CASE STUDY OF EFFECTIVE SULFATE SCALE CONTROL IN A SEVERE SCALING ENVIRONMENT UTILIZING ALTERNATIVE FIELD AND LABORATORY TECHNIQUES

Kent Caudle, Julie Hardy, Dennis Varner, and Teddy Latham
Champion Technologies

ABSTRACT

Water flooding is utilized extensively for oil recovery in the Permian Basin. Finding compatible and accessible make-up water can be problematic in some areas. In these situations, proper selection and application of scale inhibitors can enable the mixing of otherwise incompatible waters. This case study discusses the various methods used for product selection and application, including a testing methodology which can be used for direct measurement of scale inhibitor effectiveness and treatment optimization.

OVERVIEW

The Canyon Sands Formation is produced via a water flood. Table 1 displays a representative water analysis of the Canyon Sands Formation. The Canyon Sands Formation has been produced for many years (some wells are ~70 years old) and casing leaks have become increasingly problematic over the past few decades. When casing leaks occur, severe barium sulfate scaling issues result due to the naturally occurring sulfate content of the inflowing water.

Dozens of new wells were drilled in the Canyon Sands Formation in 2009. With all of the new production, water injection demands increased and the existing make-up water sources became inadequate. Additional water source(s) were needed to compensate for the new production. Two different water sources were investigated. The selection of the water source was based on several factors. The main factors were the cost of operation, accessibility, abundance, and water compatibility with the Canyon Sands Formation.

INTRODUCTION

Accumulation of scale on equipment contributes to many problems such as flow restrictions, plugging, equipment damage, and corrosion. Scale deposits are crystals of minerals that precipitate from supersaturated solutions. Changes in temperature, pressure, pH, and mixing of incompatible waters are the main factors that influence scale formation. Incompatible waters can be described as the mixing of two separate water sources in which each water source possesses complimentary electrolytes needed to form scale. For example, one water source may have an abundance of sulfate and the other barium, which when mixed will form barium sulfate scale. Scale can also form from corrosion byproducts such as iron sulfide or iron carbonate.

There are 4 basic steps in mineral scale formation[1, p. 683].

1. <u>Supersaturated solution</u> – a chemical solution that contains a greater amount of solute (Ca^{2+}, Ba^{2+}, SO_4^{2-}, CO_3^{2-}, ect.) than should be present at equilibrium
2. <u>Nucleation</u> – described as molecules in a supersaturated solution that come together randomly and form small aggregates
3. <u>Crystal Growth</u> – involves the addition of more molecules to an aggregate, forming scale crystals
4. <u>Adherence</u> – refers to scale crystals that become firmly attached to a surface

There are three general types of inhibitors used to mitigate scale issues (see Figure 1): chelating or sequestering agents, threshold inhibitors, and dispersants. Chelating or sequestering agents function by complexing with the cation (Ca^{2+}, Sr^{2+}, Ba^{2+}, ect.) so that it is unable to interact with the anion (SO_4^{2-} or CO_3^{2-}) and form scale. Threshold inhibitors work by inhibiting nucleation or crystal growth modification. The proposed principle for nucleation inhibition is that initially formed aggregates can be made unstable by adsorption of a scale inhibitor, causing the aggregate to fall apart and return the scaling ions into solution. The theory of crystal growth modification is that crystals have a preferred location of growth called an “Active Growth Site”. Crystal growth modifiers function by slowing the rate of the crystal growth, and by diminishing the ability of crystals to adhere to surfaces due to crystal distortion. Dispersants aid in preventing crystal adherence and growth by coating and dispersing formed scale crystals.

Before implementing a scale control program, the product / fluid compatibilities must be considered. Certain classes of scale inhibitors are susceptible to poisoning or deactivation in the presence of high amounts of calcium, magnesium, or iron, while others may be very resistant, but are not effective at inhibiting the particular scale that is causing issues.

WATER SOURCE A.

The first approach for supplementing the make-up water was to use water source wells containing an excess of dissolved sulfate, which would lead to a severe scaling environment. This issue was to be controlled by implementing an aggressive scale control program. This was a favorable choice for make-up water because it was easily accessible and plentiful. Scale predictions were made using ScaleSoftPitzer™, a scale modeling software[4]. Comingling the two water sources resulted in saturation indices (logarithmic function) greater than 3.0 (1000 times saturation). Through years of testing and experience in both the laboratory and field, some general guidelines have been established correlating saturation indices with scale formation. Barium sulfate scale formation often begins to occur at a saturation index of 0.3 (2 times saturation). Inadequate scale inhibition would likely result in rapid and severe scaling issues in equipment and possible formation damage at water re-injection sites.

Lab testing was performed to determine if the barium sulfate scale could be inhibited at a saturation index of 3 or greater. Three different types of scale control products were tested: phosphate ester, phosphonate, and polymer dispersant. Scale inhibitor polymers were not considered due to the high cost and difficulty in monitoring low level residuals. In addition, phosphate ester and phosphonate based scale control chemistries have been used in West Texas for many years with success.

