THE USE OF ACROLEIN FOR IMPROVED WATER QUALITY, CONTROL OF MIC, AND ENHANCED INJECTIVITY IN SECONDARY OILFIELD RECOVERY SYSTEMS

Joseph Penkala, John Mosley, Mark Baker and Leo Castro
Baker Petrolite Corporation

ABSTRACT

Acrolein (2-propenal) is a potent biocide and sulfide scavenger which has been used to mitigate bacterial and iron sulfide problems in secondary oilfield recovery systems. The effectiveness of acrolein is due to its α,β-conjugated double bond which reacts with sulfhydryl and amine groups on bacterial proteins as well as irreversibly reacting with sulfide ions in hydrogen sulfide (H_2S) and iron sulfide (FeS). This paper discusses the applications of acrolein in water injection systems to control bacteria, H_2S, and FeS scale problems impacting water clarity, injection flowline integrity, and injection well performance. Data are presented on four case studies which describe: 1) the reduction in injection well failures due to acid producing bacteria (APB), 2) the control of bacteria and related biomass in injection wells via batch and squeeze applications to improve injectivity, 3) remediation of FeS formation face damage in injection wells via squeeze applications, and 4) reduction of H_2S levels and remediation of FeS fouled injection wells via a topside batch treatment program and downhole squeeze application.

INTRODUCTION

Challenges to Maintaining Water Quality and Injectivity

Secondary oil recovery often implements strategic injection of produced water or source water to physically sweep the displaced oil to adjacent production wells while maintaining reservoir pressure to enhance production. Paramount to a successful water injection system is maintaining high quality of the injected water to ensure integrity of the injection lines, downhole tubulars, and the formation rock receiving the water. Major challenges to maintaining this level of water quality stem from the formation or transport of scales and solids, proliferation of micro-organisms and associated by-products, oil carry-over, and corrosion.

Sulfides are particularly problematic to oilfield injection water. H_2S is corrosive, resulting in damage to metal surfaces and failure of lines or equipment. It also reacts readily with soluble iron to form FeS scale. Deposition of this FeS scale can reduce throughput when it occurs in the injection lines, filters, and tubulars. It can also lead to underdeposit corrosion. Ultimately the FeS scale can cause formation damage and loss of injectivity.

Often these sulfides are biogenic, generated by sulfate reducing bacteria (SRB) that populate the injection water and proliferate at various points in the system due to ideal temperatures and nutrients. Besides generating H_2S and FeS via the reaction of soluble iron with the former, SRB are responsible for some forms of microbiologically influenced corrosion (MIC). Furthermore, the SRB in association with other types of bacteria present in bulk waters form adherent colonies on surfaces, such as tank bottoms, pipes, tubulars and formation rock. The biofilm that is established can be very harmful to the injection system and is most difficult to eradicate.

Notorious among the bacteria which co-colonize the biofilm with the SRB are the APB which can generate aggressive acids that can lead to MIC. These fast growing organisms are pivotal in the establishment of biofilms, due to rapid proliferation and the secretion of a protective exopolysaccharide slime (EPS) material that helps form the matrix of the biofilm. They also form a synergism with SRB in the biofilm and generate metabolites that serve as nutrients for the slower-growing SRB.

Chemical Options for Control of H_2S, FeS and Bacteria

The chemical approach to treating for H_2S, FeS and bacteria typically employs acid treatment, chelation, sulfide scavenging, and/or biocides. Each of these approaches has merits as well as limitations. Although acids are effective at dissolving FeS deposits, they are extremely corrosive and in some cases allow redeposition of the FeS downstream in the system once the acid is spent. Chelation of soluble iron is another approach which can inhibit FeS formation, but the reaction is reversible and impacted by the presence of H_2S. Sulfide scavengers target the sulfide ion and have the benefit of both removing H_2S and inhibiting Fe_xS_y formation. However, with traditional triazine-based scavengers this reaction can be inefficient and often results in solids formation which can be detrimental to downstream filters and injection wells. Biocide treatments are able to target the SRB populations and mitigate the source of biogenic sulfides; however, not all biocides are effective at penetrating oil-wet solids and biofilms to attack persistent bacterial populations established in vessels, lines, and the well bore. Furthermore, most biocides have little capacity to directly remove both H_2S and FeS scale already existent in the system (One exception is tetra-kis hydroxymethyl phosphonium sulfate (THPS) which has iron-chelating properties but still does not react with sulfides). Ultimately, none of the conventional chemicals described have the capacity to provide a comprehensive treatment for bacteria, H_2S, and FeS.

Acrolein as a Comprehensive Option

One chemistry that can provide a comprehensive approach for treating oilfield water injection systems fouled by bacteria and sulfides is acrolein, or 2-propenal. The key to this approach is three-fold: Acrolein is a potent microbiocide; it scavenges H_2S and it dissolves FeS scale. This versatility of the acrolein molecule is due to its α,β-conjugated double bond which renders it extremely reactive with sulfhydryl and amino groups in bacterial proteins and DNA, and with sulfides in general.[1-7] Acrolein is an extremely potent, water soluble biocide effective against a broad spectrum of bacteria including SRB, showing cost effective best performance in 89% of all kill tests conducted.[6] Acrolein's ability to partition into the oil phase renders it highly effective in penetrating oil-wet solids and biofilms to target sessile bacteria.[7] As a sulfide scavenger, acrolein reacts in a 2:1 molar ratio to form water soluble, irreversible sulfide-containing reaction products. The reaction with H_2S is rapid,[3] whereas the reaction with Fe_xS_y is slower due to dependence on the shift from Fe_xS_y to H_2S and soluble iron whereby it scavenges the H_2S.[5-6] The fact that acrolein is non-corrosive and non-surfactant[6-7] in nature makes it compatible with surface and downhole equipment and oil-water separation systems.

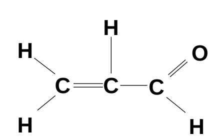
As a result of its 3-fold capability, acrolein has been used successfully in treating a variety of operational problems caused by bacteria and sulfides.[6] These applications include:

- Downhole treatment of production and injection wells to control Fe_xS_y solids, H_2S, bacteria, pump failures, and MIC
- Treatment of oil storage tanks, settling tanks, heater treaters and free water knockouts (FWKO) to improve oil-water separation and control bacteria
- Treatment of water storage air flotation units, water storage tanks, and surge tanks to control sulfide solids and bacteria
- Treatment of filters to control bacteria, Fe_xS_y solids and improve filter run times
- Protection of flow lines and water injection lines by controlling bacteria, Fe_xS_y solids, MIC, H_2S, and underdeposit corrosion

The scope of this paper is to discuss strategies for using acrolein to help manage water injection system performance and to highlight some of these applications in four case studies: 1) The first case study discusses the biocidal control of aggressive APB populations corroding the tubing strings of a water injection system. 2) The second study describes the control of bacteria and related biomass in injection wells via batch and squeeze applications to improve injectivity. 3) The third study discusses the remediation of FeS formation face damage to improve injectivity in several injection wells. 4) Finally, the fourth case study describes how acrolein is used to reduce H_2S levels and improve injectivity by FeS remediation.

PROPERTIES OF ACROLEIN THAT ENABLE IT TO FUNCTION IN DIVERSE TREATMENT ROLES IN WATER INJECTION SYSTEMS

Acrolein is a low molecular weight compound (MW = 56), a 3-carbon vinyl aldehyde, that is highly reactive chemically due to a carbon-carbon double bond conjugated with the double bond of an aldehyde carbonyl:[1] It reacts readily with sulfhydryl groups and the dissociated HS^- form of H_2S.[1,2-4] It also reacts with amino groups, including those present on bacterial proteins.[1-2] These reactions are rapid and irreversible.

