THE DEVELOPMENT AND IMPLEMENTATION OF A SCALE INHIBITOR FOR HIGH IRON SYSTEMS

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ABSTRACT

The control of mineral scales such as calcium carbonate, calcium sulfate, and barium sulfate are easily controlled with the use of the materials identified as phosphonates. Generally the phosphonate inhibitors are applied to the water stream at levels of 5 to 25 parts per million (ppm). If a significant amount of soluble iron (ferrous iron) is present in the water, the required amount of inhibitor is substantially increased or the inhibitor is rendered ineffective.

When presented with a project to treat a waterflood and produced water system where calcium carbonate and calcium sulfate scales were a definite possibility and the formation water contained 500 ppm soluble iron, inhibition of the scale formation was questionable.

BACKGROUND INFORMATION

Information supplied to the laboratory indicated the injection water was relatively light brine with a chloride level of approximately 4000 milligrams per liter (mg/l). Calcium was measured at 550 mg/l Ca. The sulfate value was 1270 mg/l sulfate (SO_4). (Table 1)

In contrast to the injection water, the formation water was heavy brine with 207,500 mg/l chloride and 16,500 mg/l calcium, (Ca). The dissolved sulfate value was reported to be 280 mg/l sulfate (SO_4). (Table 2)

It was anticipated that the mixture of the waters (injection water and formation water) at the time of break-thru at the producing wells, would be on the order of 10% injection water and 90% formation water. To access the severity these scaling tendencies which would result with the mixing of the two waters the Rice University ScaleSoftPitzer™ computer program was utilized. The program predicted the formation of calcium carbonate at both surface and injection well under various temperature and pressure conditions when the waters were mixed.

One of the criteria of the selected scale inhibitor(s) was that it must demonstrate good solubility in both the injection water and the formation water and all mixtures of the two waters.

Another requirement was that the inhibitors selected must provide inhibition at temperatures of 50 ^oC (122 ^oF) and 90 ^oC (195 ^oF).

Because of the high soluble iron content of the formation water, it was necessary to run all tests under anaerobic conditions. Initially the waters were purged with nitrogen in an effort to remove the dissolved oxygen in the sample. There was some doubt as to the oxygen level remaining after purging and it was decided to employ a purge of argon for more complete removal. This treatment resulted is a substantially oxygen free sample was employed for all of the test work.

The producer indicated initially it was anticipated the system would handle a mixture of 10% produced water – 90% injection water, it was decided to employ this mixture as the standard for all of the testing.

LABORATORY TESTING

To provide some mechanism for the elimination of the most incompatible materials bulk samples of the formation and source waters were prepared in accordance with the formulations given tables 1 and 2. For this series of evaluations, no soluble iron was added was added to the formation water, and no effort was made to remove the oxygen from the sample.

A total of twenty four (24) scale inhibitor bases were initially examined. These materials were generally classified as phosphonates, and polymers (acrylic acid polymers, maleic anhydride polymers, phosphophino carboxlyic acid polymers, etc).

Each material was prepared as a 30% solution of the inhibitor. No adjustment in the pH of the inhibitor was made, thus the pH of the inhibitor solution ranged from pH < 1.0 to pH 7.5.

One milliliter (1.0 ml) of the formation water and nine milliliters (9.0 mls) of the injection water were mixed in a one ounce French square bottle. One (1.0) milliliter of the inhibitor was added to the brine mixture, the bottle capped, thoroughly shaken, and placed in a 180 °F (82°C) oven overnight.

Samples thus prepared contained the equivalent of 10,000 parts per million of the scale inhibitor.

Those samples which showed no evidence of turbidity or solids formation after heating to 180 °F (82°C) were then evaluated in the tube blocking test mechanism.

Of the initial twenty four potential materials, only five (5) were soluble in the formation water and were carried forward for additional evaluation.

Initially, a screening of twenty-four (24) available scale inhibitors were evaluated at 1000 and 5000 ppm in the injection water. With the exception of one compound, all inhibitors were found to be acceptable.