Testing (see Figure 2) was performed by mixing the sulfate containing water with the barium containing water. Both water samples were filtered prior to testing using a 0.45 um millipore filter. The barium containing water was treated with the respective scale inhibitor at a dosage of 100 ppm. The samples were filtered after a period of time to remove any barium sulfate precipitate that may have formed, and analyzed for the presence of dissolved barium using atomic absorption spectroscopy. The barium content of the samples were compared to the original barium containing water sample. The remaining barium content in the treated samples indicates how effective the scale inhibitor was at preventing scale deposition. The results were reported as percent inhibition. Results from the test indicated that the phosphate ester scale inhibitor was superior to the phosphonates and polymer dispersant at preventing barium scale formation. The phosphonates were minimally effective and the polymer dispersant was not effective in preventing barium scale formation.

Further testing was done using the phosphate ester and dispersant to determine the particle sizes of the scale agglomerates that formed (see Table 2 and Figure 3). Particle size distribution tests were performed on samples treated with the phosphate ester, dispersant, and a mixture of phosphate ester and polymer dispersant.

The particle size was determined on the treated and untreated sample. The purpose of this test was to determine what impact the scale inhibitors would have on the amount and size of any particles that formed. It is important that the suspended particles be minimal in abundance and size to prevent formation damage and ensure the water injection system integrity. The phosphate ester chemistry exhibited the best results by having both the lowest count per 100 mL and smallest size of particles. Based on the results, the phosphate ester would be used field wide to control barium scale. Sulfate containing water should not be used for make-up due to the high risks associated with barium sulfate scale formation. A water source well was drilled to meet the additional make-up water requirements.

WATER SOURCE B.

As an alternative to using the sulfate containing water the Lower Canyon Sands Formation, a water bearing formation only, was drilled and utilized for make-up. Water from this formation did not have a significant impact on the saturation index for barium scale making it an ideal candidate for make-up water. Table 3 shows a representative water analysis of that formation.

The calcium, magnesium, chloride, and iron content were substantially higher in the Lower Canyon Sands water compared to the Canyon Sands Formation. The phosphate ester was not compatible with this water, nor was the phosphonate scale inhibitors. It was eventually determined that the phosphate ester was reacting with the dissolved iron and precipitating out. This was accomplished by running millipore filtrations and analyzing the accumulated solids. Solids from multiple millipore filtrations were collected from a water injection line in order to accumulate enough solids for analysis. The millipore filters were soaked in warm HCl at a pH of 4. The eluent was then analyzed for the presence of phosphate, calcium, and iron (see Figure 4).

Initially, the precipitated phosphate ester was thought to be carbonate scale with respect to millipore filtrations. Millipore filtration tests were being done monthly to monitor the water quality. Qualitative and quantitative analyses of the suspended solids were performed. The acetic acid soluble content, which is generally categorized as carbonate, was high because the precipitated phosphate ester would re-dissolve in acetic acid solution.

The precipitation of phosphate ester with dissolved iron was further confirmed through additional lab testing. Phosphate ester was added to a water sample from the Lower Canyon Sands Formation and left static for approximately 24 hours. The precipitate was filtered and dried. The precipitate was then dissolved in acidized deionized water. The dissolved iron and phosphate content was then determined using standard bench test methods. Results indicated a high concentration of both species. The standard phosphonate and phosphate ester chemistries that are typically used to control scale in this area were all incompatible with the Lower Canyon Sands water. Polymer scale inhibitors were then considered as an option for treating commingled Canyon Sands and Lower Canyon Sands Formation water.

The polymer scale inhibitor was selected based on additional properties of resistance to deactivation via ferric iron. Performance tests were performed on the phosphate ester and polymer using synthetic brine. Product comparison was done by performing dynamic scale loop tests. Both fluids were tested at 35, 30, and 25 ppm, respectively. The dynamic flow scale loop (see Figure 5) works by commingling a synthetic brine containing barium with a synthetic brine containing sulfate. The synthetic brines were made based on an analysis of the formation water. The scale inhibitor is initially started at a high dosage rate and then incrementally decreased until scale begins to form in the scale coils. This method of dosing is commonly referred to as sequential dosing. Scale formation is determined by monitoring the line pressure on the inlet and outlet of the scale coils. When scale begins to form and adhere to the internal surface of the scale coils, a difference in pressure occurs where the inlet pressure increases and the outlet pressure decreases. This is an indication that the inhibitor is below the minimum effective dosage.

The polymer exhibited a minimum effective dosage of 35 ppm. The phosphate ester had a minimum effective dosage of less than 25 ppm. Compatibility tests were performed on the phosphate ester and polymer to compare product compatibilities. Although the phosphate ester outperformed the polymer in effective minimum dosage, the phosphate ester was not recommended because it was incompatible with the Lower Canyon Sands Formation water.

The phosphate ester exhibited incompatibility issues at dosages as low as 10 ppm in the Lower Canyon Sands Formation water. The polymer scale inhibitor did not show any signs of incompatibility until the concentration reached 1000 ppm. This was significantly higher than the recommended target treating dosage of 35 ppm. Detailed results can be found in Figure 6.