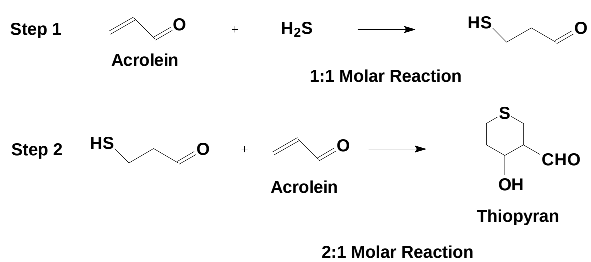


Acrolein

2-Propenal

Acrolein as an H_2S Scavenger. The reaction of acrolein with H_2S is rapid and reaches completion within 5-20 minutes, although 80-90% is consumed within the first 5 minutes.[3] The reaction is irreversible and the reaction products which include thiopropanal, thiodipropanal, and thiopyran, are water soluble[1,3]. This eliminates the concerns with solids as seen with the triazine scavengers. For applications, generally 2 moles of acrolein react with 1 mole of H_2S, which is approximately 4 ppm of acrolein per 1 ppm of H_2S on a weight basis.

Acrolein Reaction with Sulfide



Acrolein as an FeS Remover. Similarly, with FeS, acrolein can dissolve this solid by reacting with H_2S that is in equilibrium with soluble iron and sulfide and follows the same reaction process[5-6] as described above for H_2S. It can also prevent its formation by scavenging H_2S upstream. The net result is the resolution of issues such as black water, FeS scale and plugging, FeS-stabilized emulsions contributing to high oil-in-water, and formation damage. [6]

Acrolein as a Biocide. Acrolein has been used successfully for control of sessile bacteria in waterflood systems. This non-surfactant water soluble biocide demonstrates excellent oil solubility, thereby allowing for penetration of oil-coated surfaces and biofilms to effectively target sessile bacteria. [6-7] In a recent report, in 26 out of 29 planktonic time kill studies when compared to conventional biocide chemistries, acrolein was the most cost effective biocide for control of general aerobic and facultative anaerobic bacteria (GAB) and SRB.[6] The mechanism of microbial attack by acrolein is via denaturing of protein and enzyme systems in bacterial cells by reacting with protein sulfhydryl and amine groups. [2] As a small molecule with oil solubility, acrolein can penetrate oil-wet surfaces and transport through EPS slime to contact sessile bacterial populations. [6]

ACROLEIN APPLICATIONS IN WATER INJECTION SYSTEMS

Acrolein Treatment Strategies

To treat or protect waterfloods against damage from bacteria, H_2S and/or FeS, chemicals are applied in batch or continuous applications, or for remediation such as for a tank or well, a shut-in treatment may be designed. Acrolein is well suited for all of these types of applications and can be used at practically any point in the system that is required to target the fouling agent.

Water Plant Treatment. In the water injection plant, acrolein may be applied to any affected vessels that require cleaning due to sulfides or bacteria. It can be used to treat FWKO's with FeS-stabilized emulsions to prevent oil carry-over into the separated water. It can also be applied into tanks to deal with FeS solids or resistant sessile bacteria, thereby improving water quality. Often, acrolein is applied into the water storage tanks feeding the injection system, thereby allowing a residual to be distributed to the injection lines and injection wellheads. The fact that it can penetrate oil films and biofilms aids in the mitigation of deposits of bacteria or FeS solids that are inaccessible to other conventional chemistries. Its non-surfactant and non-corrosive properties prevent undesirable consequences that some chemistries might produce. For instance, surfactant biocides, although excellent at penetrating oil films, can cause foaming and system upsets. Likewise, low pH products such as THPS can increase the potential for corrosion.

Injection Line Treatments. In managing the water injection lines, it is often difficult to control the build up of biofilms and FeS over the long transit time to the injection wells due to throughput of the chemical and accessibility to deposits and biofilms. This often leads to deterioration of the water quality and injection integrity downstream, and culminates in fouling of the injection wells. Acrolein is typically applied at the water injection feed tank or suction to the injection pumps to address these concerns. Throughput is excellent although its half-life (8-24 hrs) can be an issue for very long transit times of the injection water.

Injection Well Treatments. Injection wells are best managed by maintaining water quality leaving the plant and affording biocidal protection of the injected water. Besides upstream treatments with acrolein, well remediation can be performed. During these squeeze treatments, the acrolein is targeted at a 3 to 6 foot radial penetration and the well is shut in for 24 to 72 hours. This type of application can be done to treat for FeS damage or for near well bore contamination of bacteria.

Field Studies Highlighting Range of Acrolein Applications in Waterfloods

A number of studies have been published documenting the successful use of acrolein to improve injection water quality and remediate injection well damage. Successful applications of acrolein as a biocide in oilfield systems have been reported by several authors.[8-12] The field performance of acrolein has been consistent with laboratory screening tests described earlier. Palacios and Riccobono[8] report a 3 year evaluation of acrolein, glutaraldehyde, THPS, and a quaternary amine to reduce MIC and control SRB growth in a produced water facility which received make-up water from a contaminated pit. Acrolein batch treatments were able to reduce MIC to < 0.01 mil per year (MPY), whereas the other biocides (> 0.2 MPY) could not meet the facility's specifications of 0.13 MPY. Harless[9] describes the successful mitigation of sessile SRB and GAB in the guard filters of a production facility by continuous treatment with 5-20 ppm acrolein. Another account of sessile bacterial control is reported by Van der Wende et al.[10] where a water injection system is batch treated with acrolein and the performance is measured via corrosion coupons which are monitored for sessile bacterial growth and solids deposition. The treatment resulted in a 79-97% reduction in MIC and a >80% reduction in solids. Additional studies documenting the maintenance of injection water quality and protection of injection flow lines from MIC are reported by Johnson et al.[11] and Law et al.[12] In the latter study, an acrolein batch treatment program successfully replaces a previous program with continuous injection of a diamine quaternary amine that could not adequately control SRB populations resultant from high sulfate make-up water mixed with the injection water.

Among more recent studies it was shown that, at the 92,000 m^3 per day water flood facility in Rincon de los Sauces, Argentina, acrolein maintained control of sessile SRB and GAB in a system exhibiting up to 12 hours transit to outlying wells in an economic fashion for the 3 year period of the study.[13] The control was exerted via a single injection point into the terminal water tank in the injection plant. Dickinson et al[14] showed that by varying acrolein treatment strategies and injection points that SRB and associated sulfides could be controlled adequately at a waterflood facility in Elk Hills, California that ultimately resulted in a 100% increase in throughput volumes, a 50% decrease in sulfides, an 87% decrease in suspended solids, and an improvement in injectivity from 70,000 BWPD to 105,000 BWPD. At an offshore facility near Thevenard Island, Australia, acrolein was compared with a dual glutaraldehyde-quaternary amine biocide (GQB) and a THPS biocide in a trial on an offshore production facility to control SRB and associated sulfides on an offshore and an onshore production facility.[15] Results demonstrated a reduction from 90% to 30% in the number of SRB samples taken throughout the plant that exceeded 100 SRB per ml as well as a decrease in associated iron and H_2S. The conversion of the traditional GQB and THPS-based bacteria management programs to an acrolein treatment program resulted in a projected cost savings of 40%.

Finally, in a clear illustration of acrolein remediation of SRB and associated H_2S and FeS, Penkala et al[16] discuss a program designed to manage a water disposal facility serving a 200 MCFSD gas plant receiving offshore production. The disposal system was fouled with SRB-generated FeS to the point that the disposal wells were completely plugged. A three-phase program was implemented to: 1) remediate the injection wells by acrolein squeeze stimulations, 2) remove FeS pads from the tankage and build-up on the disposal lines and mitigate SRB by aggressive acrolein batch treatments, and 3) provide preventive maintenance using continuous and batch treatment programs of acrolein in the water disposal plant. Merits of the program are reflected in a 30% increase in well capacity following the squeeze stimulations, a 400 to 500% improvement in filterability of the water, a 90% decrease in H_2S, and an 82% reduction in cartridge filter changeouts.

