Evaluation of Scale Inhibitors in Marcellus High-Iron Waters

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Summary

The Marcellus waters of Pennsylvania and West Virginia commonly contain elevated levels of calcium, barium, and iron. Theoretical analyses of these waters indicate a propensity toward the formation of calcium carbonate, barium sulfate, strontium sulfate, and iron-related scales. The high level of dissolved iron commonly present in the water adversely affects the ability of the scale inhibitor to inhibit calcium carbonate scale. In this study, the inhibition performance of two new chemicals and some commercial products was evaluated under static and dynamic test conditions using synthetic Marcellus waters at varying iron concentrations. It was shown that both new chemicals were able to control calcium carbonate scale effectively in the presence of dissolved iron up to 200 ppm, whereas the performance of polycarboxylic acid, amino tri(methylene phosphonic) acid, and carboxymethyl inulin dropped sharply even in the presence of small amounts of Fe^{2+} (5 ppm). The inclusion of iron-sequestering agents with these chemicals and the effect of iron upon calcium sulfate inhibition are also discussed in this paper.

Introduction

Mineral-scale formation is a problem for oil and gas operations that can result in the deterioration of assets, increased lifting costs, and lost production. Common mineral scales such as calcium carbonate, calcium sulfate, or barium sulfate can precipitate from produced water and create blockages in perforations, production tubulars, and equipment. The most common method of scale control is the use of low concentrations of specialty chemicals (inhibitors) that catalytically prevent the precipitation of solids. These chemical inhibitors are referred to as "threshold" inhibitors because they prevent scale formation at concentrations that are typically hundreds to thousands of times less than the concentration required with acid or chelate addition.

The Marcellus formation does not produce water naturally. The composition of the water recovered during production is a function of the fracture-water source and the chemical reaction that occurs with the shale. This reaction takes place during the fracturing process and through contact of the fracture water with the fracture face over time. The first water produced from the wells is described as flowback water and is characterized by gradually increasing total dissolved solids (TDS) over time. Eventually, the TDS reach plateaus. Significant but variable quantities of calcium, barium, strontium, and iron are present in the waters recovered from the wells. The amount of calcium present in the waters ranges from approximately 10 000 to 25 000 mg/L. The barium present will range from 3000 mg/L in West Virginia and southwestern Pennsylvania to 17 000 mg/L in northeastern Pennsylvania. Strontium commonly falls in the 3000- to 6000-mg/L range, but can run over 10 000 mg/L. Dissolved iron is present in the waters from approximately 50 to 300 mg/L. For one group of 80 Marcellus shale water samples, 43% reported sulfates of 0 mg/L, 15% were in the 1- to 10-mg/L range, 24% were from 11 to 20 mg/L, and 18% were from 21 to 79 mg/L.

Theoretical analyses of these waters indicate a propensity toward the formation of calcium carbonate, barium sulfate, strontium sulfate, and iron-related scales. To date, the scale deposits analyzed have comprised calcium carbonate, iron-related scales, and sodium chloride. The saturation indices calculated for barium sulfate scales in various parts of the play can be in the hundreds or thousands, thereby potentially overloading the scale inhibitor. At the same time, a high level of dissolved iron (200 ppm) commonly present in the water may be reducing the scale-inhibitor performance.

It has been well known for some time that the presence of soluble iron has an adverse effect upon the performance of conventional scale inhibitors against calcium carbonate scale, whereas inhibitors show effective control against barium sulfate scale in the presence of iron (Hill et al. 2000; Dyer and Graham 2000; Graham et al. 2003; Johnson et al. 2005; Kriel et al. 1994; Guan et al. 2009; Stoppelenburg and Yuan 2000). For example, Graham et al. (2003) reported that the addition of 10 ppm Fe^{2+} to test brine caused the observed minimum inhibitor concentrations (MICs) to increase more than 100-fold when tested against calcite scale using the common phosphonate scale inhibitor diethylenetriamine-penta (methylene phosphonic) acid (DTPMP). An increase in the performance of DTPMP on barium sulfate scale control in the presence of iron was observed by another group (Stoppelenburg and Yuan 2000) because anaerobic conditions were strictly maintained in a specially designed test apparatus.