The remaining twenty-three (23) inhibitors were then evaluated in the formation brine without the added iron. Of these twenty-three, three materials appeared to be acceptable.

To further define the effectiveness of the materials a series of static tests were initiated. In this series, 10 ppm of the inhibitor in question was placed in a four ounce French square bottle. Each bottle was flushed with a stream of argon to remove any oxygen. Under an atmosphere of argon, to each bottle 90 milliliters of the de-aerated injection water was then added. This was immediately followed by the addition of 10 milliliters of the de-aerated formation brine, which did not contain any added iron.

A second set of samples was prepared as before with the exception that 500 ppm soluble iron was added to the formation brine.

The samples were immediately tightly capped and place in a 195 ^{o}F (90 ^{o}C) oven overnight. At the end of approximately twelve (12) hours the bottles were removed and allowed to cool undisturbed.

The contents were then filtered under an-aerobic conditions through a weighed 0.45 μm filter. The weight of the precipitate was determined and the composition of the material was determined by X-ray fluorescence.

LABORATORY TEST RESULTS

Results of the static inhibitor evaluations are as follows:

Samples without added iron	Samples with 500 ppm iron added
Blank – no chemical	Blank - no chemical
Weight retained – 76 mg/liter	Weight retained - 79 mg/liter
Solids:	Solids:
Calcium – major	Iron – major
Manganese – major	Sulfur – major
Chlorine – trace	Sodium – trace
Sulfur – trace	Silica – trace

Inhibitor A - 10 ppm

Weight retained - 33 mg/l

Solids:
Sodium – major
Calcium – major
Manganese – major
Chlorine – minor
Silica – trace
Sulfur – trace
Phosphorus – trace

Inhibitor A – 10 ppm

Weight retained -115 mg/l

Solids:
Iron – major
Sodium – trace
Silica – trace
Calcium – trace
Chlorine – trace
Sulfur – trace

Inhibitor B - 10 ppm

Weight retained - 30 mg/l

Solids:
Sodium – major
Manganese - major
Sulfur – minor
Calcium – minor
Silica – trace

Inhibitor B – 10 ppm

Weight retained -104 mg/l

Solids:
Iron – major
Sodium – trace
Silica – trace
Sulfur – trace
Calcium – trace
Chlorine - trace

Inhibitor C - 10 ppm

Weight retained - 30 mg/l

Solids:
Sodium – major
Sulfur – major
Manganese – minor
Silica – trace
Calcium – trace
Chlorine – trace
Chlorine – trace

Inhibitor C – 10 ppm

Weight retained -101 mg/l

Solids:
Iron – major
Sulfur – major
Sodium – minor
Phosphorus – minor
Silica - minor
Phosphorus - minor

(Note: All inhibitors were adjusted to pH 4.0.)

Results of these tests indicated the primary precipitating salt was calcium, probably as calcium carbonate. The presence of manganese is plausible, since fifty (50) parts per million manganese was added to the formation water.

Inhibitors B and C each showed low amounts of calcium in the precipitate, indicating effective inhibition of the calcium ion.

The iron added samples showed essentially the same results except the major component of the deposit was iron, which was to be expected.

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TUBE BLOCKING TESTING

The next step in the evaluation process was to determine the effectiveness of each material using the tube-blocking test. Specifications for this test were as follows:

Test coil – stainless steel – 0.02” inside diameter (id) one meter in length

Pumps – a peristaltic pump was used to pump the injection water sample and an ISCO syringe pump was used for the formation water sample

Fluid flow – the injection water was pumped a t a rate of 9.0 milliliters per minute and the formation water was pumped at 1.0 milliliter per minute.

The two brines were injected into a mixing tee and thence to the test coil. A pressure transducer connected to a data logger collected the pressure on the test coil versus time.

Runs were made at temperatures of 122 ^{o}F (50^{o}C) and at 195 ^{o}F (90^{o}C)

Based on results of the tube blocking tests, inhibitor C appeared to be the better of three candidates, however, inhibitor C did not fully prevent pressure increases in the test as shown in figure 7.