NEW APPLICATIONS OF ACROLEIN IN MANAGEMENT OF WATER INJECTION PERFORMANCE

To illustrate the performance of acrolein as a biocide in field applications, four new field case histories are presented. A brief review of each field study highlighting some of the unique application benefits of acrolein in each is discussed below:

CASE HISTORY I: ACROLEIN CONTROLS APB-RELATED MIC IN A WATER INJECTION SYSTEM IN SOUTHERN OKLAHOMA

Problem: The first case study describes an acrolein treatment program to obtain control of an aggravated problem of APB established in the water injection system in a southern Oklahoma oil lease. The field was producing 1,700 BOD and 130,000 BWD. Approximately 130,000 barrels produced water and 5,000 barrels make-up water per day were being injected via an array of 120 injection wells. The water injection plant schematic is shown in Figure 1, detailing the produced water path through 5 FWKO's and 5 coalescers before passing to a 10,000 bbl tank where it is sent to the injection system that consists of 8 branch lines. Prior to 1997, the facility exhibited high levels of FeS solids developing in the plant and critical numbers of corrosion failures in the injection well tubulars. Based on bacterial data from serial dilution cultures and microscopy, it was determined that high levels of APB and SRB were established in the system. Various biocide programs were implemented utilizing glutaraldehyde, quaternary amines or THPS. However, none of these treatments were able to mitigate the MIC. Several bacterial kill studies conducted for biocide selection indicated that acrolein showed the most cost effective performance for kill of the GAB and SRB. Subsequently, a recommendation was made to treat the system with an 80 gallon slug of acrolein into one of the 5 FWKO's every two weeks, rotating the FWKO treated. This program, which amounted to 160 gallons of acrolein per month, caused a sharp decrease in MIC failures in the first year of treatment from 90 injection well failures per year down to 51 failures per year and leveled off to 40 failures per year for 2002 and 2003 (Figure 2).

In February 2003, due to budgetary constraints, a cut back in the program was made to 132 gallons of acrolein per month. In an effort to optimize the treatment, the bi-weekly batch was split into 1) a 33 gallon acrolein bi-weekly treatment upstream of the FWKO's (rotating the FWKO treated each cycle) and 2) a 33 gallon bi-weekly treatment into the 10,000 bbl surge tank coinciding with the upstream treatment. The downstream treatment was implemented to give extended acrolein residual out to the injection wells, since there was concern that the residuals would be reduced after passing through the tank trains and since the FeS solids and bacteria in the water plant had been reduced during the first stage of the program. The goal of the downstream injection system was to maintain control of sessile bacteria at the injection wells and prevent an increase in incidence of MIC failures.

In January of 2004, the failure rate had dramatically increased to 25 injection well failures for the month. This trend continued into February giving a projection of 106 failures per year. Careful examination of the failure records and pipe sections indicated that the vast majority of these failures were due to APB-mediated MIC (Figure 3). As a response to the emergency, supplemental treatments of acrolein were made during the off-week of the treatment cycle at the 10,000 bbl tank or downstream to the injection system. However, this did not affect the increasing trend in failures.

Considerable field testing was undertaken to determine what factors were contributing to the decline in the injection system other than the possibility of under-treating due to the cutback in chemical volume. The water quality reflected by total suspended solids (TSS) and filtration rates through a 0.45µm pore size membrane filter had not deteriorated during the treatment cut backs in 2003; hence the underlying cause for the increase in failure rates was not readily evident. Bacterial analysis conducted within the system revealed a 100-fold increase in planktonic bacteria from the input (1.91x 10^4/ml) to the water plant to injection well heads (2.71 x 10^6/ml) (Figure 4) and the majority of injection wells sampled were contaminated with > 10^6 planktonic bacteria/ml (Figure 5) with an average of 3.41 x 10^8 sessile bacteria/in^2 (Figure 6). Measurement of acrolein residuals during application indicated that the 10,000 bbl tank was being greatly under-treated during the reduced chemical program: 35 ppm as compared to the 200 ppm in the previous treatment. In addition, the duration of acrolein residuals out in the injection system was marginal: ~60 ppm residual for 1 hr compared to the 120 ppm for 2 hours mandated by the kill studies. Furthermore, one leg of the injection system was receiving less than 10 ppm residual to several of the wells, indicating that almost no biocidal treatment was being received by these wells due to the flow of water to this branch of the system.

Examination of operational changes that occurred during 2003 indicated that a number of producing wells had been shut in for months, leaving stagnant conditions for bacterial build up. These wells were then brought back on production at the end of 2003 and the contaminated fluids flowed into the water plant. In addition, a source well that had been shut-in, along with the associated transfer line, was reactivated and the water diverted to the 10,000 bbl tank. These factors, in conjunction with the chemical cut back, all contributed to a severe build up of sessile bacteria out in the injection system and this population was continually being replenished by the bacteria present in the 10,000 bbl tank which was not being controlled. It was evident that all of the factors, including reduced treatment and operational changes, had provided an opportunity for the sessile bacterial to become strongly established in the injection system. As this was a biological phenomenon, however, it required time, in this case approximately 9 months, before the impact to the injection system would be realized by the surge in failures as seen at the beginning of 2004. By the same logic, any enhanced treatment would require several months to be reflected by the reduction in failure rates since much of the damage had already occurred. As an intermediate step, aggressive acrolein biocide treatments were made at the 10,000 bbl tank and out to the injection system to try to obtain control of the MIC.

Solution: A new program was put in place in September of 2004. Based on an economic analysis of the cost of failures it was decided prudent to increase the treatment volume beyond that of the original program initiated in 1998. Acrolein slug treatments at 80 gallons on bi-weekly cycle into the FWKO's were resumed, with an additional treatment of 24 gallons at the exit to the 10,000 bbl tank on the opposite week of the cycle. The total treatment volume per month was 208 gallons. This program addressed delivery of a biocidal residual to the 10,000 bbl tank and delivery of biocidal residuals to the injection system every week, with a moderate treatment during the upstream application and a rigorous treatment with the downstream application.

A new sessile bacteria monitoring program was initiated to evaluate the effectiveness of the treatment program (Figure 7), since during the upset it was discovered that the few injection wells that were being monitored for sessile bacteria were in a part of the system exhibiting low or no failure rates. Additional sets of wells were added to the monitoring program, including representation from the different legs of the injection system and including sets of wells that were high in sessile bacterial counts and prone to failures.

Results: Overall, the initial acrolein program resulted in improved water quality throughout the field. Benefits realized from the program include:

- Lower hydrogen sulfide concentrations
- 99.99% reduction in planktonic SRB and APB concentrations
- Elimination of sticking floats and valves due to iron sulfide
- Savings of $28,000/yr due to elimination of solids from tank bottoms
- 34% reduction in total suspended solids
- Reduction in facility line leaks and injection line leaks
- 50% reduction in injection well failures

The net economic impact of the first stage of the program equated to a greater than $500,000 per year savings in operational costs. The enhanced acrolein program implemented in September of 2004 not only regained control of MIC failure problem as reflected by the drop in injection well failures to 36 in 2005 and 37 in 2006, but in 2007 reduced the failure rate by another 50% over the initial program down to 22 failures per year.

CASE HISTORY II: COMPREHENSIVE ACROLEIN TREATMENT OF WATER INJECTION SYSTEM OVERCOMES BACTERIALLY MEDIATED LOSS OF INJECTIVITY

Problem: This case study describes how acrolein was used in both batch and squeeze applications to improve injectivity problems caused by bacteria contamination. An independent producer operating a waterflood near Whiteface, Texas was having difficulty injecting water and had observed an abnormal decline in production. The production system consisted of approximately 350 barrels of produced fluid from the West Production Header and 650 barrels of the produced fluid from the "M" Battery being transferred to the FWKO at the injection station. The produced water is separated at the FWKO and sent to the produced water tank. Water from the produced water tank flows into one of two surge tanks. Approximately 4,000 barrels of fresh supply water is mixed with the produced water in the surge tanks prior to injection into 27 injection wells (Figure 8). The injection system was operating at a steady-state condition for several years.