The two principal test methods used in the industry for measuring the efficiency of scale inhibitors are the static bottle test and dynamic tube-blocking test. Dynamic tube-blocking tests are commonly used to evaluate the performance of scale inhibitors in the presence of iron because examination of the system in the presence of dissolved iron can be achieved more easily than in static tests (Dyer and Graham 2000). However, dynamic tests evaluate scale inhibitors under very short residence times (generally less than 10 seconds), whereas the residence times are longer in oilfield applications and may typically range from minutes to days. Moreover, a relatively small increase in residence time within a dynamic test system caused contradictory findings to be seen in previous studies. For instance, Dyer and Graham (2000) and Hill et al. (2000) recorded that calcium carbonate scale inhibition using poly (vinylsulfonate) (PVS) was less affected in the presence of low iron levels, whereas Graham et al. (2003) found that the MIC of PVS increased from 5 to 10 ppm to 50 ppm as 10 ppm iron was added. The authors concluded that the different findings on PVS arose from the longer residence time involved as a result of increasing the length of scaling coil from 1000 to 3000 mm. In this study, to conduct a balanced assessment, both static bottle tests and dynamic tube-blocking tests were performed to evaluate the performance of scale inhibitors in a typical Marcellus water **(Table 1).** The scaling

TABLE 1—SYNTHETIC MARCELLUS WATER COMPOSITION	
	Concentration (ppm)
Sodium	63,863
Calcium	16,200
Magnesium	1,200
Potassium	314
Barium	1,000
Strontium	500
Iron	0 to 200
Chloride	130,607
Bicarbonate*	1,050
pH	7.1

TABLE 2—COMPOSITION OF LOW-TDS WATER	
	Concentration (ppm)
Sodium	1,940
Calcium	600
Magnesium	125
Potassium	61.7
Barium	0
Iron	100
Strontium	8.08
Zinc	0
Chloride	3,744
Sulphate	1,170
Bicarbonate	60

potential of this brine can be expressed as saturation index (SI), which is defined as the logarithm of the ratio of scaling ion activity product to the thermodynamic solubility of a scale. At 65°C, the SI of calcium carbonate and iron carbonate scale (in the presence of 200 ppm iron) is 2.98 and 2.84, respectively, which indicates that the amount of precipitate of calcite and iron carbonate is approximately 790 and 410 mg/L, respectively, at equilibrium conditions. The Marcellus produced waters also contain significant amounts of barium, and almost any produced water with a detectable quantity of sulfates will present an SI indicating a potential for barium sulfate deposition, which will be discussed in our future work.

Methods. Two new phosphonate-based scale inhibitors were selected for this application. Johnson et al. (2005) found that aminophosphonate with an alcohol group or carboxylic acid group inhibited carbonate-scale formation in the presence of 200 ppm iron. Unfortunately, the structure of these chemicals was not disclosed. The phosphonate-based scale inhibitors used in this study were modified phosphonate compounds that do not contain an alcohol group or carboxylic acid group. Polycarboxylic acid (PAA), amino tri(methylene phosphonic) acid (ATMP), and carboxymethyl inulin (CMI) were chosen as representative common inhibitors for protection against calcium carbonate scale. Table 1 lists the composition of the synthetic Marcellus water used for static bottle inhibition tests.

Static Bottle Tests. Synthetic Marcellus waters were made and split into anionic-water (AW) and cationic-water (CW) components. Each of the AW and CW brines contained twice the concentration of the anionic and cationic salt, respectively, as well as the original concentration of sodium chloride. When the AW and CW brine were mixed at a 1:1 ratio, they produced a brine with the desired composition. The AW and CW brines were filtered twice through 0.45-μm membrane filters to minimize the amount of insoluble particles. These brines were then sparged continuously with a combination of 96%-oxygen-free N2 and 4% carbon dioxide (CO_2) to adjust the brine pH to approximately 7.1 and remove the dissolved oxygen. After flowing the CW brine with N2 and CO_2 for several hours, 50 ppm of ascorbic acid was added to function as an oxygen scavenger, followed by the addition of oxygen-sensitive Fe^{2+} salt.

The desired amount of inhibitor was added into each test cell using the 2 wt% dilutions. The pH of these inhibitor stock solutions was adjusted to 6.5 before use. Fifteen milliliters of anionic solution was added to a 1-ounce test cell, which was previously sparged with oxygen-free N2 to remove O2, followed by 15 mL of cationic solution. The mixing solution was capped immediately and stirred using a Teflon-coated magnetic stirring bar. The inhibition time was the time lapse between the start of mixing the anionic with the cationic solution and the first noticeable turbidity occurring in the solution measured by visual inspection through a laser beam. Because

it was difficult to prevent iron oxidation, and the effect of ferric iron has been debated in different studies (Johnson et al. 2005), all static bottle tests were conducted at room temperature (25°C) to minimize the in-situ oxidation of iron. No obvious iron oxidation was found within 90 minutes by using this testing procedure. The difference in inhibition efficiency between various scale inhibitors could also be examined within this time period.

