MICROEMULSION ADDITIVES ENHANCE FLUID RECOVERY, PROVIDE H2S MITIGATION, AND PREVENT FORMATION DAMAGE FOR STIMULATION, DRILLING, AND REMEDIATION OPERATIONS

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ABSTRACT

A new generation of microemulsion additives have been developed that are effective in remediating damaged wells and is highly effective in fluid recovery and relative permeability enhancement when applied in drilling and stimulation treatments at dilute concentrations.

The microemulsion is a unique blend of biodegradable solvent, surfactant, co-solvent and water. The nanometer sized structures are modeled after Veronoi structures which when dispersed in the base treating fluid of water or oil permit a greater ease of entry into a damaged area of the reservoir or fracture system. The structures maximize surface energy interaction by expanding to twelve times their individual surface areas to allow maximum contact efficiency at low concentrations (.1-.5%). Higher loadings on the order of 2% can be applied in the removal of water blocks and polymer damage.

Lab data is shown for the microemulsion in speeding the cleanup of injected fluids in tight gas cores. Further tests show that the microemulsion additive results in lower pressures to displace frac fluids from propped fractures resulting in lower damage and higher production rates. This reduced pressure is also evident in pumping operations where friction is lowered by 10-15% when the microemulsion is added to fracturing fluids. Field examples are shown for remediation and fracture treating of coals, shales and sandstone reservoirs, where productivity is increase by 20 to 50% depending on the treatment parameters. Drilling examples are shown in horizontal drilling where wells clean up without the aid of workover rigs where offsets typically require weeks of workover.

INTRODUCTION

Oil and gas wells are stimulated using many techniques involving solvents and/or surfactants. These conventional solvent/surfactant systems have demonstrated effective and efficient stimulation results when used during fracturing, acidizing, and remedial operations. Various types of these conventional solvents and/or surfactants have been successfully used in a variety of downhole stimulations and remedial treatments in oil and gas well reservoirs worldwide. Often treatments are based solely on prior history and practices in an area without regard for the reservoir's uniqueness. Understanding the hydrocarbon habitat and the potential for temporary or permanent damage from drilling and /or completion methods has spawned an industry seemingly saturated with chemical and mechanical solutions which, when applied correctly, provide some increased productivity of reservoir fluids. However, many so-called optimized treatments are not designed to adequately deal with all the issues within a particular well or reservoir, and as such, may actually create or cause a more damaging scenario than originally existed. Moreover, with increased awareness for human and environmental safety, formulations once considered optimal and effective are now being used less frequently or have been completely omitted because of potential safety hazards. Solvent/surfactant/aqueous micro-emulsion systems have been created to address these issues more effectively.

Surface activity (i.e. surface /interfacial tension /contact angle/ wettability) is one of the major properties associated with surfactants, but is not exclusive to them. Other organic liquids such as plant derived solvents; with diverse solubility properties have excellent surface activity (i.e. 20-25 dynes/cm. in aqueous systems), especially when blended with other compatible and natural based surfactants. This synergistic activity when utilized at an optimal concentration for a specific well application either as a solvent/surfactant/aqueous system, or when blended as a microemulsion using aqueous fluids, produces a versatile treatment system, a micellar solution or microemulsion, capable of many simultaneous functions among which are the following:

1) Reduced surface tension / interfacial tensions in aqueous or acidic fluids to less than 25 dynes/ cm. and 0.1 – 1.0 dynes/cm. respectively. Contact angle can be made zero or 90 degrees as required and wettability essentially “neutral”, which are more critical issues in reservoir rock or solid substrate compatibility issues.
2) Provides maximum penetration, contact efficiency and dispersion of various paraffins, asphaltenes, scales, bacterial films, and concentrated gel filter-cakes, formation fines, drilling fluids, etc.
3) Allows uniform fines suspension in wellbore breakdown treatments (i.e. acidizing) to aid in solids/damage recovery and subsequently production increase and/or recovery.
4) Maximizes heavy or complex hydrocarbon (paraffins, asphaltenes, etc.) Breakdown and dissolution, when pumped with various acids, CO_2, water, as well as hydrocarbon based carrier fluids.
5) Controls and maintains ideal reservoir wettability resulting in effective surface cleaning without permanent alteration to maximize subsequent treatment efficiency.
6) Retards inorganic/organic acid (i.e. HCl / Acetic) reactions and provides effective reaction kinetics control.
7) Provides an enhanced fluid loss control mechanism in fracturing and acidizing fluid systems.
8) Significant friction reduction in aqueous, acidic, carbon dioxide, or nitrogen stimulation fluids when pumped through treating tubular goods.

