a low rate (3 to 4 BPM) in order to minimize the increase in water production.

**Table 3** lists the stabilized production responses before and after the treatments. **Figure 5** illustrates the production history of Well #1. Oil production was increased by an average of 113% while water cut increased an average of 2% on Wells #1 and #2 and decreased by 13% on Well #3.

## SECOND STUDY AREA

This area of interest (**Figure 3**) had four wells in the San Andres that were treated. The characteristics of the wells and the treatment volumes are listed in **Table 4**. All of these wells had been acidized several times over their producing lives (approximately 10 years) and as in the First Study Area above, they were prime candidates for this new treatment. A summary of the two different treatment schedules pumped on these wells is listed in **Table 5**. An example of the rate and pressures observed on each of these different methods are illustrated in **Figure 5 and Figure 7**.

**Table 6** lists the stabilized production responses before and after the treatments. Oil production was increased by an average of 106% with Well #4 having no improvement after production had stabilized. Water cut decreased an average of 2.5% over the four wells, with only Well #4 having an increase in water cut of 5%.

## THIRD STUDY AREA

This area of interest (**Figure 3**) had two wells in the San Andres that were treated. The characteristics of the wells and the treatment volumes are listed in **Table 7**. Both of these wells had been acidized several times over their producing lives (approximately 12 years) and as in the other study areas above, these were prime candidates for a low rate Acetic Acid treatment. An overview of the treatment schedule pumped on each these wells is listed in **Table 8**. An example of the rate and pressures observed are illustrated in **Figure 8** for Well #1.

**Table 9** lists the stabilized production responses before and after the treatments. Oil production was increased 133% in Well #2, while Well #1 had no apparent improvement after production had stabilized. The operator believes that the production on both wells will come up as they are having water injection problems. Water cut increased by an average of approximately 1%. Well #2's water production is significantly higher than pre-treatment rates and the operator feels confident that this will decrease.

## CONCLUSIONS

1. Production increases of 106% to 133% was achieved using the changes in equilibrium of 30% acetic acid on the San Andres wells that had been previously acidized several times using hydrochloric acid.
2. Low treatment rates along with the use of the slower reacting acetic acid controlled the water cut changes to within 2%± in each of the areas and resulted in an overall an insignificant change.

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Table 1
Summary of Wells in First Study Area

| | **Well #1** | **Well #2** | **Well #3** |
|---|---|---|---|
| Casing | 5-1/2" – 14# | 5-1/2" – 14# | 5-1/2" – 15.5# |
| Depth | 4900' | 4840' | 4834' |
| Tubing | 2-7/8" – 6.5# | 2-3/8" – 4.7# | 2-3/8" – 4.7# |
| Perforations Depth (Number) | 4802' – 4828' (78) | 4802' – 4810' (40)<br>4816' – 4830' (52) | 4800' – 4820' (40)<br>4824' – 4834' (20) |
| Treatment | 750 gals HCl<br>2000 gals Acetic<br>770 bbls Flush | 750 gals HCl<br>2000 gals Acetic<br>850 bbls Flush | 750 gals HCl<br>2000 gals Acetic<br>850 bbls Flush |

| Table 2<br>Overview of Treatments of Wells in First Study Area | | |
|---|---|---|
| **Stage** | **Stage Function** | **Fluid Description** |
| 1 | Load hole and establish injection rate | Fresh Water |
| 2 | Acid | 15% HCl + Ball Sealers |
| 3 | Flush | Fresh Water |
| 4 | Surge Balls off Perforations | |
| 5 | Acetic Acid | 30% Acetic Acid |
| 6 | Flush | Fresh Water |

| Table 3<br>Summary of Production Response of Wells in First Study Area | | | |
|---|---|---|---|
| | **Well #1** | **Well #2** | **Well #3** |
| Oil Before | 10 BOPD | 2 BOPD | 2 BOPD |
| Gas Before | 2 MCFD | 1 MCFD | 1 MCFD |
| Water Before | 47 BWPD | 18 BWPD | 7 BWPD |
| Oil After | 14 BOPD | 3 BOPD | 7 BOPD |
| Gas After | 5 MCFD | 3 MCFD | 2 MCFD |
| Water After | 77 BWPD | 35 BWPD | 13 BWPD |