UTILIZING AND MONITORING POLYMER SCALE INHIBITORS

Presently, there is extensive research being done with purpose of developing economical and time-saving methods for monitoring low ppm residuals of polymer scale inhibitors. One of the more popular methods being exploited presently is by tagging the polymer with an inert molecule that will fluoresce[3]. Monitoring low ppm residuals in non-polymer based chemistries has been the standard approach in the oil and gas industry for decades. This practice is a secondary method for validating a scale inhibitor program. In using this method, a minimum inhibitor concentration is assumed based on results from lab testing and field history. There is no practical way of determining the minimum inhibitor concentration for treated fluids on a per location basis using scale inhibitor residuals alone[2]. Scale stress testing has the potential to overcome these limitations.

An alternative method for monitoring and validating scale inhibitor programs is presently being developed for use in the Permian Basin. This method is referred to as a scale stress test. A scale stress test by definition determines the capacity of treated fluids to inhibit scale formation. The limiting reactant (in this case sulfate) is added incrementally to the treated fluids until there is no longer enough scale inhibitor to prevent scale formation. Unlike scale inhibitor residual testing, this new method measures the capacity of the treated fluids to prevent scale formation on an individual location basis. Scale stress tests are presently being used to monitor the polymer scale inhibitor treating regime for the Canyon Sands Formation.

Water from the Canyon Sands Formation has an abundance of naturally occurring barium. Stress tests are routinely performed on Canyon Sands water that has been treated with polymer scale inhibitor. The test is conducted by adding known amounts of sulfate (SO_4^{2-}) at different concentrations to the treated water. The amount of dissolved barium is determined in samples that have been spiked with a known amount of the limiting reactant (sulfate). The barium content is also determined in one sample that is not spiked. A significant decrease in the dissolved barium content indicates that the inhibitor concentration was not high enough to prevent barium scale formation and the sample failed the stress test. The test directly quantifies how much additional sulfate the treated fluids can tolerate before scale begins to form. By determining the threshold at the point where barium sulfate scale begins to form, a minimum effective dosage can be established empirically on a sample point by sample point basis in a relatively short amount of time.

One of the main goals of the scale stress test is to develop a procedure that does not require additional analytical equipment, involves a simple procedure, and can be completed in a timely manner. For these reasons, the current desired method for interpreting scale stress test results is through visual observation. The following defines the three different results for scale stress tests through visual observation:

- Pass – no visual indication of haziness or precipitate
- Marginal – barely passed or barely failed
- Failed – sample is visibly hazy or has precipitate

This eliminates the need for sophisticated equipment that would otherwise be necessary. It can also save time because the test can be performed in the field. Figure 7 displays and compares results from visual inspection and atomic absorption spectroscopy. Certain laboratory techniques are being used to prepare samples for visual observation. These techniques are still under review and being revised, and thus will not be discussed in this paper.

In the Canyon Sands Formation study, monthly water quality testing included millipore filtration tests before and after the implementation of the polymer scale inhibitor. As evident in Figure 8, the suspended solids content improved drastically after discontinuing the phosphate ester and applying the polymer scale inhibitor. These results aided in verifying the ability of the polymer scale inhibitor to effectively mitigate barium sulfate scale and remain compatible with the water.

PROPERTIES OF BARIUM SULFATE

Barium sulfate exhibits a very low solubility compared to strontium and calcium sulfate. The solubility of barium sulfate (1.1×10^{-10} K_{sp}) is 2.5 mg / L at 20 ºC[1, AP11]. Strontium sulfate (3.2×10^{-7} K_{sp}) and calcium sulfate (2.4×10^{-5} K_{sp}) have a solubility of 104 mg / L and 667 mg / L at 20 ºC, respectively[1, AP11]. Figures 9 – 12 illustrate some of the different properties of barium sulfate with respect to the scaling tendencies, pH, pressure, and temperature.

The scaling index for barium sulfate increases significantly with only a small increase in the concentration of sulfate (see Figure 9). This can be used as a tool to determine what impact the addition of sulfate has on the scaling tendencies of fluids. It is also important to understand what impact pH, pressure, and temperature has on scaling tendencies. These factors were taken into consideration when designing scale stress tests.

Based on the software model results, barium sulfate scale formation is unaffected by pH (see Figure 10). Thus, it is not considered when performing stress tests. Although it has relatively low impact compared to other factors, an increase in pressure decreases the scaling tendencies for barium sulfate formation (see Figure 11). Temperature plays an important role in the determination of barium sulfate scaling tendencies. As the temperature increases, scaling tendencies for barium sulfate decrease significantly (see Figure 12).

Stress testing on Canyon Sands Formation water is done at room temperature (~75 ºF) at 1 atmosphere. The temperature range for this formation is 90 to 105 ºF. Performing the stress tests at room temperature results in a more severe test because the lower the temperature, the higher the scaling index for barium sulfate, as seen in Figure

12. Test conditions can be changed to better mirror system conditions. As observed above, pH and pressure have minimal or no impact, while temperature plays a significant role on scaling tendencies for barium sulfate. Performing stress tests is superior to residual testing because a minimum level of capacity to inhibit scale can be set on an individual location basis. With respect to the Canyon Sands Formation, this is beneficial because some of the wells are as much as 70 years old and susceptible to casing leaks. When casing leaks have occurred in the past the inflowing water has had an abundance of sulfate content. Stress tests are performed such that not only do the fluids have enough inhibitor to prevent scale in normal conditions, but the fluids still remain inhibited with an excess of sulfate. In short, scale inhibitor programs can be augmented via stress test to offer additional inhibition to fluids to protect against other anomalies such as casing leaks.