Robert Schechter et. al. investigated micellar solution / microemulsion systems as primarily chemical or surfactant enhanced oil recovery aids. In his text Oil Well Stimulation [1] he addresses their value as mechanisms for improving the efficiency and cost effectiveness of the specific purposes of virtually any well treating system. Schechter defines a micelle as:

“An aggregate of a large number of surfactant molecules in which the hydrophilic (water loving) portions of the molecules are arranged so that they are in contact with water. The hydrophobic (water hating) portions are collected together so that they form a separate phase that excludes water molecules. It has been found that the solubility of a variety of hydrocarbon based substances, which are not normally very soluble in water, can be enhanced to a remarkable extent by the addition of specific surfactants in specific concentrations. These hydrocarbon substances are then incorporated into the interior of these micelles, or groups of micelles, and carried along with the treatment fluid or exposed to the maximum-targeted benefit of the treatment fluid. Micelles are extremely small and are invisible to the eye, being roughly the length of the surfactant’s tail (i.e. 2 – 4 nanometers). Micellar solution treatments will easily pass through most pores in sedimentary rocks, and are easily injected as treatment fluids.”

A natural solvent, micellar solution/microemulsion additive can be created for optimum effectiveness in the various applications listed previously, with improved synergistic benefits not found using conventional surfactant and/or solvent systems. The natural microemulsion additive product formulations dramatically increase the system’s effectiveness, and augment its environmental compatibility and chemical safety standards to surpass most, if not all, products currently being used in the well stimulation industry today.

The surfactant/solvent microemulsion systems are formulated as a two or three phased blend of solvent, surfactant, and water (or acid), or any two of these. The ratios can be proportioned according to the targeted treatment application. The phase containing the bulk of the surfactant at a level above the critical micelle concentration (CMC) is called a micellar solution or microemulsion. CMC is defined as the characteristic concentration of surface active agents (surfactants) in solution above which the appearance and development of micelles brings about sudden variation in the relation between the concentration and certain physiochemical properties of the solution (such as surface tension). Above the CMC the concentration of singly dispersed surfactant molecules is virtually constant and the surfactant is at essentially its optimum level of activity for many applications (also known as the critical micellization concentration). These micellar blends of surfactants and solvents can be formulated to be either oil in water, water in oil, or equilibrium water and oil. Figure 1 shows the 3 types of formulas possible. The reported work uses a Windsor type III microemulsion, which can be applied in either water or oil based fluids [2] .

The unique properties of the proprietary nonionic surfactant and natural solvent derivative causes the normally unstable “equilibrium” phase to be quite stable and thus extremely active simultaneously within the treatment fluid as well as with the substrate on which the treatment is interacting. The resulting action is treatment effectiveness, without treatment “side effects” such as, formation damage from: additive adsorption/absorption losses; fluid/ product imbibition; gel filter-cake formation; emulsion blocks; undesirable wettability alteration. The ability of the microemulsion system to posses these many properties can be explained using the Voronoi type structure in Figure 2 [3]. In Figure 2 the structure on the left is a three dimensional view of a typical Voronoi polyhedron. The right hand structure is a two dimensional example. Shaded regions are occupied by oil-like material, unshaded regions by water-like material; heavy lines indicate the surfactant layer. From Talmon and Prager [3].