Further modifications were made to the inhibitor and these resulted in a product which did perform as required and had all of the solubility characteristics necessary for an inhibitor. Performance of the modified inhibitor is illustrated in fig 8.

FIELD APPLICATION

Inhibitor C was commercialized and placed in service in the field. The product has been applied at the producing wells and is added down the casing of the well with a slipstream of water to assure the inhibitor reaches bottom. Since its initiation three yeas ago, no scaling problems have been encountered in the producing system.

Approximately one year ago, it was reported that the strainers in the crude stabilizer system began to show evidence of scale formation. A sample of the scale was obtained and returned to the laboratory for analysis. The material was identified as primarily calcium sulfate and was 86 to 93 % calcium sulfate ($CaSO_4$).

The stabilizer is a system for the reduction of some of the entrained gasses in the crude stream prior to the introduction of the crude to the pipeline.

Scale inhibitor was being injected into the inlet separators on Trains 1,2 and 3. Since the scale inhibitor partitions to the water phase in the HP three phase separators, very little to no scale inhibitor is carried through to the desalters. Any residual inhibitor going to the desalters is then further diluted by the uninhibited dilution water.

It was decided that a feed of forty (40) parts per million would be made to the water tank used for the desalting operation. This single chemical injection point would provide the treated water for the desalting operation.

This additional feed was sufficient to prevent any deposition and after a period of time the screens were re-inspected and the chemical feed rate was reduced to thirty (30) parts per million. This treatment level has been maintained for the past two years and the system has remained deposit free.

CONCLUSIONS

Although in many situations, the presence of dissolved iron is detrimental to the performance of some scale inhibitors, the proper combination of inhibitors and additives can minimize or eliminate this problem.

The inhibitor described in this paper has been in use for over three years and there has been no evidence of scale deposition in the system during that time.

ACKNOWLEDGMENTS

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Table 1
Injection Water Analysis

Ion	Concentration (milligrams per liter)
Sodium	2210
Calcium	550
Magnesium	140
Potassium	64
Chloride	3830
Sulfate	1270
Bicarbonate	180

Artificial formulation of the above

Compound	Concentration (mg/l)
$CaCl_2 \cdot 2H_2O$	3011
$MgCl_2 \cdot 6\ H_2O$	2018
KCl	1171
Na_2SO_4	122
$NaHCO_3$	248
NaCl	3916

Table 2
Formation Water Analysis

Ion	Concentration (milligrams per liter)
Sodium	94,400
Calcium	16,500
Magnesium	11,500
Potassium	4,600
Iron	500
Strontium	290
Barium	13
Chloride	207,500
Sulfate	280
Bicarbonate	180
Zinc	85
Manganese	75
Acetate	50
Boron	35
Lithium	14
Silicon	12

Artificial formulation of the above

Ion	Concentration (milligrams per liter)
$NaCl$	94400
$CaCl_2 \cdot 2H_2O$	16,500
$MgCl_2 \cdot 6\ H_2O$	11,500
KCl	4,600
$FeCl \cdot 2H_2O$	500
$SrCl_2 \cdot 6H_2O$	290
$BaCl_2 \cdot 6H_2O$	13
$NaCl$	207,500
Na_2SO_4	280
$NaHCO_3$	180
$ZnCl_2$	85
$MnCl \cdot 4H_2O$	75
$NaCH_3COO \cdot 3H_2O$	50
H_3BO_3	35
$LiCl$	14
$Na_2SiO_3 \cdot 5H_2O$	12