Dynamic Tube-Blocking Tests. The dynamic tube-blocking tests were conducted in a strictly anaerobic environment. This was accomplished by continuously using a combination of oxygen-free N2 and CO_2 sparging of the fluids to bring the oxygen levels down to an acceptable level. Otherwise, the tests were conducted in accordance with the standard dynamic tube-blocking-test procedures. Because of the relatively modest scaling tendency of the Marcellus water used in the static bottle tests, dynamic tube-blocking tests were conducted using a more severe carbonate-scaling regime. Compared with the static bottle tests, a combination of 99% oxygen-free N2 and 1% CO_2 was used to adjust brine pH to approximately 7.7, and the bicarbonate concentration was increased from 1,050 to 1,200 ppm to increase the calcium carbonate scaling tendency in the test water. In addition, a 10-ft scaling coil was used in the dynamic tube-blocking tests, and the AW and CW brines were pumped separately at 2 mL/min each to further increase the residence times of the AW- and CW-brine mixture in the scaling coil.

The AW and CW brines were pumped into an oven through preheating coils, where they were heated to 65°C. The brines were then mixed in a Hastelloy C capillary tube. The mixing capillary coil had an ID of 0.75 mm. The residence time inside diameter the brine in the mixing coil was 20.35 seconds. The differential pressure was continuously measured across the mixing coil, and an increase in differential pressure was used as an indication of scale formation within the coil. The desired scale-inhibitor dosage rates were achieved by varying the ratio between the inhibitor-free AW and the inhibitor stock solution AW. The inhibitor concentration was reduced every 100 minutes, until the inhibitor failed to inhibit scale formation and the differential pressure had increased by 2.5 psi or more.

Separate dynamic tube-blocking tests were conducted to examine the impact of dissolved iron on calcium sulfate scale inhibition at 150°C. A synthetic low-TDS brine was used in this study **(Table 2)**. The synthetic AW and CW brines were sparged continuously with a combination of 92.5% oxygen-free N2 and 7.5% CO_2 to bring the oxygen levels down to an acceptable level and to adjust the brine pH to approximately 5.7, thereby minimizing the potential of carbonate-scale formation under test conditions. The inhibitor concentration was reduced every 150 minutes until the inhibitor failed to inhibit scale formation and the differential pressure had increased by 2.5 psi or more.

TABLE 3—COMPATIBILITY-TEST RESULTS AT ROOM TEMPERATURE (25°C)

Observation After 24 Hours

Inhibitor Conc. (ppm)	PAA	ATMP	CMI-1	CMI-2	RSI-1	RSI-2
25	Slight Haze	Slight Haze	Clear	Clear	Clear	Clear
50	Haze	Haze	Clear	Clear	Clear	Clear
100	Precipitate	Precipitate	Slight haze	Slight haze	Clear	Clear
150	Precipitate	Precipitate	Haze	Haze	Clear	Clear
200	Precipitate	Precipitate	Haze	Haze	Clear	Clear

TABLE 4—COMPATIBILITY-TEST RESULTS AT 65°C

Observation After 24 Hours

Inhibitor Conc. (ppm)	PAA	ATMP	CMI-1	CMI-2	RSI-1	RSI-2
15	Haze	Slight Haze	Clear	Clear	Clear	Clear
25	Precipitate	Precipitate	Slight Haze	Clear	Clear	Clear
50	Precipitate	Precipitate	Haze	Haze	Clear	Clear
100	Precipitate	Precipitate	Precipitate	Precipitate	Clear	Clear
200	Precipitate	Precipitate	Precipitate	Precipitate	Clear	Clear

TABLE 5—STATIC INHIBITION TESTS IN THE ABSENCE OF Fe^{2+}

Inhibition Time (mins)

Inhibitor Conc. (ppm)	PAA	ATMP	CMI-1	CMI-2	RSI-1	RSI-2
0	3.5	3.5	3.5	3.5	3.5	3.5
1.2	30	35	12	9	4	7
2.5	50	70	24	33	8	13
5	>80	>90	53	60	15	45
10			>80	>90	40	>120
25					>90	