From an environmental and personal safety standpoint, microemulsion systems described herein are naturally occurring, non-synthetic, non-carcinogenic, non-toxic, non-hazardous (DOT), and contain no VOC's. They need no special handling permits or transportation placarding other than a low flash point labels similar to that used for other ordinary organic solvents. The mixture itself will not burn. These standards are becoming more talked about as issues in the upstream oil and gas industry, but the microemulsion additive systems have achieved them! These environmental benefits provide the operator with another level of insulation from RECRA regulations. These systems provide a myriad of successful results based on sound and proven scientific principles without compromising safety, but rather augmenting it!
Microemulsion additive treatment quantities are custom formulated, and costs are calculated to provide the optimum performance while maintaining the necessary surfactant/ solvent, micellar properties. As little as five hundred parts per million of the microemulsion additive formulations in water, brine or acid can be effective in alleviating damage or preventing it. Concentrations necessary to accomplish optimal stimulation and /or damage removal may be between one-half and twenty percent in the treatments depending on the specific downhole issues involved.

The versatility of the micellar/microemulsion mechanism makes conventional stimulation, remediation, and / or drilling methods function more efficiently. That versatility also may allow the replacement of several non-synergistic additives with one product, thereby reducing complexity and overall cost of treatments.

LABORATORY TESTS

Several laboratory tests were performed to show the effectiveness of the microemulsion formulation in remediating damage and promoting well cleanup following stimulation. Additionally, friction reduction tests have been conducted in coiled tubing.

Core flow tests

Low permeability Sandstone plugs (1 in. diameter by 1 in. long) were saturated in 2% KCl. The permeability was measured by flowing 2%KCl in the injection direction. Nitrogen gas was then flowed in the reverse direction at 1000 psi until a stable flow rate was achieved. This was used as the baseline test. The core was restored to full saturation and was then treated in the injection direction with 2% KCl containing 2 gal/1000 gal (gpt) of microemulsion. Nitrogen gas was flowed in the production direction at 1000 psi until a stable rate was achieved. The results are shown in Figure 3. With 2% KCl only, the gas perm was .02 md. When the 2%KCl + 2 gals. microemulsion (ME) per 1000 gallons was injected the gas permeability increased to .04 md. This is consistent with several observations in which the gas flow rate and relative permeability to gas is 50 to 100% higher than without the microemulasion additive [4]. Several lab tests have been run on coal and shale samples showing similar results using the standard GRI test [5].

Fracture Cleanup tests. A series of tests were conducted at an independent testing laboratory comparing a 35 lb CMHPG + Zr at 250 F with and without 2 gpt microemulsion. The tests are run by statically leaking off the gel while closing on a 2 lb/sq ft pack of 20/40 Light Weight Ceramic. 2%KCl is flowed back through the core and pack to simulate flowing back the well for 6 hours. Gas is then flowed at simulated rates of 50 MCFD to 1 MMCFD (Nitrogen gas). This is the standard test for proppant pack regain [6].

In Figure 4 the x-axis shows units of the gas density *velocity /viscosity so that the cleanup can be predicted with any gas properties. The test without microemulsion cleans up to 43% while the test with 2 gallons microemulsion additive per 1000 gallons cleans up to 74%. Another observation is that the cleanup to near 60% is possible with very low gas rates where normally the cleanup is 30% or less. This indicates that half of the pressure is required to flow out the gelled fluid in the presence of the microemulsion. It was also observed that the filter cake is less dense with the microemulsion thus requiring less pressure to initiate flow. Pressure to initiate flow and impact on productivity is discussed in detail by Barree [7].

Friction Tests

Several tests were performed with gelled fluids with and without the microemulsion present. The fluids were pumped at 1-2 BPM through 1 in. coiled tubing at surface conditions. It was observed that the friction was decreased 8-10% when the microemulsion was added to the gelled fluids. Figure 5 shows the results that were observed.

FIELD TRIAL OBSERVATIONS

The microemulsion systems have been used successfully for drilling and completion damage removal/remediation, production rehabilitation, fracture and acid stimulation enhancement, and stimulation damage removal. They have also been combined with the application of bacterial remediation treatments. To date, various microemulsion additive treatments have been performed in nine different oil and/or gas basins, including the D.J. of Colorado, San Juan of New Mexico and Colorado, Uintah of Utah, Raton of Colorado, Green River, Pinedale, and Big Horn of Wyoming, Fort Worth of Texas and Williston of North Dakota. In the nineteen different formations in which the microemulsion additive systems have been applied, the majority of the wells for which reliable data was maintained profited from increased productivity. Thirty percent have achieved a 350 percent production improvement and over sixty-eight percent of the wells had lower lifting costs. Some specific field examples are shown below.