A bacteria survey was initiated to determine the source of injection well plugging, to determine bacteria levels throughout the production and injection system, and to recommend a treatment program to improve injectivity for the lease. The survey showed that the bacteria levels were increasing from the production to the injection system (Figure 9). An analysis of solids plugging the filters at the injection system indicated severe bacterial contamination. Epi-fluorescence microscopy also indicated severe bacterial contamination in the injection system and the water supply well.

Solution: An acrolein treatment program was recommended to treat the water supply well and the injection system. The initial treatment was for one cylinder (52 gallons) of acrolein pumped into the water supply well over one hour. To treat the injection system, half a cylinder (26 gallons) of acrolein was pumped into the production tank at the injection system and the remaining half cylinder into the commingled surge tanks at the injection system. The subsequent treatments at the injection system consisted of one cylinder into the commingled surge tanks and one cylinder into the water supply well.

Two problematic injection wells were chosen for squeeze treatment. The wells were back-flowed for two tubing volumes and preparations were made for a chemical squeeze treatment down the injection string. The squeeze solution consisted of one cylinder of acrolein and 5 gallons of a nonionic surfactant mixed into 100 barrels of fresh water. The squeeze solution was over-flushed to the formation face where it remained undisturbed for 24 hours and returned to injection. The application provided for approximately 8.6 feet of radial penetration of a 1.2% concentration of acrolein into the formation.

Results: Hall plot curves were generated from cumulative injection volumes and cumulative injection pressure data collected daily from each injection well in the system for each injection well. Over 80% of the injection wells showed a positive inflection in the Hall plot trend by the second application (example in Figure 10). The remaining 20% did not show any change in the Hall plot curve at the time that this report was written. The two wells chosen for squeeze treatment also showed a positive inflection in the Hall plot trend (Figure 11).

The total amount of water filtered through a 0.45µm pore size filter increased from an average of 1,083 to 1,761 mls and the TSS dropped from 18.1 to 9.7 mg/l (Figure 12).

Production increased from 197 to 227 barrels of oil per day shortly after the program was implemented.

CASE HISTORY III: ACROLEIN STIMULATION OF INJECTION WELLS ENHANCES INJECTIVITY IN WEST TEXAS SECONDARY WATERFLOOD

Problem: This case study describes how acrolein was used in squeeze applications to remove FeS deposition in several injection wells. A large producer was experiencing low injection rates and high wellhead pressures due to FeS deposits in a West Texas waterflood. Prior acid treatments and xylene treatments had not been effective in restoring long-term injectivity. The average injection volume prior to treatment was 126 barrels per day at 1,708 psi.

Solution: For each of the water injection wells, stimulation packages were designed based on the completion of the well. According to the completion data such as tubing dimensions, perforated interval, permeability, etc., the treatment volumes utilized varied slightly. However, the general format for treating each of the injection wells was similar. As a pre-treatment to remove organic deposits, one drum of a nonionic surfactant was mixed into a water truck containing 130 barrels of 2% KCl water. The solution was pumped down the tubing where it remained undisturbed for 24 hours. The wells were back-flowed approximately two or three tubing volumes and then treated with acrolein. A high pressure pump truck was connected to the well and 20 barrels of the 2% KCl was pre-flushed into the tubing to sweep out any H_2S from the wellbore prior to the acrolein treatment. Following the pre-flush, acrolein was continuously metered into the KCl diluent at a rate of 0.52 gallons acrolein per barrel of water. A total of 52 gallons of acrolein was metered into 100 barrels of the KCl. The well was then over-flushed with 10 barrels of KCl, shut-in for 48 hours and then returned to injection. The treatment provided for a radial penetration of approximately 3 feet. The injection wells were choked back at the wellhead immediately after being returned to injection to keep the wells from taking too much fluid.

Results: Injection well data (pressures and volumes) gathered at the end of the month indicated that the average injection volume three months prior to the acrolein application increased from 126 barrels per day to 264 barrels per day. The data after the acrolein treatment was averaged six months after treatment. Data gathered during the month of the application was not averaged. The injection pressure decreased from an average of 1,708 psi before the acrolein treatment to 1,592 psi after the treatment (Figure 13).

CASE HISTORY IV: REMEDIATION OF SOUR PRODUCTION AND ENHANCEMENT OF INJECTIVITY ACHIEVED BY ACROLEIN SQUEEZE AND BATCH TREATMENTS IN SOUTHERN CALIFORNIA OIL PRODUCTION FACILITY

Mitigation of Sour Production

Problem: This case study shows how acrolein was used to reduce H_2S levels and improve injectivity. A large production facility operating a waterflood near Lost Hills, California was experiencing high H_2S levels at the inlet to their gas plant while their inlet H_2S scrubbers were out of service. A quick survey of H_2S levels at the producing wells identified the high H_2S level wells which were all supported by Header 17 of the injection system. Previous tracer surveys had demonstrated that many of the supported wells had experienced breakthrough and injected fluids could often be observed at the producer within a week. To prevent having to shut in producing wells, a plan to treat the injection header and the producing wells with acrolein was devised. H_2S levels at the injection plant were at an average of 1,153 ppm in the gas phase prior to the treatment.

Solution: An acrolein treatment program was recommended to treat the water supply header and the high H_2S level wells. To reduce the H_2S levels, the bulk water was treated with one skid (347 gallons) of acrolein. To reduce the H_2S levels in the producing wells, an acrolein squeeze program was initiated. Thirteen of the producing wells in the Header 17 injection system were treated with two cylinders (104 gallons) of acrolein, followed by 100 barrels of 3% KCl over-flush. The base fluid for the acrolein injection included 55 gallons of a pH stabilizer and 55 gallons of a nonionic surfactant per 100 barrels of injected fluid. The wells were treated with a 1.2% concentration of acrolein. The acrolein solution was injected into each producing well where it remained for 24 hours. After reaction, the wells were returned to production.

Results: The batch treatments into the injection system and producing wells resulted in statistically significant reduction of H_2S levels. These levels fell from 1,153 to 369 ppm (Figure 14). The H_2S levels remained low long enough for the scrubbers to be placed back in service and avoid having to shut in production; and while there was no extended H_2S reduction, the treatments did result in an incremental increase of 116 BOPD for a period exceeding 126 days.

Enhancement of Injectivity

Problem: At the same facility many of the injection wells were operating at the maximum allowable pressure and injection rates were below target levels. Elevated pressures were observed in the 24 injection wells receiving water from Header 17. The wells were injecting an average of 1,797 barrels of water per day at 257 psi. Backflow samples gathered from the wells confirmed a significant presence of FeS solids.

Solution: An acrolein treatment program was recommended to treat the water supply wells and the injection plant. The bulk water through Header 17 was treated three times with one skid tank (347 gallons) of acrolein for each application over a 28 day period. The acrolein was slipstreamed upstream of the header using a high pressure pump truck. There was no shut-in time during the header treatment.

To improve the injectivity for individual injection wells, acrolein squeeze stimulations were initiated. Each of the twenty-four injection wells in the Header 17 injection system was treated with two cylinders (104 gallons) of acrolein. The wells were treated with a 1.2% concentration of acrolein and included 55 gallons of a pH stabilizer and 55 gallons of a nonionic surfactant per 100 barrels of injected fluid. The acrolein solution was injected into each injection well where it was shut-in for 24 hours. After the reaction with FeS was given suitable time to react, the wells were returned to injection.

Results: The acrolein squeeze program resulted in a statistically significant injection rate increase for the 24 injection wells, increasing from an average of 1,797 to 2,130 barrels of water injected daily. The average injection pressures for these injection wells decreased slightly from 257 to 252 psi (Figure 15).