| Table 4<br>Summary of Wells in Second Study Area | | | | |
|---|---|---|---|---|
| | **Well #1** | **Well #2** | **Well #3** | **Well #4** |
| Casing | 4-1/2” – 10.5# | 4-1/2” – 10.5# | 4-1/2” – 9.5# | 5-1/2” – 14# |
| Depth | 5060’ | 5055’ | 4994’ | 5029’ |
| Tubing | 2-3/8” | 2-3/8” | 2-3/8” | 2-3/8” |
| Perforations<br>Depth (Number) | 4944’ – 72’ (29)<br>5000’ – 12’ (13)<br>5028’ – 32’ (6) | 4962’ – 88’ (20)<br>5024’ – 36’ (14) | 4964’ – 90’ | 4996’ – 5010’ |
| Treatment | 500 gals HCl<br>3000 gals Acetic<br>754 bbls Flush | 1000 gals HCl<br>2500 gals Acetic<br>884 bbls Flush | 1000 gals HCl<br>2500 gals Acetic<br>711 bbls Flush | 750 gals HCl<br>2000 gals Acetic<br>916 bbls Flush |

| Table 5<br>Overview of Treatments of Wells in Second Study Area | | | | |
|---|---|---|---|---|
| | **Method One** | | **Method Two** | |
| **Stage** | **Stage Function** | **Fluid Description** | **Stage Function** | **Fluid Description** |
| 1 | Load hole and establish injection rate | Fresh Water | Load hole and establish injection rate | Fresh Water |
| 2 | Acid | 15% HCl + Ball Sealers | Acid | 15% HCl |
| 3 | Flush | Fresh Water | Spacer | Fresh Water |
| 4 | Surge Balls off Perforations | | Acetic Acid | 30% Acetic Acid |
| 5 | Acetic Acid | 30% Acetic Acid | Diversion | 10# Brine + Rock Salt |
| 6 | Flush | Fresh Water | Acetic Acid | 30% Acetic Acid |
| 7 | | | Diversion | 10# Brine + Rock Salt |
| 8 | | | Acetic Acid | 30% Acetic Acid |
| 9 | | | Flush | Fresh Water |

| Table 6<br>Summary of Production Response of Wells in Second Study Area | | | | |
|---|---|---|---|---|
| | **Well #1** | **Well #2** | **Well #3** | **Well #4** |
| Oil Before | 2.5 BOPD | 2 BOPD | 3 BOPD | 1 BOPD |
| Gas Before | 4 MCFD | 2 MCFD | <1 MCFD | 5 MCFD |
| Water Before | 21 BWPD | 8 BWPD | 8 BWPD | 15 BWPD |
| Oil After | 4.5 BOPD | 5.5 BOPD | 7 BOPD | 1 BOPD |
| Gas After | 12 MCFD | 9 MCFD | 10 MCFD | 0 MCFD |
| Water After | 30 BWPD | 18 BWPD | 12 BWPD | 62 BWPD |

| Table 7<br>Summary of wells in Third Study Area | | |
|---|---|---|
| | **Well #1** | **Well #2** |
| Casing | 5-1/2” – 17# | 5-1/2” – 15.5# |
| Depth | 5400’ | 5400’ |
| Tubing | 2-7/8” – 6.5# | 2-7/8” – 6.5# |
| Perforations<br>Depth (Number) | 5228’ – 34’ (36)<br>5238’ – 48’ (20)<br>5253’ – 60’ (14)<br>5264’ – 76’ (24)<br>5281’ – 83’ (12)<br>5287’ – 98’ (22) | 5234’ – 40’ (14)<br>5246’ – 54’ (18)<br>5260’ – 70’ (22)<br>5274’ – 80’ (14)<br>5284’ – 91’ (16) |
| Treatment | 3000 gals Acetic<br>830 bbls Flush | 2500 gals Acetic<br>840 bbls Flush |

| Table 8<br>Overview of Treatments of Wells in Second Study Area | | |
|---|---|---|
| **Stage** | **Stage Function** | **Fluid Description** |
| 1 | Load hole and establish injection rate | Fresh Water |
| 2 | Acetic Acid + Ball Sealers | 30% Acetic Acid |
| 3 | Surge Balls off Perforations | |
| 4 | Flush | Fresh Water |