CONCLUSION

Less common lab and field methods, such as scale stress testing, particle size distribution, and percent inhibition testing via atomic absorption spectroscopy, are viable alternatives to scale inhibitor residual testing that can be used to develop, implement, and optimize scale control programs. This paper focuses primarily on the scale stress test because it offers a direct measurement of the treated water to inhibit scale, where as scale inhibitor residual testing does not. The utilization of scale stress testing has the potential to offer a more accurate assessment of a scale inhibitor program which would result in enhanced value for the producer through improved asset integrity and program optimization. Additionally, current research is investigating scale stress testing for carbonate scale control programs. Developing diverse and alternative tests for scale allow for a robust approach in providing efficient and accurate treatment for wells.

REFERENCES

(1) Harris, C. Daniel. Quantitative Chemical Analysis, 6th ed.; W.H. Freeman and Company: New York, 2003.
(2) Ramstad, K.; Rohde, H. C.; Tydal, T.; Christensen, D. "SPE 114085 Scale Squeeze Evaluation Through Improved Sample Preservation, Inhibitor Detection, and Minimum Inhibitor Concentration Monitoring"; In SPE Oilfield Scale Symposium; SPE: Aberdeen, UK, 2008.
(3) Richardson, J.; Trulear, M. G. "NACE 99630 Advances in Cooling Water Treatment and Control"; CORROSION 99; San Antonio, TX, 1999.
(4) ScaleSoftPitzer™ version 10.0 [computer software]; Rice University Brine Chemistry Consortium Energy & Environmental Institute: Houston, Texas, 2006.

Table 1
Representative water analysis of the Canyon Sands Formation.

Water Constituents	Canyon Sands Formation (mg/L)
Calcium	8180
Magnesium	1215
Barium	190
Strontium	416
*Sodium	31572
Bicarbonate Alkalinity	220
Sulfate	7
Chloride	67000
Iron	52
Dissolved CO_2	100
Dissolved H_2S	34

*calculated

Table 2
Results from particle size distribution analysis using particle analyzer.

	Untreated		**Phosphate Ester**		**Dispersant**		**Phosphate Ester / Dispersant**	
Particle Size (um)	Count/100 mL	% of Total	Count/100 mL	% of Total	Count/100 mL	% of Total	Count/100 mL	% of Total
6 - 14	338,643	17.6%	152,918	86.5%	371,150	22.2%	314,405	70.5%
14 - 21	315,327	16.4%	12,383	7.0%	391,380	23.5%	68,570	15.4%
21 - 38	1,093,790	56.8%	9,613	5.4%	883,490	53.0%	59,190	13.3%
38 - 70	177,733	9.2%	1,605	0.9%	21,820	1.3%	3,235	0.7%
> 70	603	0.0%	263	0.1%	410	0.0%	285	0.1%
Totals:	1,926,096		176,782		1,668,250		445,685	

Table 3
Representative water analysis of the Lower Canyon Sands Formation.

Water Constituents	Lower Canyon Sands Formation (mg/L)
Calcium	16521
Magnesium	2041
Barium	352
Strontium	820
*Sodium	51259
Bicarbonate Alkalinity	98
Sulfate	9
Chloride	115000
Iron	87
Dissolved CO_2	150
Dissolved H_2S	2

*calculated

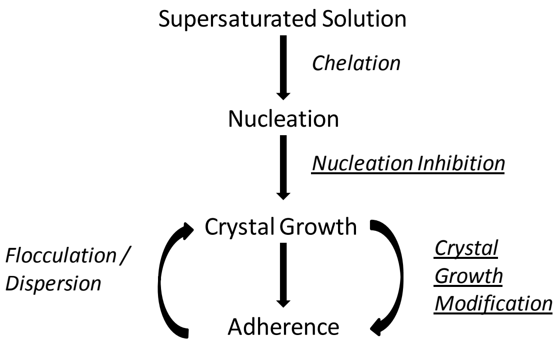


Figure 1 - Diagram of four basic steps to mineral scale formation and types of chemical intervention at each step.