SUMMARY AND CONCLUSIONS

Acrolein provides an alternate solution to chemical management of waterflood operational problems stemming from bacteria, H_2S and FeS due to its unique ability to effectively kill bacteria (both planktonic and sessile), scavenge H_2S, and dissolve FeS.

As an H_2S scavenger, acrolein reacts rapidly with H_2S to form an irreversible water soluble product and similarly removes FeS by attacking the H_2S that is in equilibrium with soluble FeS. As a biocide, it was shown to be most cost effective in 26 of 29 kills studies conducted on bacteria from various locations.

For waterflood treatments, acrolein can be applied continuously or used in batch treatments at various locations throughout the water plant, injection lines, injection manifolds or wellheads. It can also be squeezed into the near well bore to remediate formation damage due to FeS or mitigate sessile bacteria in the near well bore.

A number of publications are presented documenting these types of applications in various waterfloods throughout the world.

Four specific new case studies are described highlighting the various approaches to use acrolein for improving injection water quality and injectivity:

1) In a southern Oklahoma waterflood, a 130,000 BWD waterflood becomes contaminated with APB in the injection system that results in high numbers of APB failures per year. Acrolein is applied strategically to mitigate these failures which results in a 60% reduction in failures over the course of the program.

2) In Whiteface, Texas, a water injection system contaminated with bacteria from a water supply well resulted in a decline in injectivity and subsequent loss of production. A combination of batch treatments of acrolein to the source water and downstream co-mingled injection water plus a squeeze treatment using acrolein on two problematic injection wells resulted in a 63% increase in filterability of the water and a corresponding 15% increase in production per well.

3) A description is given of a comprehensive acrolein squeeze program in a West Texas waterflood to remediate FeS damage, where attempts with acid treatments were previously unsuccessful. The average injection pressure decreased from 1,708 psi to 1,592 psi and the average injection volume increased from 126 bbls per day to 264 bbls per day.

4) The final description reviews a program from a California waterflood to remediate sour production and enhance injectivity. High levels of H_2S, entering a gas plant where the scrubbers were out of service, were determined to come from a specific header. By squeezing the wells feeding water to this header with acrolein, the H_2S levels were reduced from 1,153 ppm to 369 ppm, thereby allowing production to continue long enough for the scrubbers to be put back in service. At the same facility, the waterflood system was operating at below target injection rates and the injection pressures were at their maximum. By treating the injection water at the header with acrolein and squeezing each of the 24 injection wells, the average injectivity per well increased from 1,792 to 2,130 BWD, while the injection pressures declined slightly.

ACKNOWLEGMENTS

The authors would like to gratefully acknowledge the contributions of Darin Horaska, Troy Yarbrough, Terry Ferrell and Ty Paris to this paper.

REFERENCES

1. Smith, C.W. 1962. Acrolein. Wiley and Sons, New York, 273 pp.

2. DeWoskin, R.S., Greenberg, M., Pepelko, W., and Strickland, J. 2003. Toxicological review of acrolein. In support of Summary Information on the Integrated Risk Information System. CAS No. 107-02-8. EPA/635/R-03/003

3. Howell, J.J. and Ward, M.B. 1991. The use of acrolein as a hydrogen sulfide scavenger. SPE Paper No. 2172. Presented at the Production Operations Symposium, Oklahoma City, Oklahoma, April 7-9, 1991

4. Kissel, C.L., Brady, J.L., Clifton Gottry, H.N., Meshishnek, M.J., and Preus, M.W. Factors contributing to the ability of acrolein to scavenge corrosive hydrogen sulfide. 1985. SPE Paper No. 11749. California Regional Meeting of the Society of Petroleum Engineers of AIME, Ventura, California.

5. Salma, T. 2000. Cost effective removal of iron sulfide and hydrogen sulfide from water using acrolein. SPE Paper No. 59708. Presented at SPE Permian Basin Oil and Gas Conference, Midland, Texas, March 21-23, 2000.

6. Penkala, J.E., Law, M.D., Dickinson, A.L., Horaska, D., Conaway, J., and Soto, H. Acrolein, 2-propenal: a versatile microbiocide for control of bacteria in oilfield systems. NACE Paper No. 04749, NACE International Corrosion/2004, New Orleans, LA, March 30-April 2, 2004.

7. Kissel, R. 1984. Acrolein as a biocide and sulfide inhibitor. Presented at NACE, Bossier City, Louisiana, November 1984.

8. Palacios, C.A. and Riccobono, C.C. 2003. Field experiences for SRB-MIC control in water injection plants having continuous pit recovered fluids. NACE Paper 03547. Presented at NACE International Corrosion 2003, San Diego, April 2003.

9. Harless, M.L. 1996. An acrolein pilot plant treatment program for Exxon Pipeline Company's Grand Isle, Louisiana Water Treatment Facility. American Filtration Society Produced Water Seminar, League City, Texas, January 1996.

10. Van der Wende, E., De Rienzo, C.L., Harless, M.L., Paakkonen, S.T., Simons, P.B., and Summerfelt, F.F. 1996. The effect of acrolein treatment on the corrosion rates of mild steel piping of a secondary recovery produced water flood. NACE International Canadian Region Western Conference, Anchorage, Alaska, February 1996.

11. Johnson, M.D., Harless, M.L., Dickinson, A.L., and Burger, E.D. 1999. A new approach to mitigate sulfide production in oilfield water injection systems. SPE Paper No. 50744, Presented at the International Symposium on Oilfield Chemistry, Houston, Texas, February 16-19, 1999.

12. Law, M.D., Burger, E.D., Kretsinger, M.B., Schoenenburger, J.G., and Ullman, M.A. 2001. A field case history: Chemical treatment of a produced-water injection system using anthraquinone improves water quality and reduces costs. SPE Paper No. 65023. Presented at SPE International Symposium on Oilfield Chemistry, Houston, Texas, February 15, 2001.

13. Penkala, J.E., Soto, H., Carranza, D., and Gimenez, C. 2005. Acrolein (2-Propenal) mitigates sessile biofilm and biogenic sulfides in a large waterflood in Neuquen Province, Argentina. ASVENCOR Paper No. 5140 . Presented at the ASVENCOR Congreso Internacional de Corrosion in Lecheria, Edo. Anzoategui, VZ, 22-26 November 2005.

14. Dickinson, A., Peck, G., and Arnold, B. 2005. Effective chemistries to control SRB, H2S, and FexSy Problems. SPE Paper No. 93087. Presented at SPE Western Regional Meeting, Irvine, CA 30 March – 1 April.

15. Shield, M., Charlesworth, M., and Paakkonen, S. 2005. Field Experiences using acrolein (2-propenal) for control of SRB and MIC in an offshore production flowline and onshore production facility in Western Australia. 16th International Oil Field Chemistry Symposium, Geilo, Norway, 13-16 March 2005.

16. Penkala, J.E., Reed, C., and Foshee, J. 2006. Acrolein application to mitigate biogenic sulfides and remediate injection well damage in a gas plant water disposal system. SPE Paper No. 98067. Presented at the 2006 SPE International Symposium and Exhibition on Formation Damage in Lafayette, LA 15-17 February, 2006.