| Table 9<br>Summary of Production Response of Wells in Third Study Area | | |
|---|---|---|
| | **Well #1** | **Well #2** |
| Oil Before | 4 BOPD | 3 BOPD |
| Gas Before | 3 MCFD | 3 MCFD |
| Water Before | 55 BWPD | 85 BWPD |
| Oil After | 4 BOPD | 7 BOPD |
| Gas After | 4 MCFD | 4 MCFD |
| Water After | 58 BWPD | 325 BWPD |

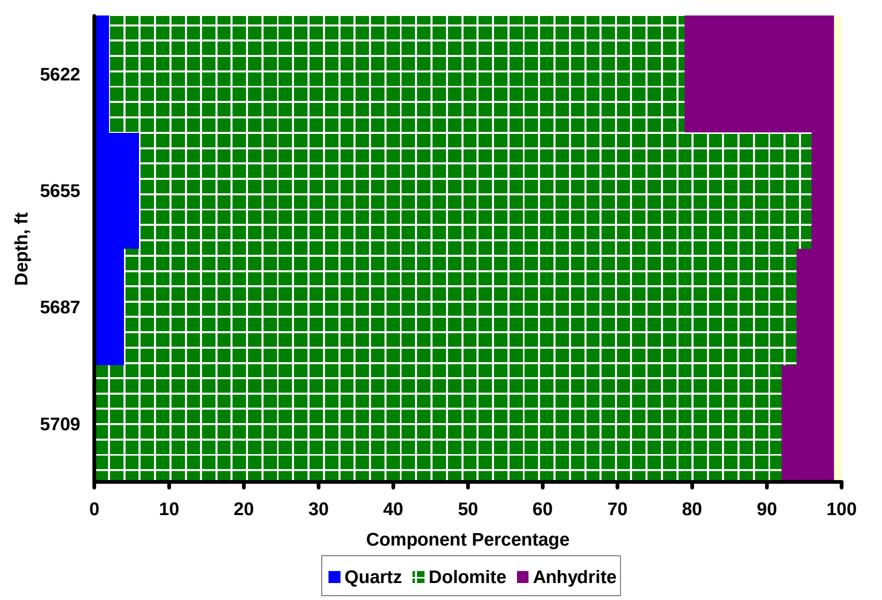


Figure 1 – Variance in lithology of San Andres.

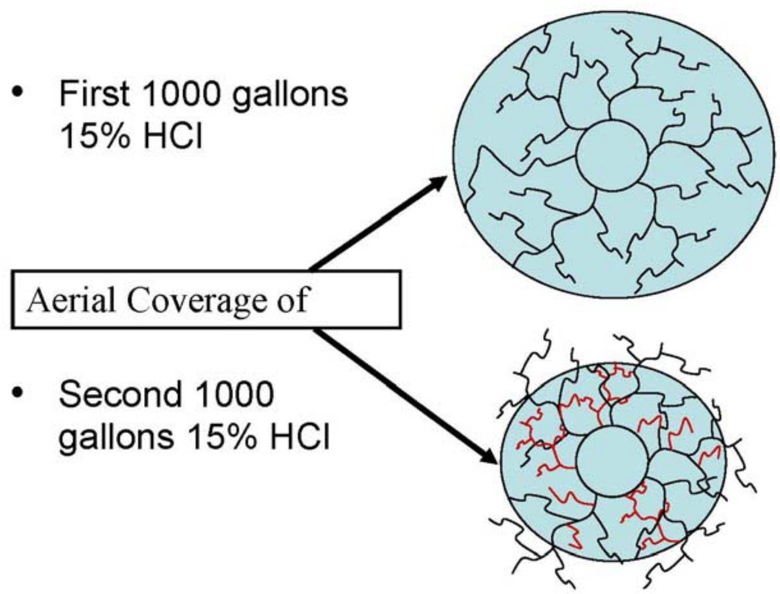


Figure 2 – Difference in acid effectiveness.