Table 3

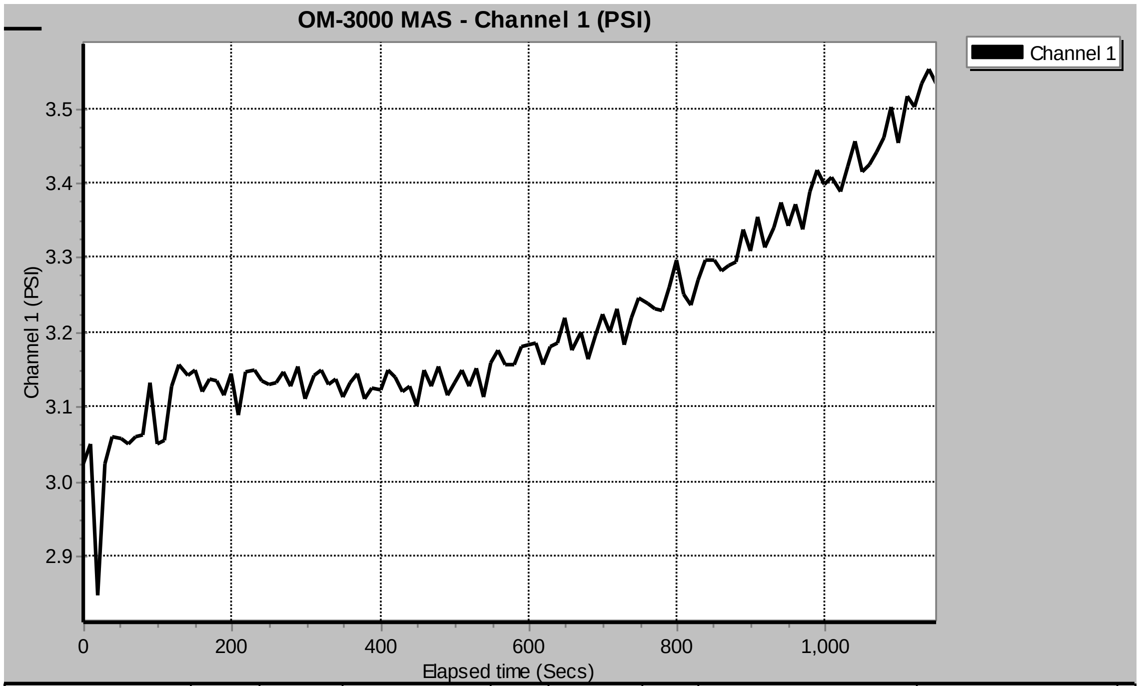
Analysis of Solids Taken from the Suction Strainers on Train1, 2,and 3 Crude Stabilizer

Calcium Sulfate ($CaSO_4$)	86 – 93%
Magnesium Sulfate ($MgSO_4$)	1 – 3 %
Strontium Sulfate ($Sr\ SO_4$)	0 – 2 %
Iron Oxide (Fe_3O_4)	2 – 4 %
Sodium Chloride (NaCl)	1 – 2 %
Sand	3 - 8 %

Figure 1

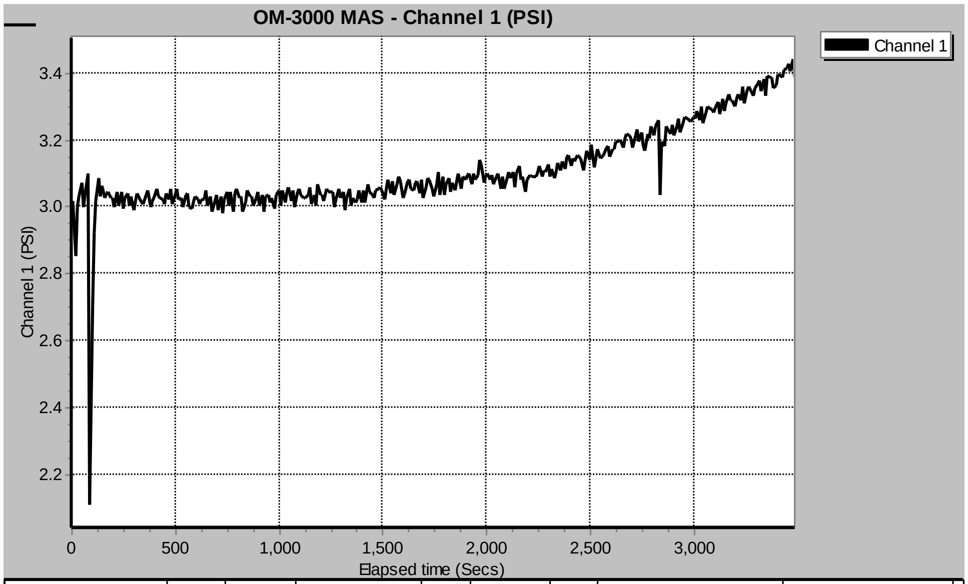
Train 1,2,3 Crude Stabilizer Tower Suction Strainer