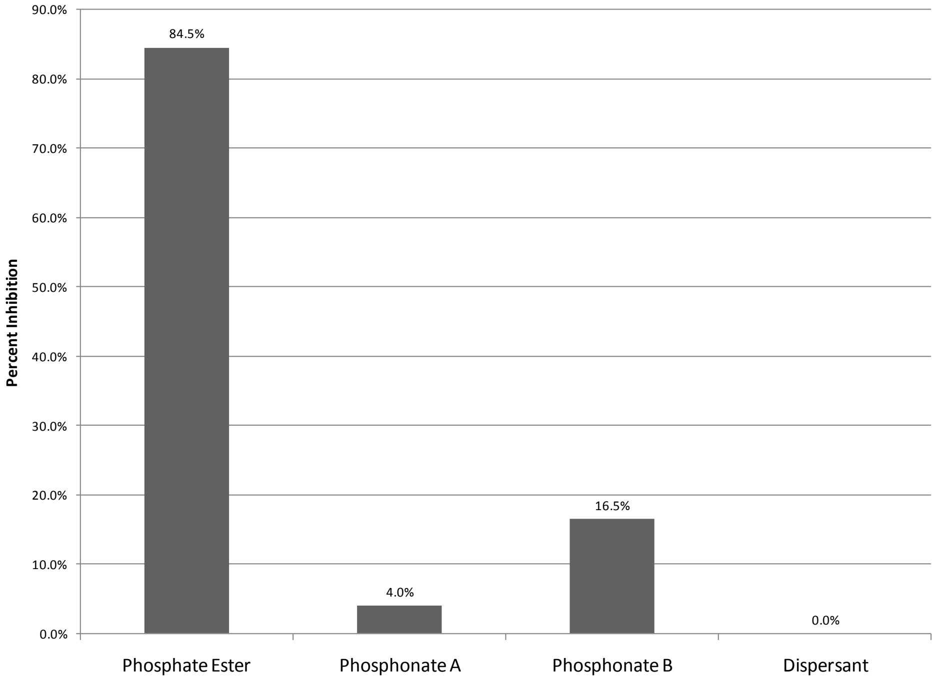
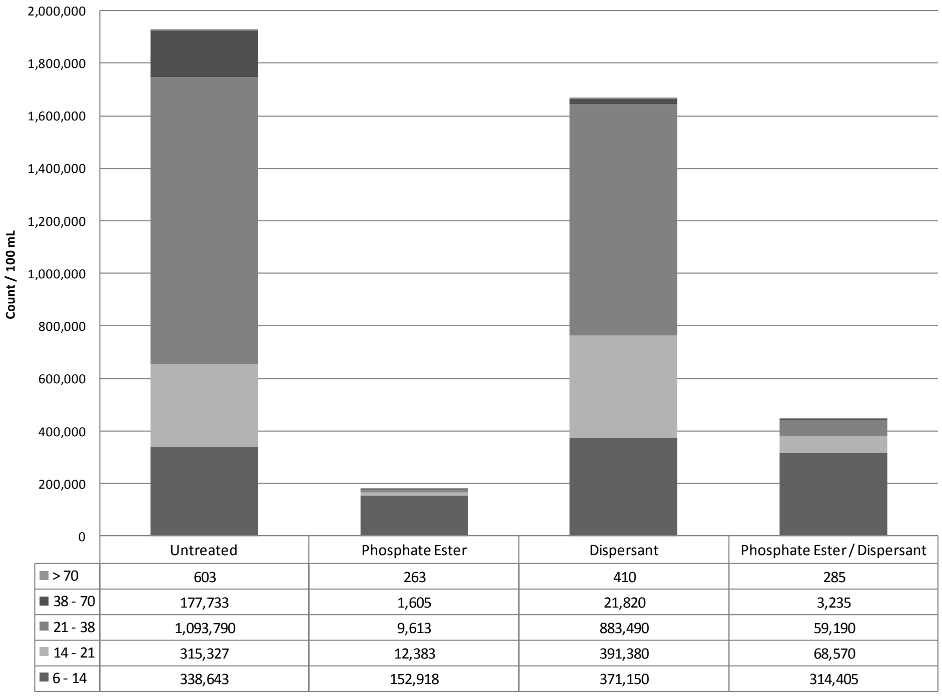


Figure 2 - Barium sulfate Inhibition performance test using atomic absorption spectroscopy.



	Untreated	Phosphate Ester	Dispersant	Phosphate Ester / Dispersant
■ > 70	603	263	410	285
■ 38 - 70	177,733	1,605	21,820	3,235
■ 21 - 38	1,093,790	9,613	883,490	59,190
■ 14 - 21	315,327	12,383	391,380	68,570
■ 6 - 14	338,643	152,918	371,150	314,405

Figure 3 - Results from particle size distribution analysis using particle analyzer.

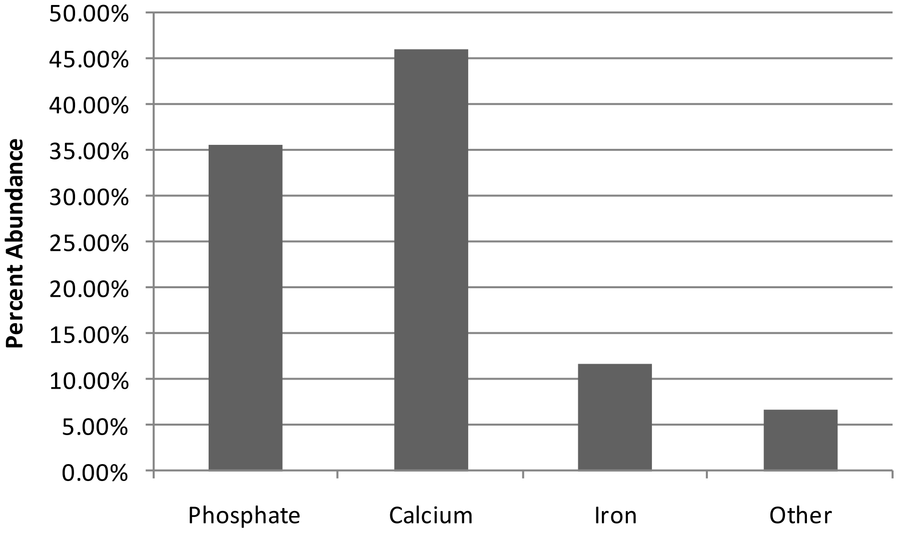


Figure 4 - Percent abundance of phosphate, calcium, and iron from millipore filtration tests.