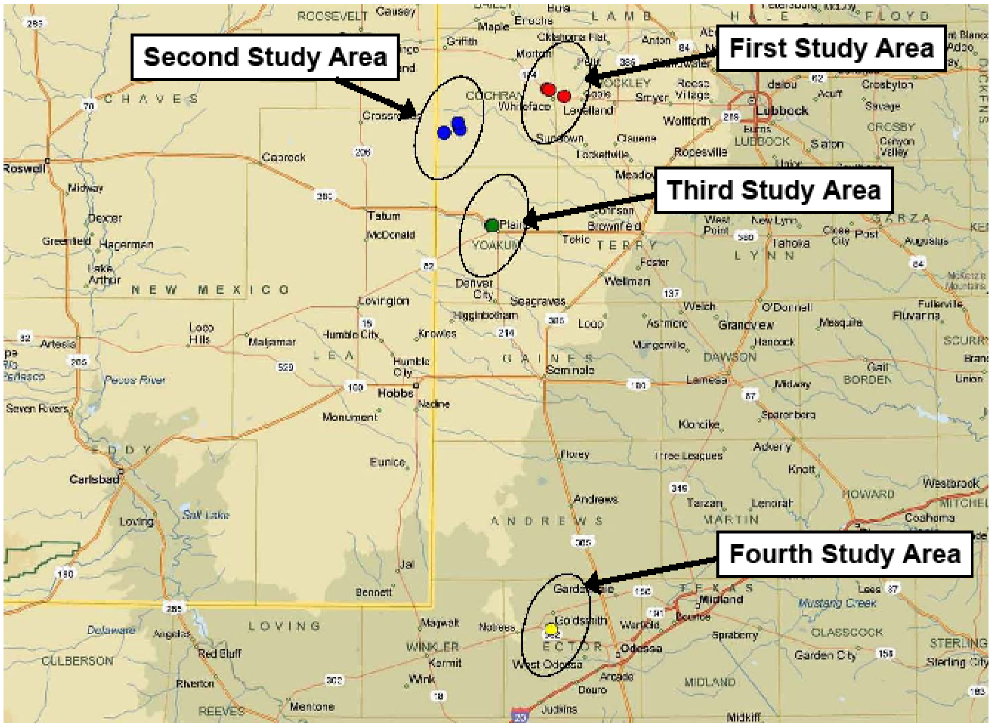


Figure 3 – Map of Study Areas.

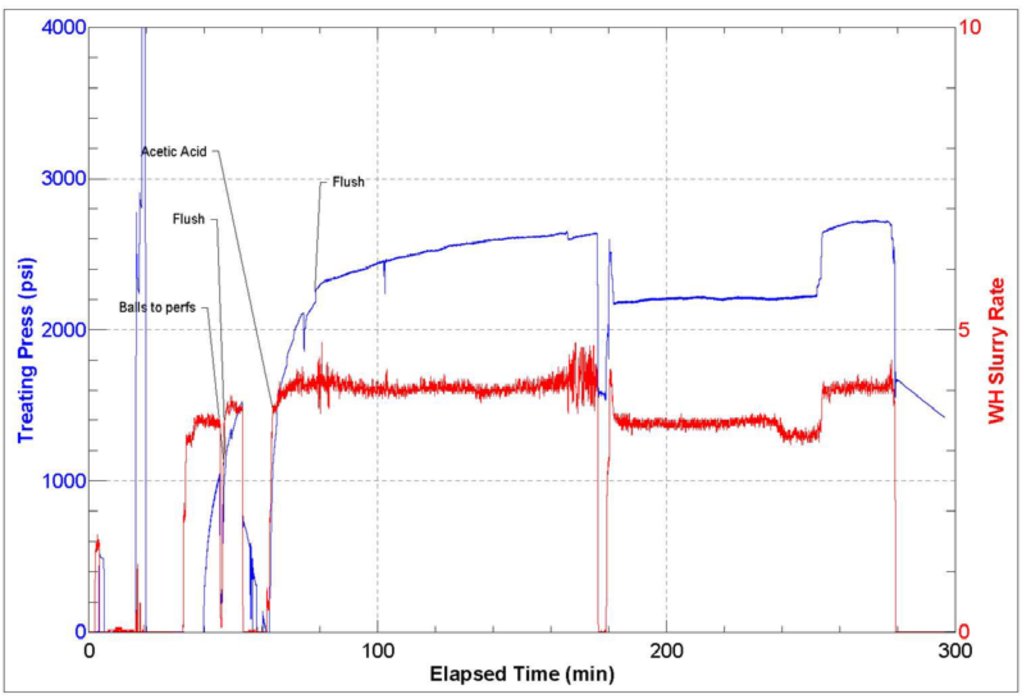


Figure 4 - Plot of Rates and Pressures during treatment of Well #3 in the San Andres in the First Study Area.