FIELD TRIAL A

A coalbed methane (CBM) well in the Four Corners area of northwestern New Mexico was originally drilled and fracture stimulated in 1990 and was selected for a field trial using the microemulsion technology. This selection occurred as result of data review which led to a suspicion that the original fracture stimulation did not clean up properly. This property had gone through a series of ownership changes and was being produced at rates of approximately 65 MCFPD and 2 BWPD. The well was producing from the Fruitland Coal with perforations at 1172' to 1190', had a porosity of 10%, and was on a rod pump with 2 3/8" tubing for water removal. The well was squeeze treated with 30 barrels of 2% calcium chloride water containing 30 gallons of the microemulsion additive and pumped at 5 barrels per minute. Pump in data was gathered but nothing of significance was revealed. The well was shut in for seven days to allow for optimal effects and returned to production.

The water production increased immediately to 10 barrels per day and the gas production immediately improved to about 95 MCFPD. The improvements continued until production reached an average of 155 MCFPD. The fluid recovered immediately after the Microemulsion treatment was analyzed and found to contain gel residue believed to be from the original fracture stimulation and subsequent samples were found to contain only water. The enhanced production continued for over a year before data was no longer tracked [4,8].

The data gathered after this project and similar projects has lead to shorter shut in periods, inclusion of the microemulsion technology into fracture stimulation and additional remediation treatments with attendant improvements in production. The sampling and testing of the flow back fluids has also led to a better understanding of the interfacial mechanisms occurring between the rock and the fluid.

The project costs totaled $1500.00 and were amortized within the first 30 days of the treatment. The success of this project provided an additional $75,000.00 in incremental income to the operator during the first year.

FIELD TRIAL B

A (second) coalbed methane (CBM) well in the Four Corners area of northwestern New Mexico was originally drilled and fracture stimulated in 1991 and was selected for a field trial using the miroemulsion technology. This selection occurred as result of data review, and similar to Field Trial A, the well appeared to have been damaged from the original fracture stimulation which did not clean up properly. This property had gone through a series of ownership changes and was being produced at rates of approximately 35 MCFPD and 2 BWPD. The well was producing from the Fruitland Coal with perforations at 1180' to 1198', had a porosity of 10%, and was on a rod pump with 2 3/8 tubing for water removal. The well was squeeze treated with 30 barrels of 2% calcium chloride water containing 30 gallons of the microemulsion additive and pumped at 2 barrels per minute. Pump in data was gathered but nothing of significance was revealed. The well was shut in for seven days to allow for optimal effects and returned to production.

The gas increased immediately to 70 MCFPD while the water production was unchanged at 2 barrels per day. The production remained at that level for ten months and fell to 50 MCFPD, whereupon the well was squeeze treated again with 30 barrels of 2% calcium chloride water containing 30 gallons of the microemulsion additive per 1000 gallons. The well was shut in for seven days to allow for optimal effects and returned to production.

The well responded from the second application with a gas increase to 75 MCFPD and over the succeeding 60 days continually improved to 100 MCFPD. The fluid recovered immediately after the first microemulsion treatment was analyzed and found to contain some gel residue believed to be from the original fracture stimulation and subsequent samples were found to contain only fines. The fluid recovered immediately after the second microemulsion treatment was analyzed and found to contain only water. The enhanced production continued for over a year before data was no longer tracked.

Each project's expenses totaled $1500.00 and these costs were amortized within the first 30 days of each treatment. The success of this project provided an additional $83,000.00 in incremental income to the operator during those two years [4,8].