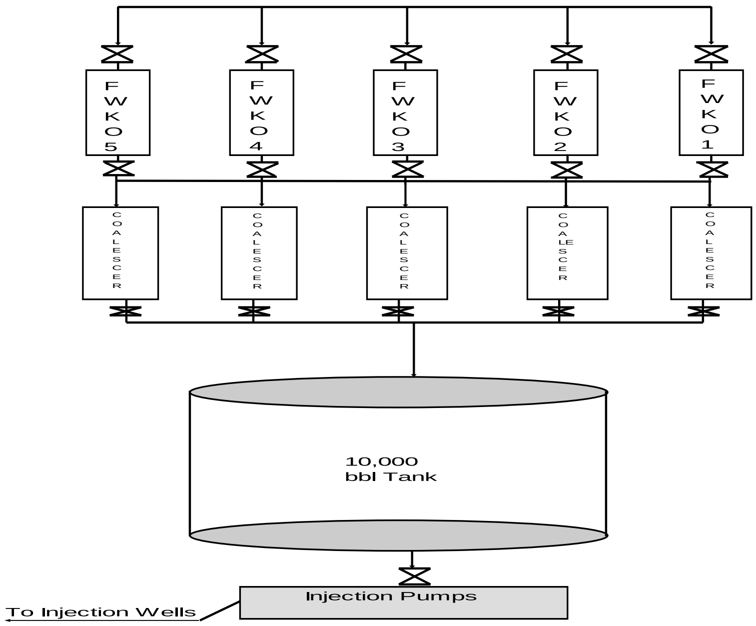


Figure 1 – Water injection Station

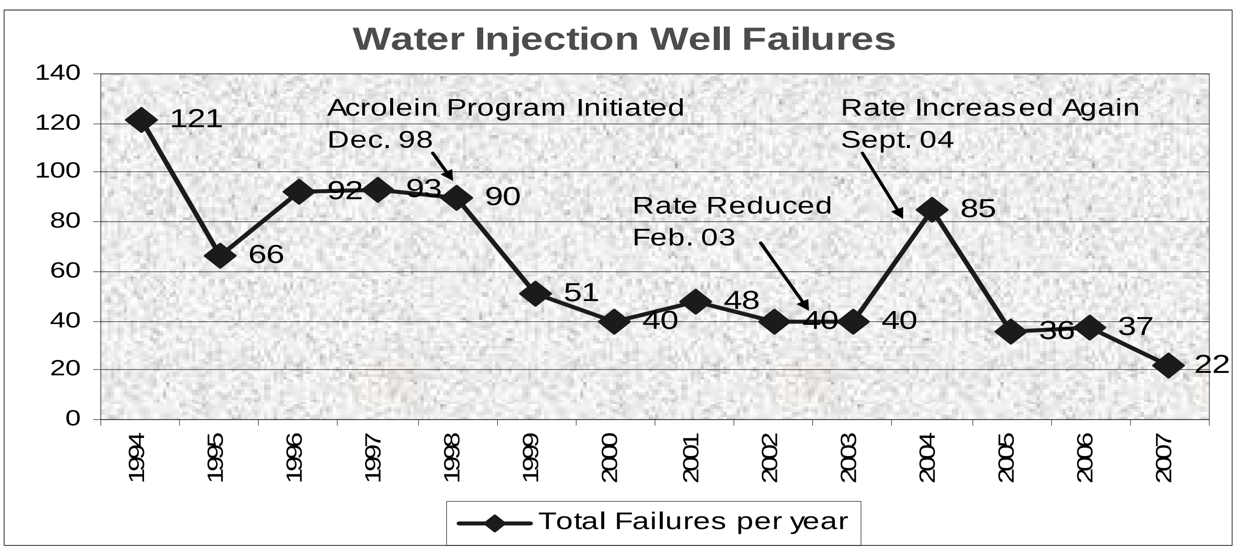


Figure 2 – Injection Well Response to Acrolein Program

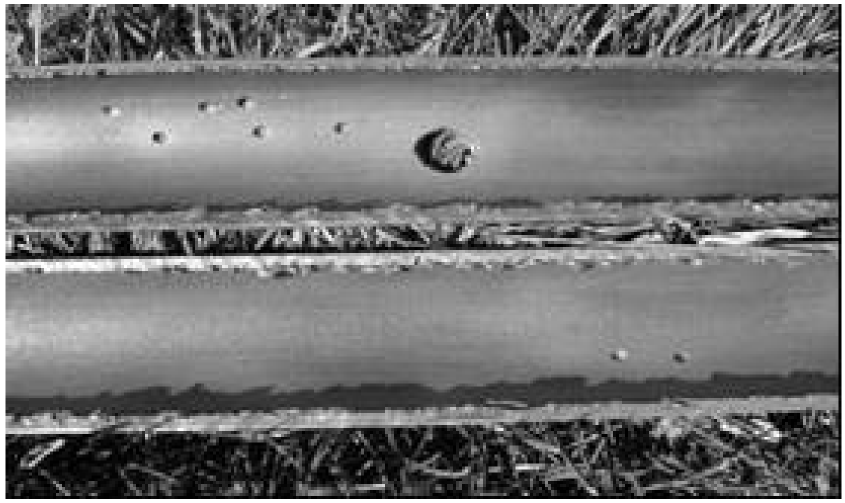
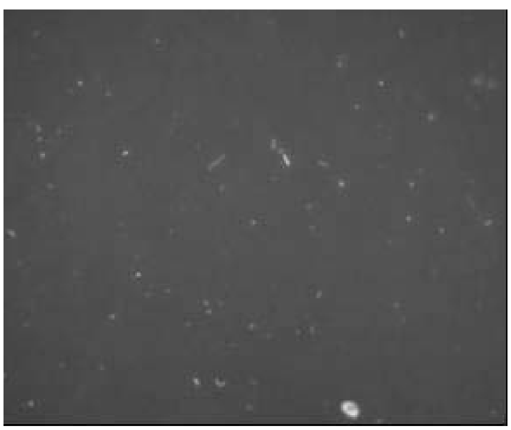


Figure 3- MIC (Acid Producing Bacteria) Corrosion in Injection Tubing



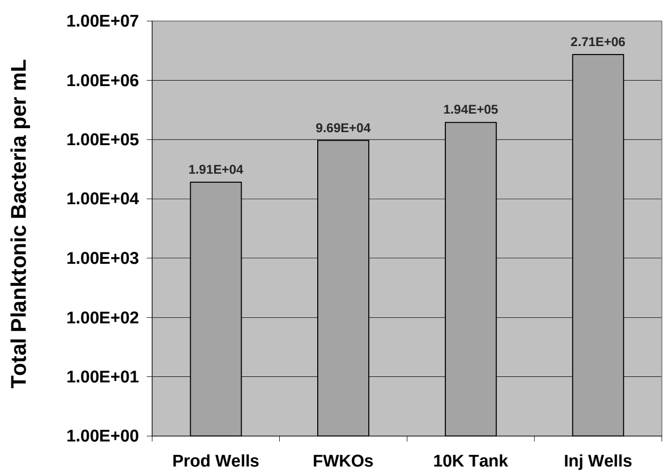


Figure 4 – Planktonic Bacteria Levels Increasing Through System – Photomicrograph of Planktonic Bacteria in the Production System

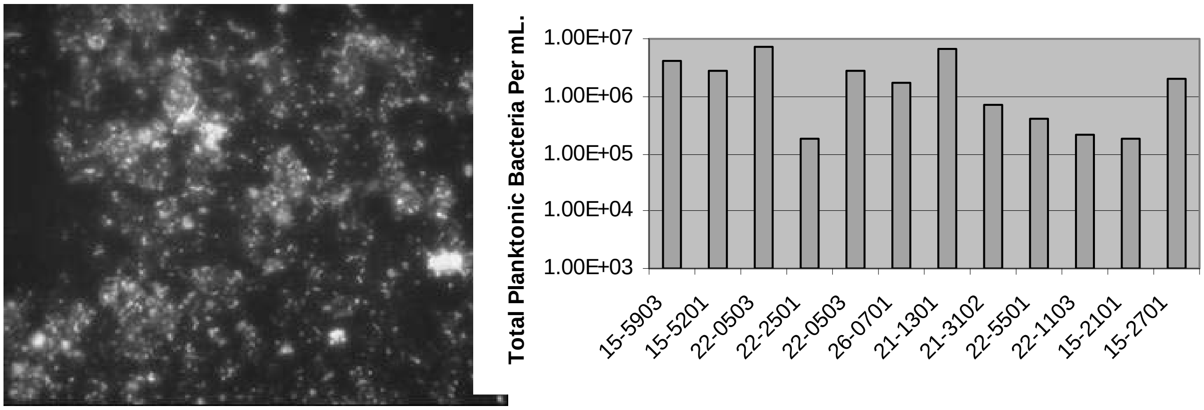


Figure 5 - Planktonic Bacteria Levels in the Injection System – Photomicrograph of Bacteria in the Injection System