Figure 3 - Train 1 Stabilizer Pump Strainer After
30 – 40 ppm Inhibitor C Scale Inhibitor Treatment



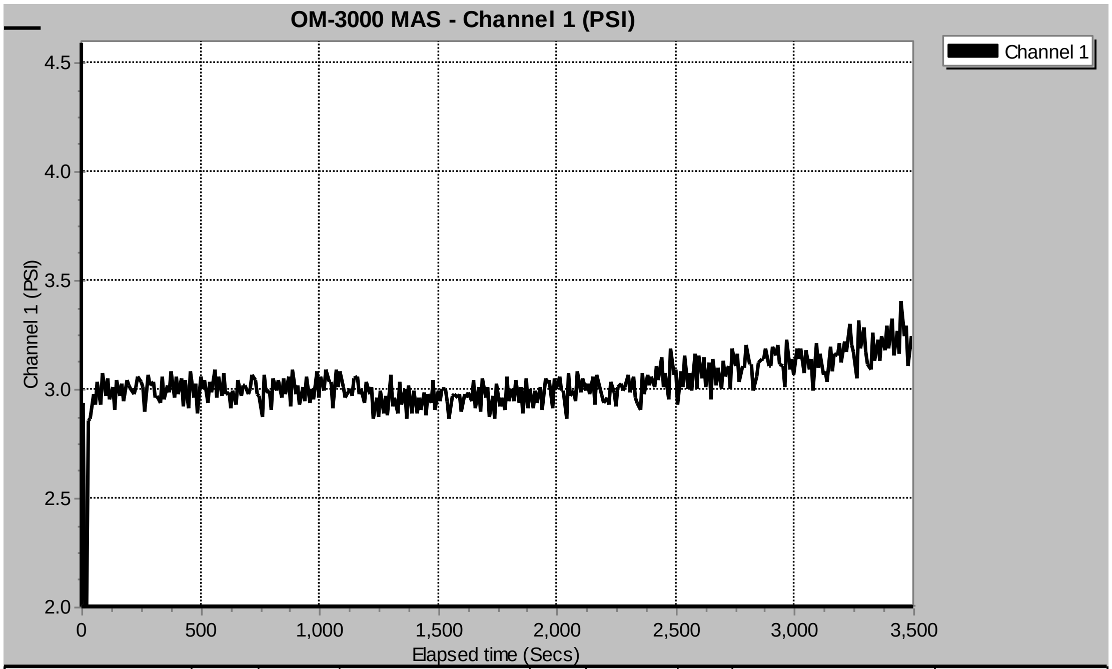
Company	Plot	Folder	Recording	Chan	Ch. Label	Type	Recording start	Recording size	R
BJ Chemical Services	■	Lab data	Project 20050377	1	Channel 1	PSI	28 Feb 2003 (1:33:08 pm)	116 samples at 10 Secs	