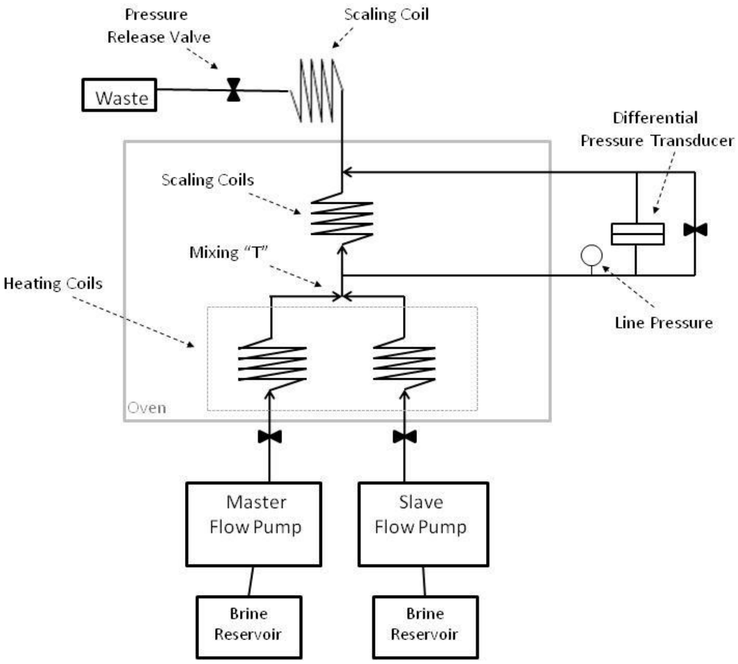
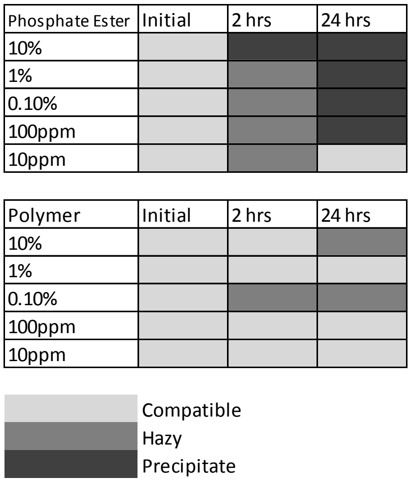


Figure 5 - Diagram of Dynamic Flow Scale Inhibitor Efficiency Test Apparatus.



Phosphate Ester	Initial	2 hrs	24 hrs
10%	░	▓	▓
1%	░	▓	▓
0.10%	░	▒	▓
100ppm	░	▒	▓
10ppm	░	▒	░

Polymer	Initial	2 hrs	24 hrs
10%	░	░	▒
1%	░	░	░
0.10%	░	▒	▒
100ppm	░	░	░
10ppm	░	░	░

░ Compatible
▒ Hazy
▓ Precipitate

Figure 6 - Results from water / scale inhibitor compatibility test.

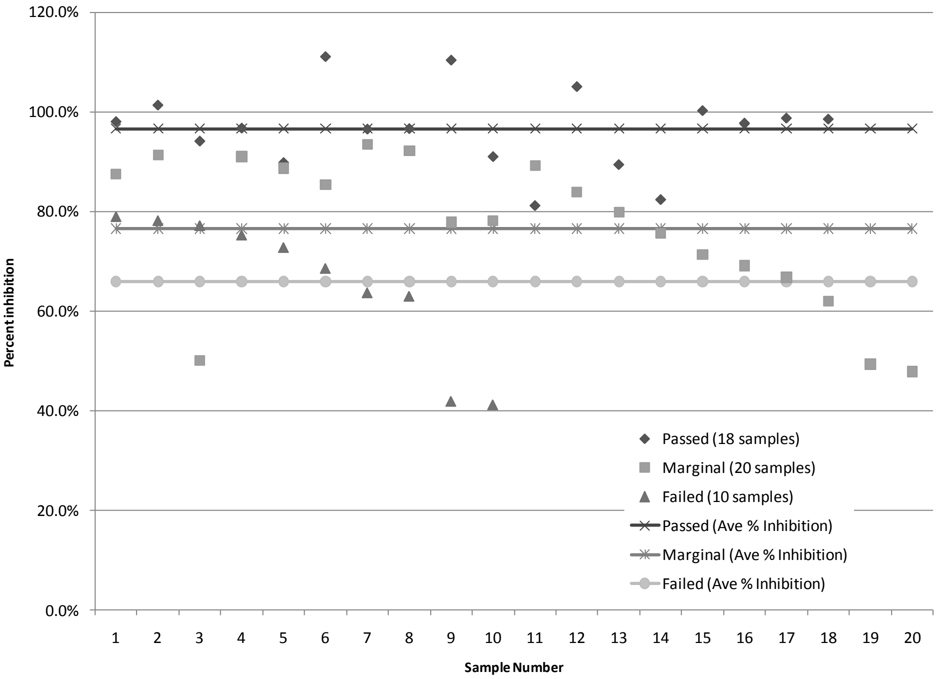


Figure 7 - Each data point represents one sample that underwent the scale stress test. Observations were made categorizing each sample as Passed, Marginal, or Failed. The percent inhibition was determined using atomic absorption spectroscopy. The graph is a comparison of visual observations vs. atomic absorption spectroscopy. The vertical axis denotes the percent inhibition. The horizontal axis represents the sample number.