FIELD TRIAL C

A "D" Sand well in the DJ Basin of northeastern Colorado was originally drilled and fracture stimulated in 1973 and was selected for a field trial using the miroemulsion technology. This selection was based upon a data review which pointed towards a heavy hydrocarbon deposition at the near well bore region. This property had gone through a series of ownership changes and was being produced at rates of approximately 1 BOPD and 7 MCFPD. The well was producing from the D Sand with perforations at 7096' to 7102', had a porosity of 12%, and was on a rod pump in 2 3/8" tubing. The well was squeeze treated with 30 barrels of 2% calcium chloride water containing 30 gallons of the microemulsion and pumped at 2 barrels per minute. Pump in data was gathered but nothing of significance was revealed as the well went on a vacuum. The well was shut in for two days to allow for optimal effects and returned to production [8].

Over the succeeding 2 weeks after the treatment, the oil production steadily increased to about 2 barrels per day and the gas production improved to about 30 MCFPD. The fluid recovered immediately after the microemulsion treatment contained significant amounts of debris, including fines. Subsequent samples contained only clean water. The enhanced production continued for over 6 months at which time the operator has remediated the well again. The data is just now being collected and is unavailable at the time of this paper.

The data gathered after this project has contributed to a better understanding of the effects that can be obtained from the proper use of the microemulsion technology in older oil and gas producing wells. The sampling and testing of the flow back fluids has also led to a better understanding of the interfacial mechanisms occurring between the rock and the fluid.

The project costs totaled $900.00 and were amortized within the first 30 days of the Treatment.The success of this project provided an additional $17,500.00 in incremental income to the operator during this six month period.

FIELD TRIAL D

The Barnett Shale section in the Fort Worth Basin in north central Texas has been a very active play for almost a decade and the operator wanted to investigate the microemulsion technology as another chemical additive to improve both production and (frac) water recoveries in the field development. This new well was selected for a field trial by integrating the miroemulsion technology in the fracture stimulation job. This selection occurred as result of the strategic decision coinciding with the drilling and completion schedule. The well was to produce from the Barnett Shale with selective perforations in a gross interval covering 6873' to 7156', and had porosities ranging from 10% to 13%.

The well was fracture stimulated using a 28,000 barrels of a slick water system incorporating the microemulsion technology at rates of up to 65 BPM down 5.5" casing. The fracture stimulation utilized 40/70 Ottawa sand for proppant at up to 2 pounds per gallon. The well was flowed back immediately. The gas production stabilized at rates of 1.9 MMCFPD after 1 week and fluid recoveries were 80% improved over past data pools [4].

The microemulsion added approximately 10% to the fracture stimulation costs, however, the operator reports that this well's production is approximately 20% improved from offsetting wells. The production is being tracked by the operator for further evaluation as the project continues and all successive wells after this Field Trial have used the microemulsion as part of the fracture stimulation.

Several fracturing treatments have been performed in other tight gas reservoirs with Similar responses, that is, improved load recoveries and gas production rates that are 20 to 100% higher than offset wells treated with the same size treatment without the ME additive. The higher increases are in wells with crosslinked frac fluids. This data corroborates the lab data where pressures to cleanup crosslinked fluids were cut in half with the ME resulting in the ability to cleanup more of the fracture and thus increase productivity by as much as 2 fold over wells without the ME present.

FIELD TRIAL E

A horizontal well was drilled in the four corners area of the US. Typically these wells are drilled with a starch based drilling fluid. Several barrels of fluid are lost to the formation during the drilling process that is not recovered. Normally, a workover rig is required to cleanup the well prior to production for a period of 2 weeks. A well was drilled with the same drilling fluid with the exception of adding 2 gal/1000 gal of the microemulsion. This well flowed back all of the drilling fluids over the period of one week without the aid of a workover rig, and was put on production. The production was 2 times as high as offsets. This is attributed to the microemulsion creating a lower pressure to cleanup the drilling fluid, and thus more area can be cleaned up.