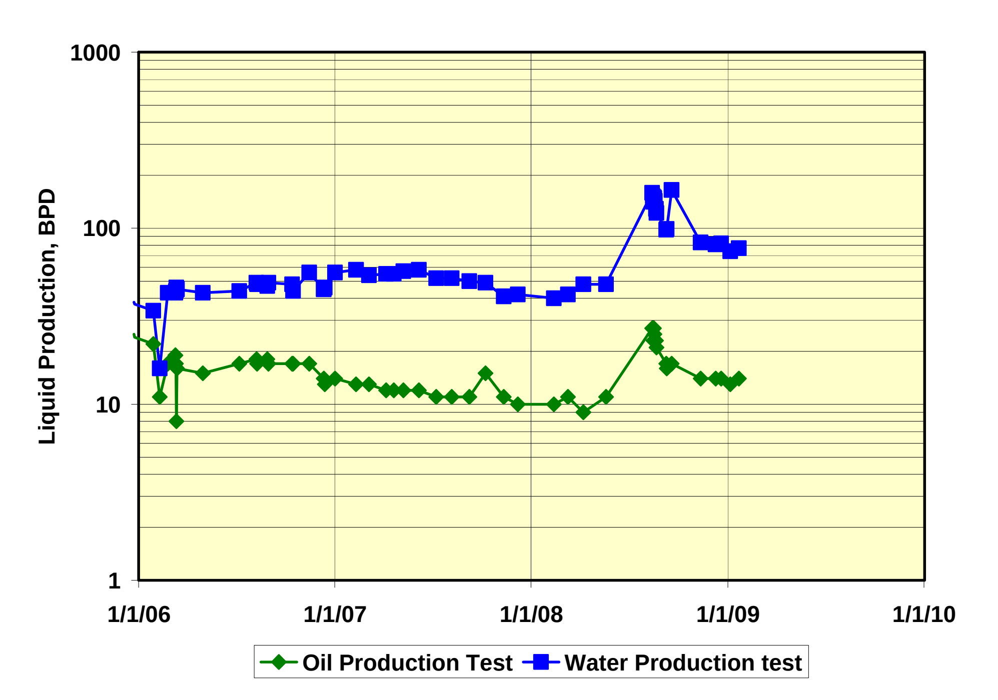


Figure 5 – Production history Well #1 of the San Andres wells in the First Study Area.