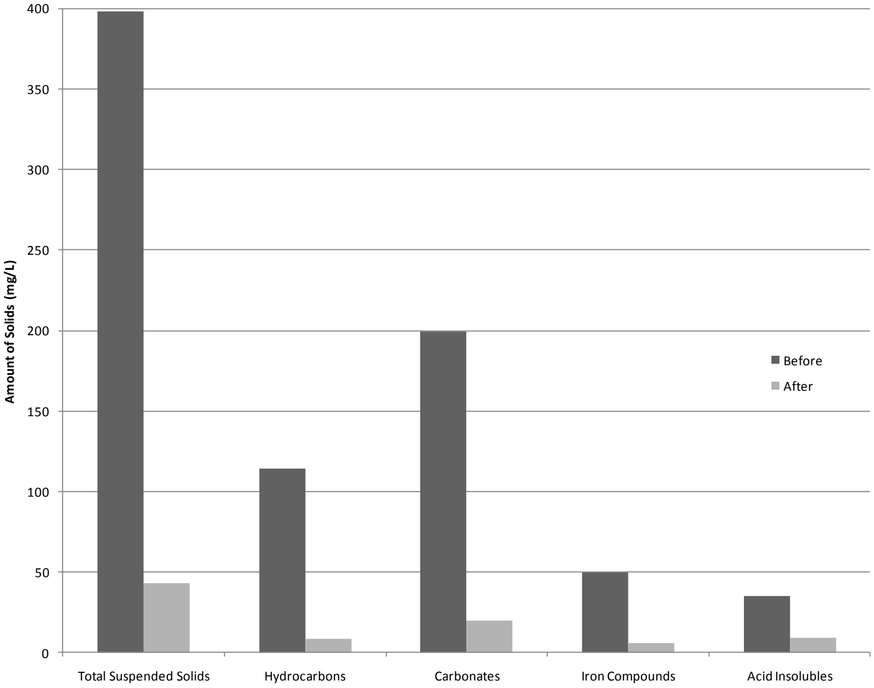


Figure 8 - Millipore filtration results before and after implementing the polymer scale inhibitor.

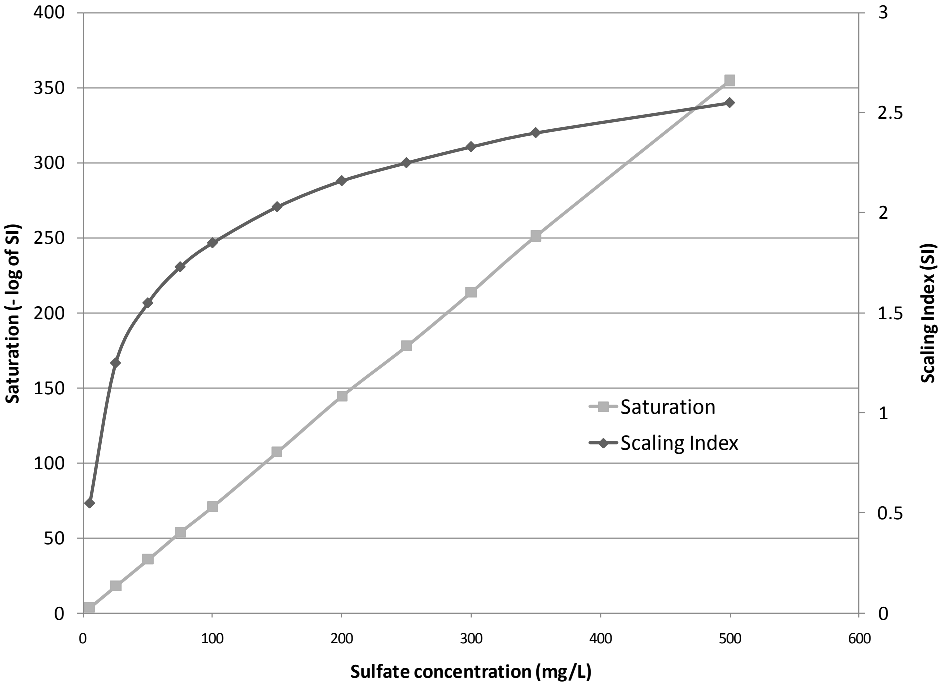


Figure 9 - ScaleSoftPitzer™ was used to model the change in the barium sulfate scaling index with the addition of sulfate using water analysis data from Table 3[4].