TABLE 6—STATIC INHIBITION TESTS IN THE PRESENCE OF 5 ppm Fe^{2+}

Inhibition Time (mins)

Inhibitor Conc. (ppm)	PAA	ATMP	CMI-1	CMI-2	RSI-1	RSI -2
0	3.5	3.5	3.5	3.5	3.5	3.5
1.2	6.5	7.0	8	4	4	5.5
2.5	10	15	9	5	5.5	10
5	12	16	8.5	8.5	8.5	16
10	15	17	9.5	9	11.5	26
25			10.5	9	28	42
50			11	10	60	70

TABLE 7—STATIC INHIBITION TESTS IN THE PRESENCE OF 10 ppm Fe^{2+}

Inhibition Time (mins)

Inhibitor Conc. (ppm)	PAA	ATMP	CMI-1	CMI-2	RSI-1	RSI-2
0	3.5	3.5	3.5	3.5	3.5	3.5
1.2	5.5	7	4	4	4	4
2.5	6	8	4.5	4.5	6	8
5	7	9.5	5.5	4.5	7.5	14
10	7.5	10	6	6	9	22
25			7	6	24.5	36
50			7.5	6.5	45	62
75					>80	>80

TABLE 8—STATIC INHIBITION TESTS IN THE PRESENCE OF 25 ppm Fe^{2+}

Inhibitor Conc. (ppm)	Inhibition Time (mins)					
	PAA	ATMP	CMI-1	CMI-2	RSI-1	RSI-2
0	3.5	3.5	3.5	3.5	3.5	3.5
1.2	4.5	5	4	4	4	4
2.5	4.5	6	4.5	4.5	5.5	9
5	5.5	8	4.5	4.5	7	14
10	6.5	8.5	4.5	4.5	8	18
25			4.5	5.0	21.5	28
50			5.5	5.0	43	49
75					61	68
100					>80	>80

TABLE 9—STATIC INHIBITION TESTS IN THE PRESENCE OF 50 ppm Fe^{2+}

Inhibitor Conc. (ppm)	Inhibition time (mins)					
	PAA	ATMP	CMI-1	CMI-2	RSI-1	RSI-2
0	3.5	3.5	3.5	3.5	3.5	3.5
2.5	4.5	5.0	4.0	4.0	5.0	5
5	5	5.5	4.0	4.0	6.5	9
10	5.5	6.5	4.0	4.0	8.5	12
25			4.5	4.5	18.5	19
50			4.5	5.0	38	40
75					46	58
100					70	>80

Experimental Results and Discussions

Static Compatibility Tests. The Marcellus water used contained a high calcium concentration (16,200 ppm), which may lead to incompatibility problems when exposed to high inhibitor concentrations at elevated temperatures. These incompatibilities may cause the formation of a low-solubility calcium-inhibitor precipitate, and thus reduce the effective concentration of the inhibitor in the brine. Therefore, a static compatibility test was conducted first to determine the upper limit of the scale-inhibitor concentration selected for static-inhibition testing. In this compatibility test, the pH of the inhibitor stock solution was adjusted to 6.5, and the anionic scaling ion (bicarbonate) was not added to the synthetic solution to avoid incompatibilities caused by the formation of scale deposits. Because Ca^{2+}, Mg^{2+}, Ba^{2+}, and Sr^{2+} were the predominant divalent cationic ions in this water and it was difficult to prevent iron oxidation at high temperatures during prolonged testing, iron was omitted from these experiments. The results were summarized in **Tables 3 and 4,** with inhibitor concentrations quoted in this study on the basis of the active inhibitor concentration. The test results indicated that PAA and ATMP were poorly soluble in Marcellus water, whereas the modified phosphonate scale inhibitors RSI-1 and RSI-2 were very compatible with the high-TDS brine. The Marcellus water tolerated 200 ppm or more of active RSI-1 and RSI-2 at 65°C.