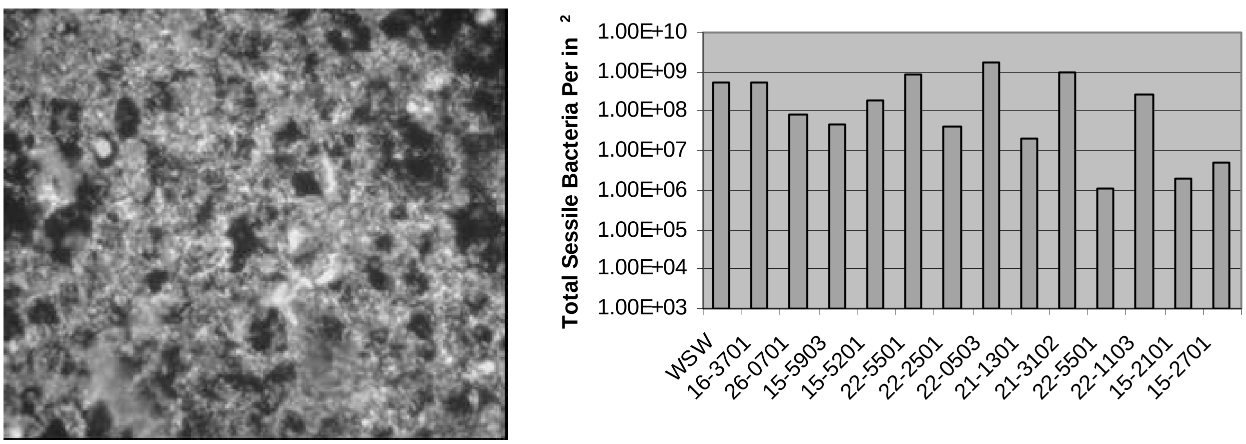


Figure 6 – Sessile Bacteria Levels in the Injection System – Photomicrograph of Sessile Bacteria in the Injection System