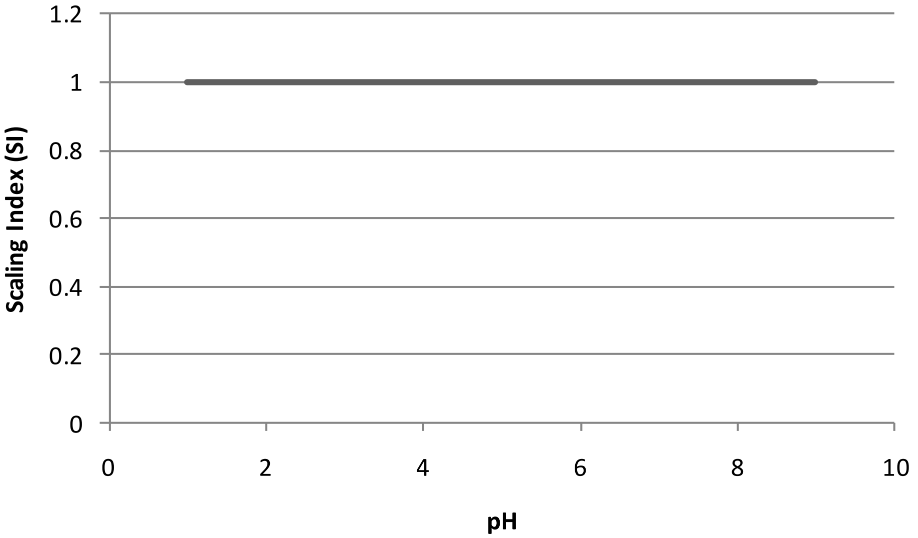


Figure 10 - Diagram describing the effect of pH in barium sulfate scaling tendencies using ScaleSoftPitzer™[4].

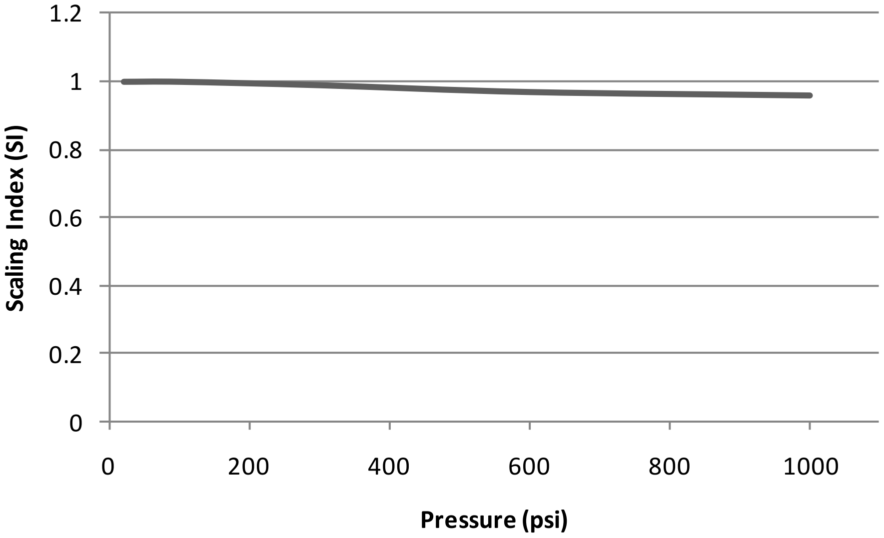


Figure 11 - Diagram describing the effect of pressure on barium sulfate scaling tendencies using ScaleSoftPitzer™[4].

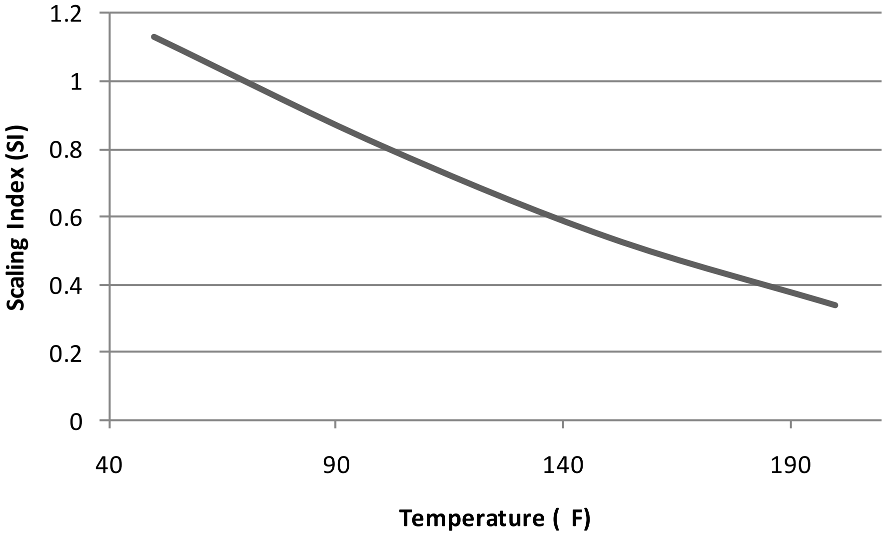


Figure 12 - Diagram describing effects of temperature on barium sulfate scaling tendencies using ScaleSoftPitzer™[4].