Static Bottle Tests. Static bottle tests were first conducted to evaluate the inhibition performance of the selected chemicals in the absence of iron **(Table 5).** The results showed that PAA and ATMP were the most effective inhibitors against calcium carbonate scale, which was consistent with previous observations (He et al. 1999). Approximately 2.5 ppm of ATMP offered more than 1 hour of protection time, whereas 10 ppm of RSI-1 provided 40 minutes of protection time. However, a significant change in the inhibition efficiency of PAA and ATMP was observed as 5 ppm of Fe^{2+} was added to the brine **(Table 6).** At 5 ppm ATMP, the inhibition time decreased dramatically from more than 90 minutes to 16 minutes in the presence of 5 ppm iron. Increasing the ATMP concentration from 5 to 10 ppm only had a negligible effect upon inhibition time. The presence of 5 ppm of iron also significantly decreased the performance of CMI-1 and CMI-2 (CMI from different sources). Fifty parts per million of CMI-2 offered only 10 minutes of inhibition time in the presence of 5 ppm iron, whereas the inhibition time of 10 ppm CMI-2 was approximately 90 minutes in the absence of iron. The presence of 5 ppm of iron also had an adverse effect upon the performance of the modified phosphonate inhibitors RSI-1 and RSI-2. However, this effect was moderate, and 50 ppm RSI-2 still prevented the formation of calcium carbonate scale for 1 hour in the presence of 5 ppm iron.

Tables 7 through 11 list the performance of selected scale inhibitors in the presence of various Fe^{2+} concentrations. The efficiency of all scale inhibitors decreased as Fe^{2+} concentration increased. The test results showed that PAA, ATMP, and CMI did not work in the presence Fe^{2+} at 50 ppm or more. However, the presence of Fe^{2+} showed much less affect upon the performance of RSI-1 and RSI-2, and this reduced response was offset by increasing the inhibitor concentration in the brine. Tables 10 and 11 showed that 100 ppm of RSI-2 was able to prevent the formation of scale for 1 hour even in the presence of 100 to 200 ppm Fe^{2+} in the Marcellus water. It seems that increasing the dosage of the inhibitor provided only a negligible improvement upon the inhibition efficiency of CMI in the presence of Fe^{2+} (greater than 25 ppm). It was difficult to add 20 ppm or more of PAA or ATMP into the brine because of the poor compatibility of these chemicals.

The dramatic reduction in inhibition performance for certain scale inhibitors in the presence of iron had been ascribed to the formation of insoluble Fe-inhibitor complexes [i.e., physical in-

TABLE 10—STATIC INHIBITION TESTS IN THE PRESENCE OF 100 ppm Fe^{2+}

Inhibitor Conc. (ppm)	Inhibition Time (mins)					
	PAA	ATMP	CMI-1	CMI-2	RSI-1	RSI-2
0	3.5	3.5	3.5	3.5	3.5	3.5
2.5	3.0	3.5	3.5	3.5	5	5
5	3.5	3.5	3.5	3.5	5.5	6.5
10	3.5	4.0	3.5	3.5	6.5	8
25			3.5	3.5	13	15
50			4.0	4.0	32.5	33
75					53	54
100					65	>70

TABLE 11—STATIC INHIBITION TESTS IN THE PRESENCE OF 200 ppm Fe^{2+}

Inhibitor Conc. (ppm)	Inhibition Time (mins)					
	PAA	ATMP	CMI-1	CMI-2	RSI-1	RSI-2
0	3.5	3.5	3.5	3.5	3.5	3.5
2.5	3.0	3.5	3.0	3.5	5	4.5
5	3.5	3.5	3.5	3.5	5.5	5.5
10	3.5	4.0	3.5	3.5	6.5	7.5
25			3.5	3.5	11.5	13
50			4.0	4.0	21.5	27
75					30.5	43
100					51	64

TABLE 12—EFFECT OF CITRATE ADDITION ON THE INHIBITION PERFORMANCE OF RSI-1 AND RSI-2 IN THE PRESENCE OF 200 ppm Fe^{2+}

Inhibitor Conc. (ppm)	Citrate Conc. (ppm)	Inhibition Time (mins)	
		RSI-1	RSI-2
0	0	3.5	3.5
10	5	16.5	10
20	10	27	18
30	15	39	43
50	25	65	74

compatibility (Johnson et al. 2005)]. However, there are only a few publications in the literature that describe the interaction of common scale inhibitors with Fe^{2+}. Kan et al. (2008) reported that the alkaline earth cations are classified as Pearson hard cations, which form strong ionic bonds with Pearson hard bases common in natural brines and inhibitors (e.g., OH^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, $H_nPO_4^{n-3}$, and carboxylates). Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} are classified as borderline hard and soft acids, and their bonding shows increasing covalency with soft bases such as the amine group in the aminophosphonates. The metal-ligand complex stabilities increase in the order of Ca<Mn<Fe<Co<Ni<Cu, and this order is often referred to as the Irving-Williams order. The stability constant of ferrous carboxylate is more than two orders of magnitude higher than that of the corresponding Ca complex. Furthermore, the stability constants for the iron ion with aminomethylphosphonate, ATMP, and ethylenediamine tetra (methylene phosphonate) are much higher than that for alkaline-earth-metal ions. The work of another group (Kriel et al. 1994) also indicated that Fe^{2+} had a larger stability constant than either calcium or magnesium for 1-hydroxy ethylidene-1,1-diphosphonic acid, a common scale inhibitor. From the preceding study results, one may conclude that the strong interaction between aminophosphonate and carboxylate with Fe^{2+} may affect the inhibition properties of certain inhibitors.