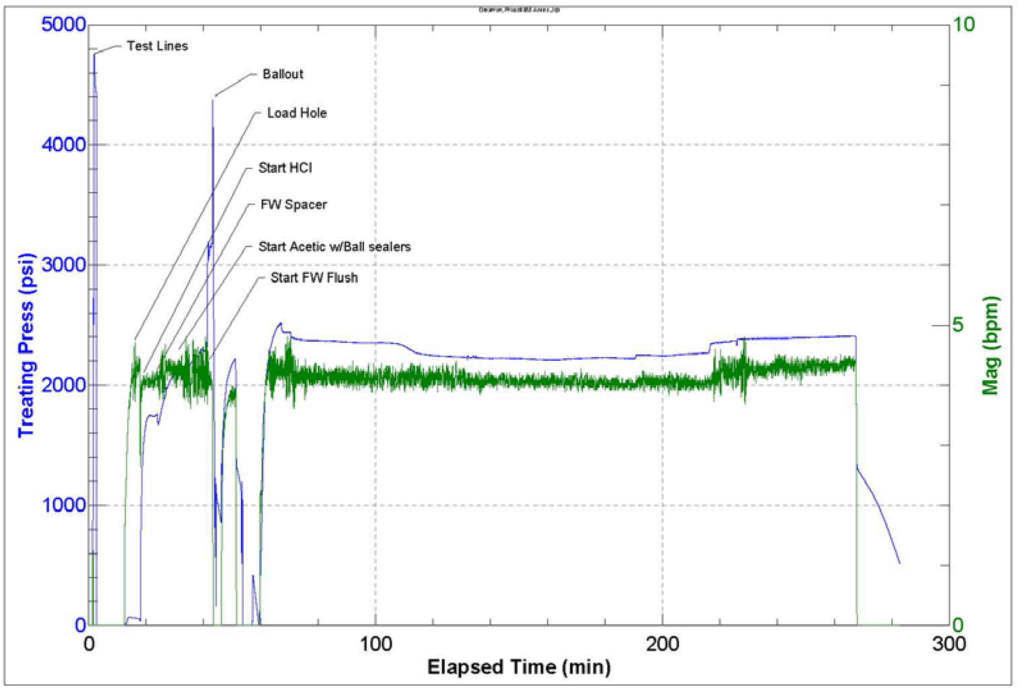


Figure 6 - Plot of Rates and Pressures during treatment of Well #2 in the Second Study Area using Method One.

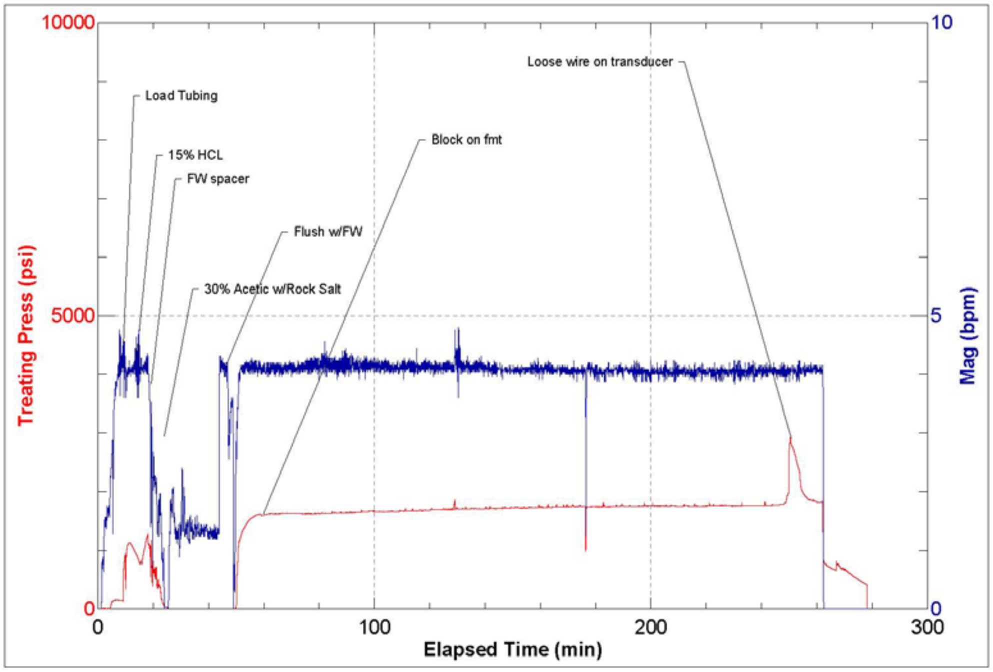


Figure 7 - Plot of Rates and Pressures during treatment of Well #4 in the Second Study Area using Method Two.