Figure 4 - Tube Blocking Test results with no Chemical



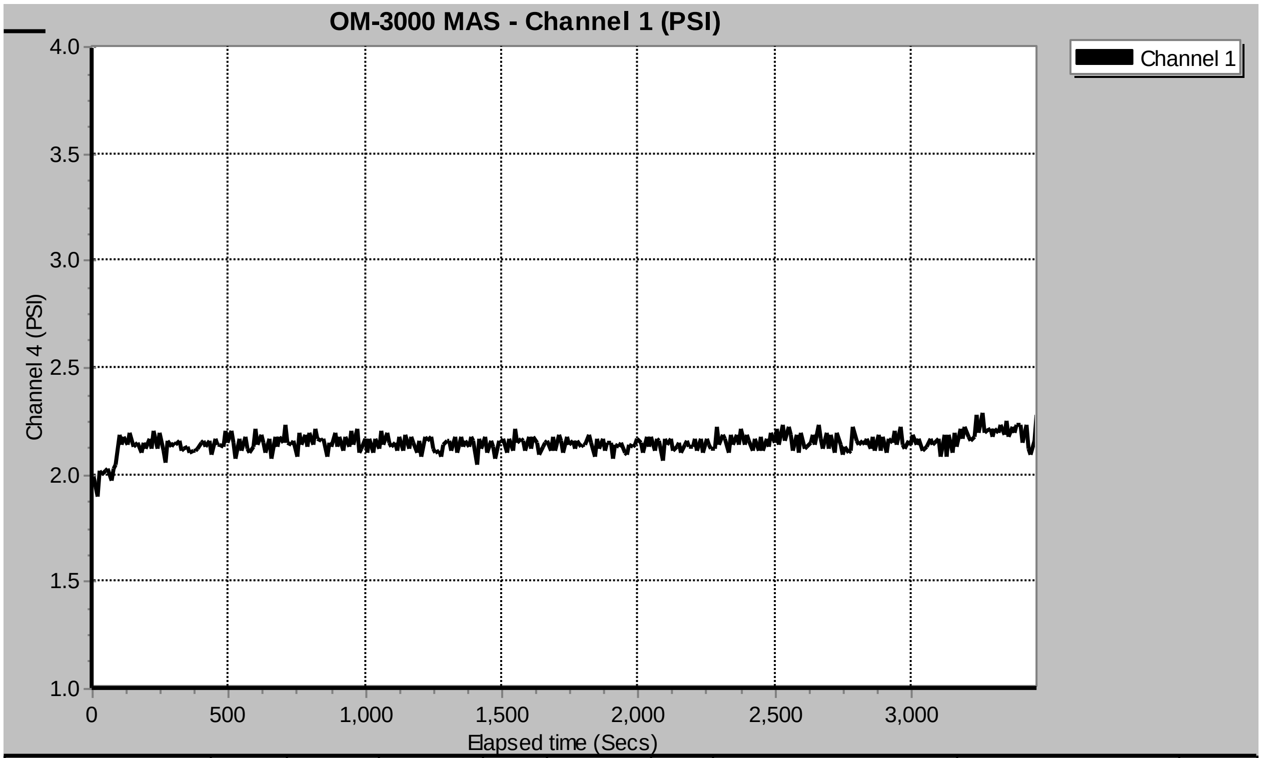
Company	Plot	Folder	Recording	Chan	Ch. Label	Type	Recording start	Recording size
BJ Uncihem Chemical	▬	Lab data	Project 20050377	1	Channel 1	PSI	28 Feb 2003 (2:45:43 pm)	350 samples at 10 Secs

Figure 5 - Tube Blocking Test Results with 5.0 Parts Per Million Inhibitor C



Company	Plot	Folder	Recording	Chan	Ch. Label	Type	Recording start	Recording size
BJ Uncihem Chemical	▬	Lab data	Project 20050377-7ppm	1	Channel 1	PSI	3 Mar 2003 (9:20:00 am)	351 samples at 10 Se

Figure 6 - Tube Blocking Test Results with 7.0 Parts Per Million Inhibitor C



Company	Plot	Folder	Recording	Chan	Ch. Label	Type	Recording start	Recording size	Remark
BJ Chemical Services	■	Lab data	Lab data	4	Channel 1	PSI	20 Mar 2002 (10:32:56 am)	347 samples at 10 Secs	

Figure 7 - Tube Blocking Test Results with 7.0 Parts Per Million Inhibitor C (modified)