As listed in Table 5, 5 ppm of ATMP or PAA was able to prevent the formation of calcium carbonate scale effectively in the absence of iron, even though the available active concentration of these inhibitors was limited by the formation of insoluble Ca-inhibitor complexes. Although the Fe^{2+}/ATMP salts were very insoluble in brine, there was no evidence showing that ATMP and Fe^{2+} may form insoluble complexes using a low dosage (less than 10 ppm) at room temperature (Friedfeld et al. 1998). However, Table 6 shows the dramatic reduction in performance of ATMP and PAA in the presence of 5 ppm Fe^{2+}, which suggests that the formation of soluble Fe-inhibitor complexes is a predominant factor in the observed reduction of performance under these conditions. Although CMI is more soluble than ATMP and PPCA in Marcellus water, its interaction with Fe^{2+} is largely unknown. Increasing the dosage from 5 to 50 ppm had little or no effect on the performance of CMI in the presence of 5 ppm Fe^{2+}, which may indicate that Fe-CMI tends to form strong complexes in the brine, and thus reduces the chemical activity necessary to achieve inhibition performance. The stability constants of the complexes formed by Fe^{2+} and the modified phosphonate inhibitors are also not available. Because RSI-1 and RSI-2 are much more soluble than ATMP and PAA in the Marcellus water, it is reasonable to expect that the stability constants of Fe-RSI are lower than those of the Fe-ATMP or Fe-PAA complexes. The reduc-
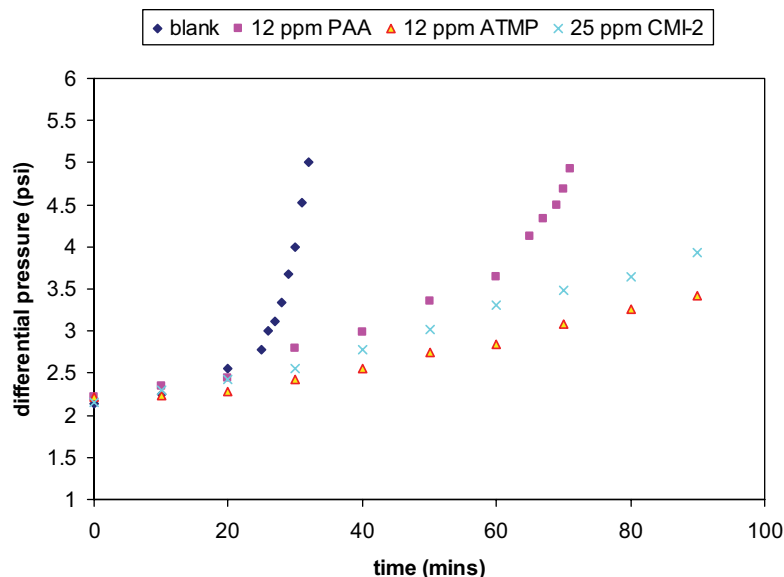
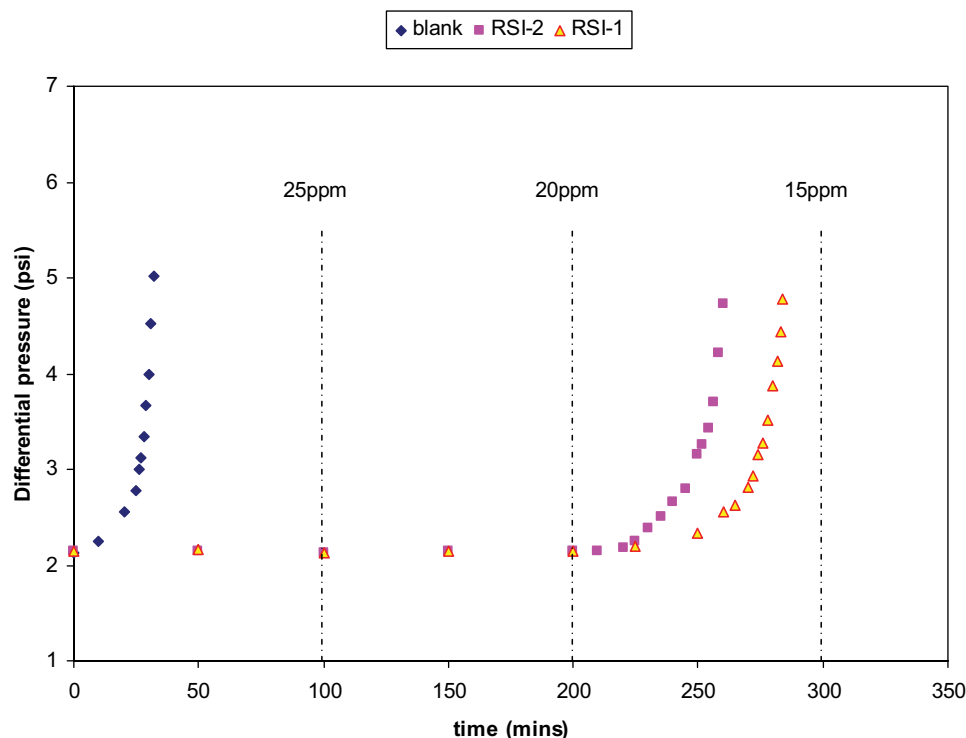Fig. 1—The performance of PAA, ATMP, and CMI-2 in the dynamic tube-blocking test in the presence of 200 ppm Fe^{2+}.