CONCLUSIONS

1. A microemulsion (ME) additive made with biodegradable solvent/surfactant/cosovlent and water has been developed fro use in well remediation and stimulation.
2. Core lab data shows that the relative perm to gas is improved when the ME is included in the formula.
3. Fracture proppant cleanup tests show that the pressure to initiate cleanup is lowered by 50% and the regained perm to gas is doubled when the ME is used in conventional gelled fluids.
4. Large scale tests and field data show that the inclusion of the ME in gelled fluids results in a 10-15% drop in friction pressures permitting higher pumping rates through coiled tubing.
5. Field data shows that squeeze jobs with the microemulsion additive have restored productivity to wells damaged by frac fluids, water blocks and heavy oils.
6. The addition of the microemulsion to fracturing treatments has resulted in improved load recoveries and enhanced gas and oil production.
7. The addition of microemulsion to a drilling fluid has resulted in greater fluid recoveries and higher production rates.

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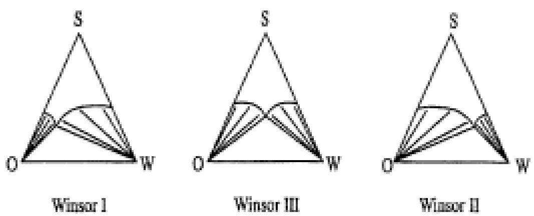

Figure 1. Schematic of ternary phase diagrams for Winsor microemulsions. In the left-hand shaded area, the microemulsion is in equilibrium with excess water, and in the right-hand shaded area, the microemulsion is in equilibrium with excess oil. The Winsor III microemulsion is in "middle phase" with an excess of both water and oil [2].

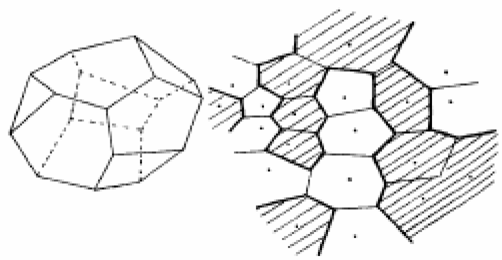

Figure 2. A Voronoi representation of a bicontinous microemulsion [3].

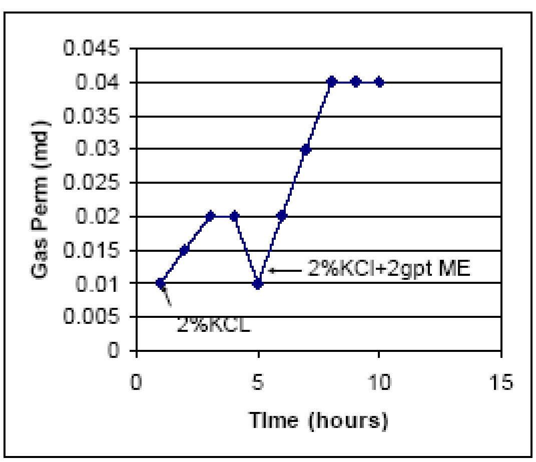

Figure 3. Gas permeability measured with N2 gas on 1 in Sandstone cores saturated with 2% KCl and injected with ME.

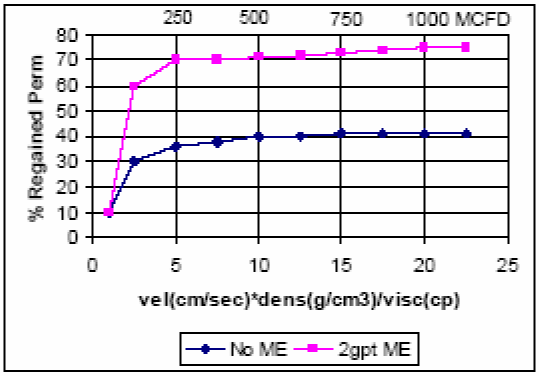

Figure 4. Regained proppant pack perm with and without 2 gal/1000 gal ME. 35 lb CMHPG+Zr in 2 lb/sq ft 20/40 Lt Wt Ceramic between Ohio Sandstone at 250 F.