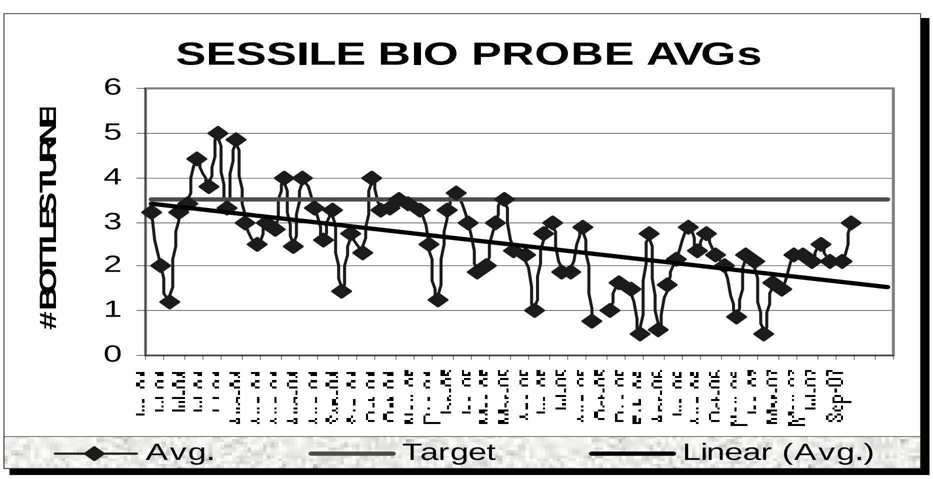


Figure 7 – Sessile Bacteria Levels after Increasing Acrolein Program

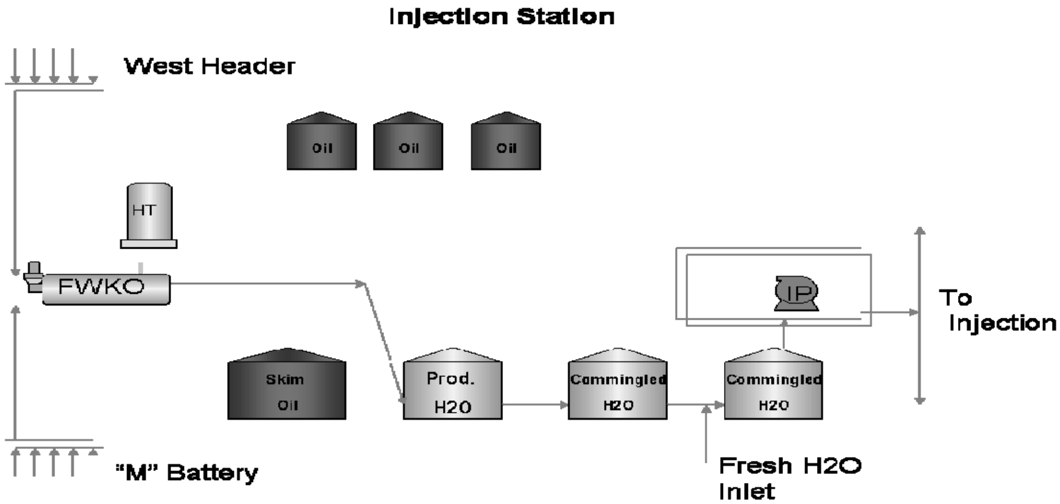


Figure 8 - Water Injection Station

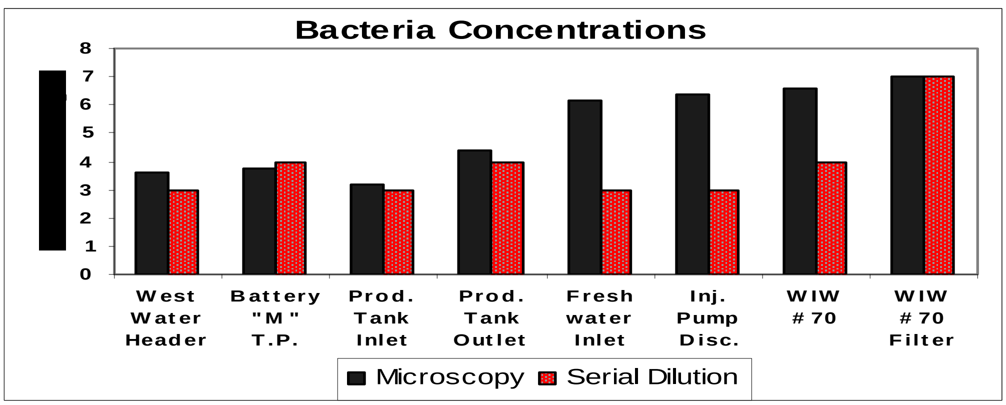


Figure 9 - Bacteria Levels Increasing Through the System

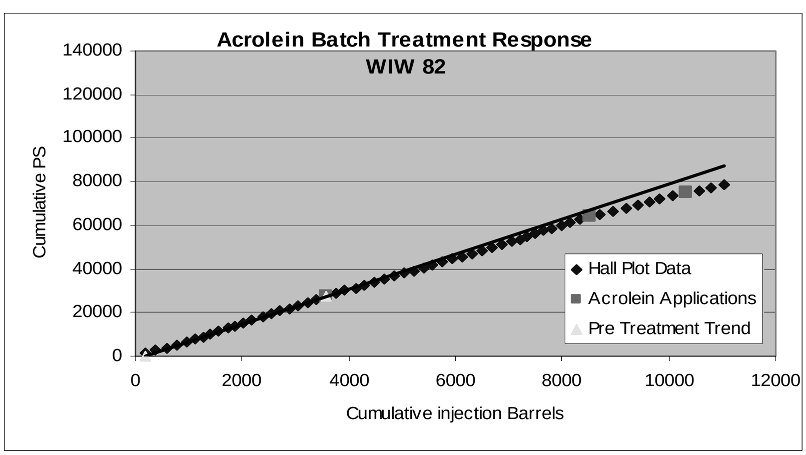


Figure 10 – Hall Plot from Acrolein Batch Treatment

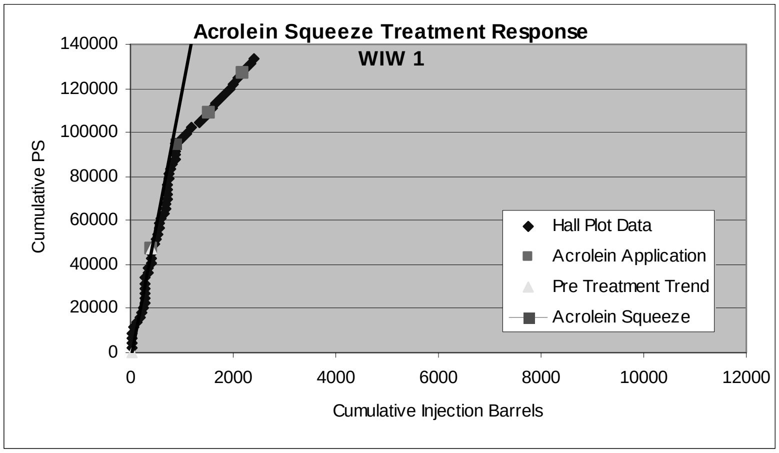


Figure 11 – Hall Plot from Acrolein Squeeze Treatment

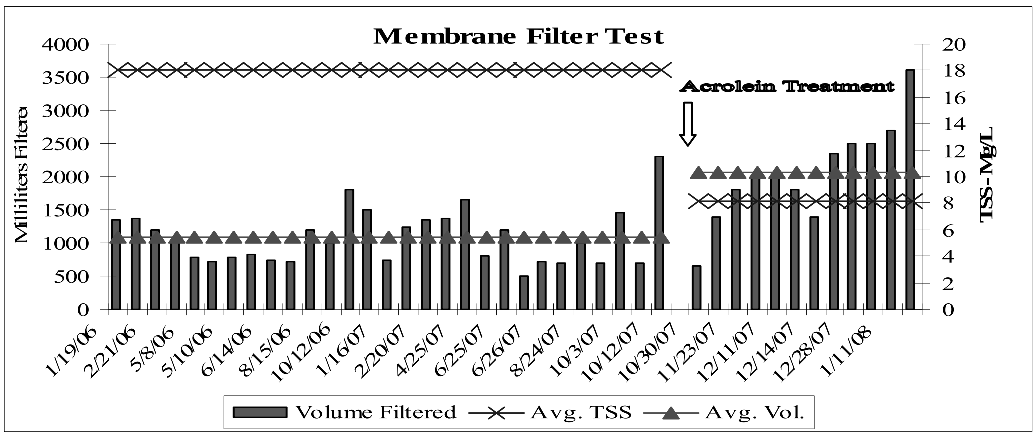


Figure 12 – Acrolein Program Results in Decrease in Total Suspended Solids and Increase in Injection Volume

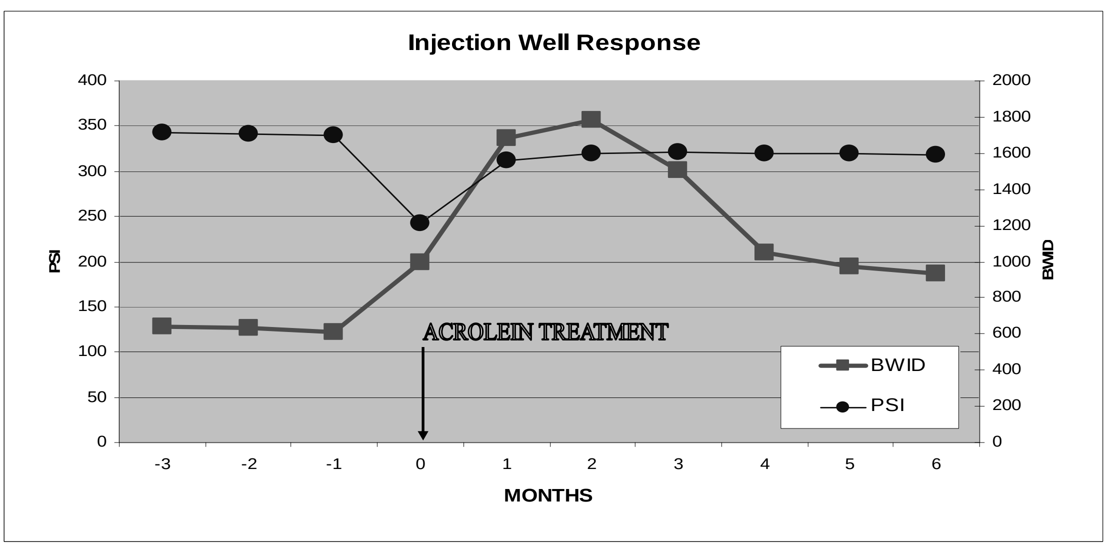


Figure 13 – Acrolein Squeeze Treatments Result in Reduction in Pressure and Increasing Injection Rates

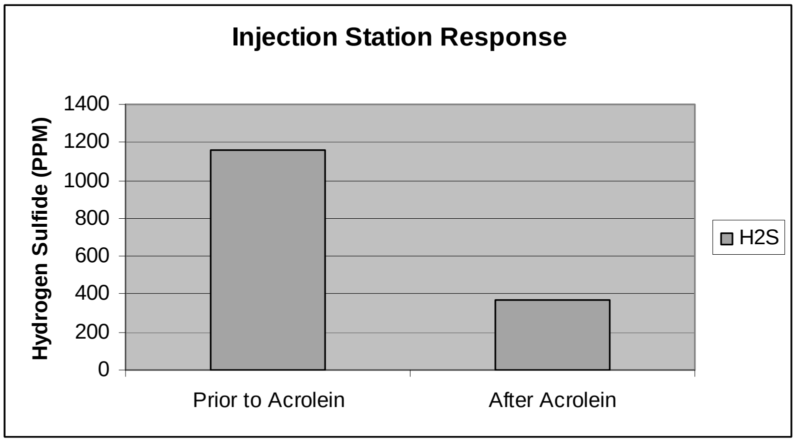


Figure 14 – Acrolein Treatment Results in Reduction of Hydrogen Sulfide

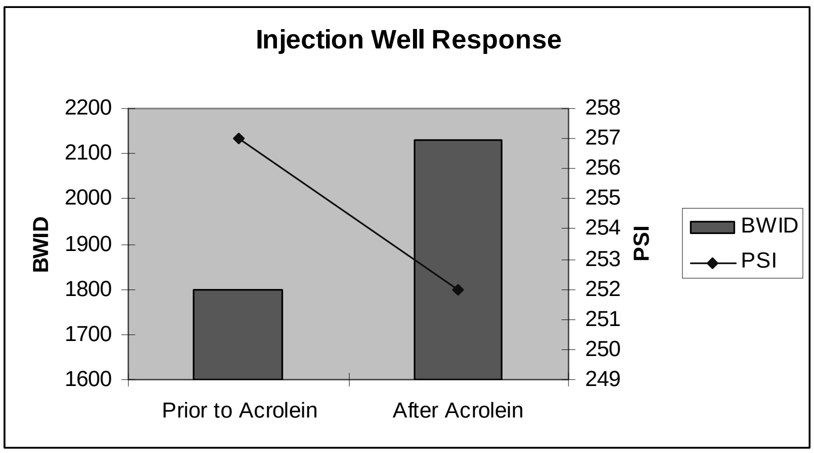


Figure 15 – Acrolein Treatment Results in Increased Injection Volume and Reduction of Pressure