Fig. 2—The performance of RSI-1 and RSI-2 in the dynamic tube-blocking test in the presence of 200 ppm Fe^{2+}.

tion of chemical activity because of the formation of an Fe-inhibitor complex could be offset partially by increasing inhibitor dosage.

The Effect of Adding Fe-Sequestering Agent (Citrate). Citrate is used widely as an iron-sequestering agent in the oil field. In addition to the formation of soluble Fe-citrate complexes, it was reported recently (Yean et al. 2008) that citrate is able to act as a kinetic inhibitor for ferrous carbonate scale control. The effect of citrate on the performance of modified phosphonate inhibitors against calcium carbonate scale was also observed in the presence of 200 ppm Fe^{2+} in this study. As shown in **Table 12,** adding citrate improved the inhibition efficiency of RSI-1 and RSI-2 significantly. It can be seen from Table 11 that RSI-1 alone provided approximately 21.5

minutes of inhibition time at 50 ppm, whereas the inhibition time had increased to 65 minutes when 25 ppm of citrate was added to the solution. The addition of citrate had little or no affect upon the pH of the solution because the pH of the citrate stock solution was adjusted to 6.5 before use. It is well established that EDTA and citrate will complex with other cations such as calcium and magnesium ions present in the solution before they complex with iron (Raju et al. 2003). Even though the entire citrate forms complexes with the iron, 25 ppm of citrate can scavenge only approximately 8 ppm of iron from this solution. Therefore, reducing Fe^{2+} activity in the solution by formation of Fe-citrate complexes is not the main factor contributing to enhanced inhibition performance. A possible explanation is that the presence of citrate could prevent the forma-
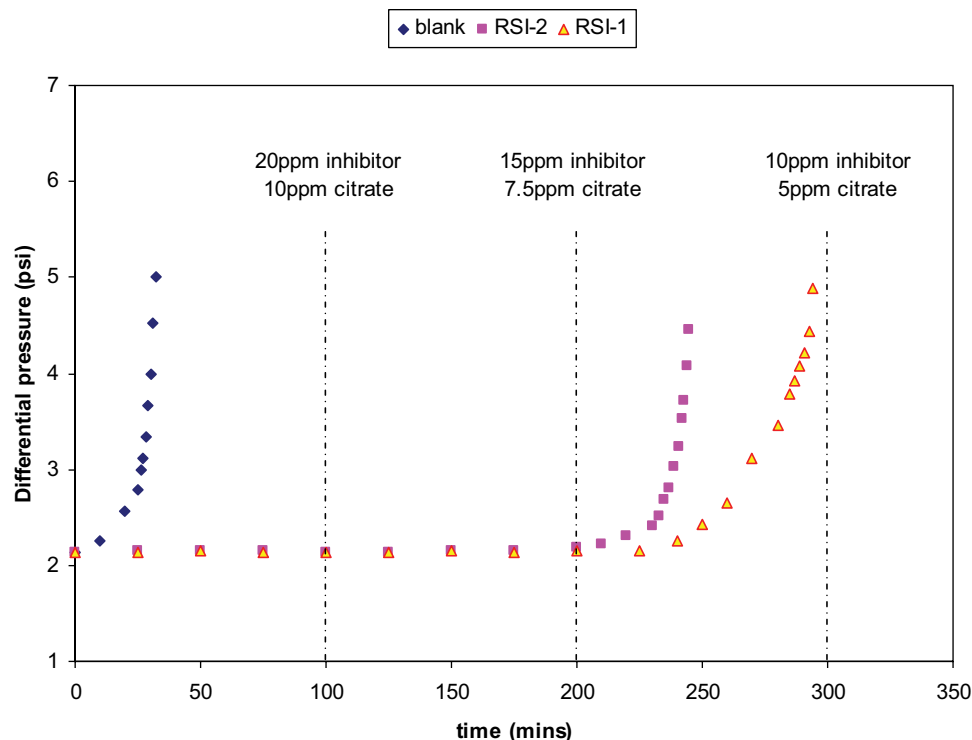
Fig. 3—The effect of citrate addition on the performance of RSI-1 and RSI-2 in the dynamic tube-blocking test in the presence of 200 ppm Fe²⁺.