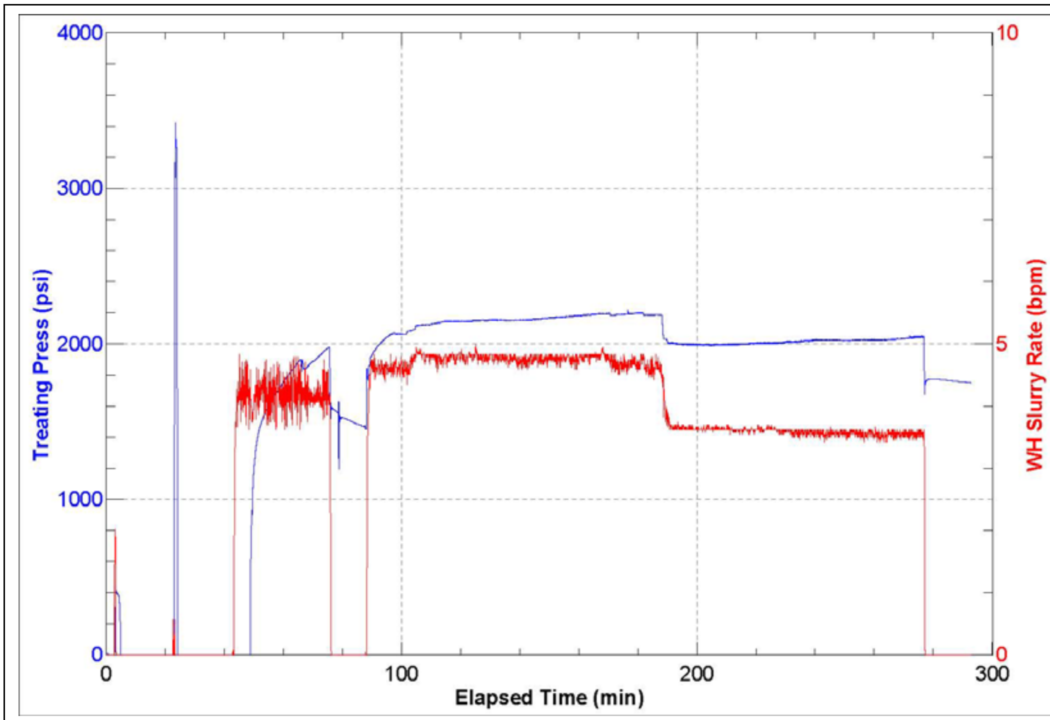


Figure 8 - Plot of Rates and Pressures during treatment of Well #1 in the Third Study Area.

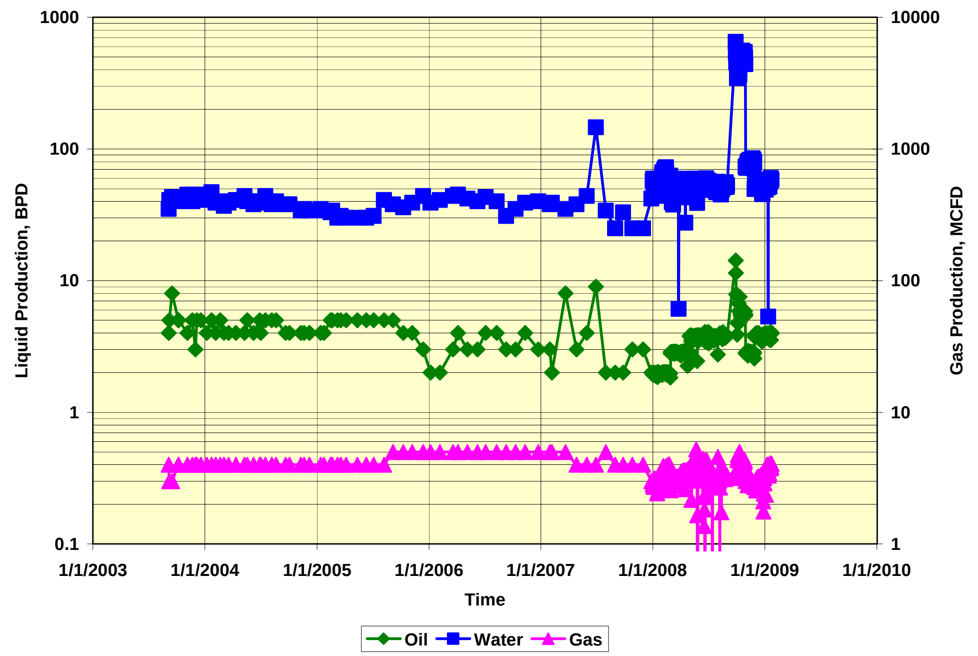


Figure 9 - Production history Well #1 of the San Andres wells in the Third Study Area.