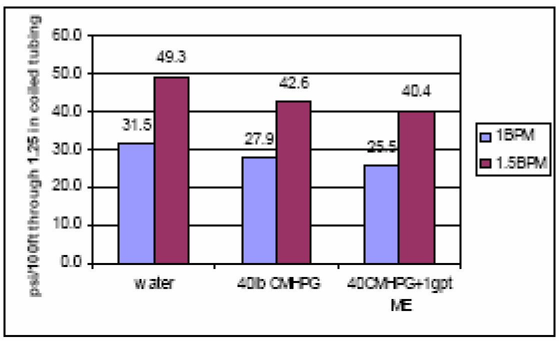

Figure 5. Friction reduction with the addition of 1gpt ME in a 40 lb CMHPG linear gel in water.

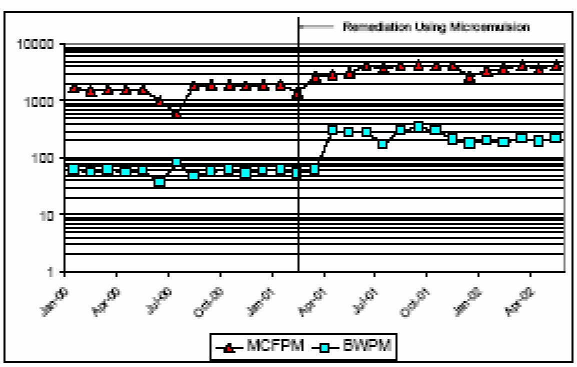

Figure 6. Remediation of damage in a coalbed metane well in the four corners area of northwestern New Mexico. Well was treated with 30 gal of ME in 30 bbl of brine.

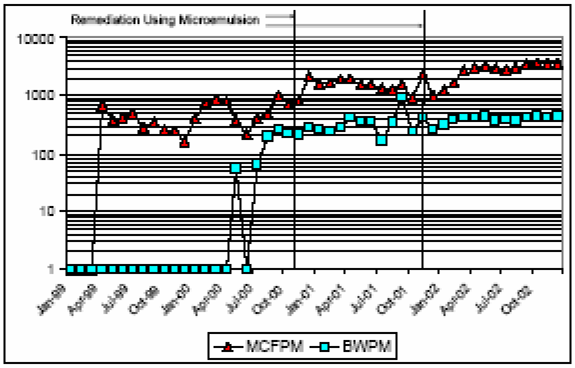

Figure 7. Remedaiton of damage in a coalbed metane well in the four corners area of northwestern New Mexico. Well was treated with 30 gal of ME in 30 bbl of brine.

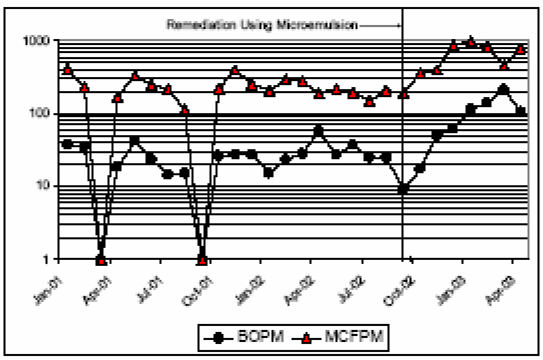

Figure 8. Remediation of a "D" Sand well in the DJ Basin of northeastern Colorado. Well was treated with 30 gal of ME in 30 bbl of brine.

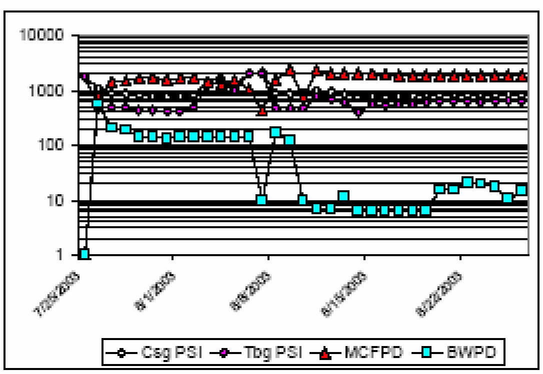

Figure 9. Production response following a hydraulic fracturing treatment of the Barnett Shale in North Texas with slick water and 2gpt ME. Load recoveries are higher and production is 20% higher than offsets.