tion of seed particles of iron carbonate, which may provide possible nuclei growth sites for calcite scale in the brine.

Dynamic Tube-Blocking Tests. To investigate calcium carbonate scale inhibition in the presence of iron under the downhole conditions with Marcellus water, dynamic tube-blocking tests were conducted at 65°C and 600 psi in a strictly controlled anaerobic system. **Fig. 1** shows the inhibition performance of 12 ppm PAA, ATMP, and 25 ppm CMI-2 against carbonate scale in the presence of iron. Under these conditions, a blank scaling time of approximately 32 minutes was recorded, whereas 12 ppm PAA failed this test after 75 minutes. A steady increase in differential pressure was recorded as 12 ppm ATMP or 25 ppm CMI-2 was examined under these conditions. The performance of these inhibitors tended to decline as dosages were increased because of the formation of insoluble Ca or Fe-inhibitor complexes. It should be noted that PAA, ATMP, and CMI showed no inhibition in the presence of 200 ppm iron in the static bottle inhibition tests, whereas ATMP and CMI were able to mildly prolong scaling time under the dynamic tests, even though the dynamic tests were conducted using a more severe carbonate-scaling regime than that for the static tests. This may be attributed to the relatively short residence time (20.35 seconds) within the scaling coil, as cationic and anionic brines were mixed under dynamic test conditions. Therefore, in order to obtain a comprehensive assessment, both static and dynamic tests should be conducted to evaluate certain inhibitors, if possible. As expected, RSI-1 and RSI-2 (**Figs. 2 and 3**) were able to prevent tube blocking when the inhibitor concentrations were above 20 ppm in the presence of 200 ppm iron. The tube blocking was prevented for more than 100 minutes when 15 ppm modified phosphonate inhibitors were combined with 7.5 ppm citrate.

The impact of dissolved iron on the performance of scale inhibitors under calcium carbonate or barium sulfate scaling conditions has been investigated by various groups over several decades. However, the effect of iron on the inhibition efficiency under calcium sulfate scaling conditions has not been reported. In this study, the performance of hexamethylenediamine tetra (methylene phosphonic acid) (HDTMP) and bishexamethylenediamine penta (methylene phosphonic acid) (BHPMP), reportedly the most effective chemicals for anhydrite scale control (Fan et al. 2010), were examined in the presence or absence of iron at 150°C along with RSI-1 and RSI-2 (**Figs. 4 and 5**). The test results indicated that all of the selected chemicals were able to offer complete inhibition at a 5 ppm concentration in the absence of iron, consistent with previous observations (Fan et al. 2010). As shown in Fig. 5, the performance of all the inhibitors tested was reduced when 100 ppm Fe²⁺ was added. Twenty-four parts per million of HDTMP or BHPMP failed to prevent tube blocking in the presence of iron, whereas the performance of RSI-1 and RSI-2 was less affected under these conditions. A lack of differential-pressure buildup was observed across the scaling coil when the concentration of RSI-2 was 16 to 20 ppm. When citrate was added to the test brine containing the modified phosphonate inhibitors, coil pressure buildup occurred at low inhibitor concentrations in a manner similar to that observed with carbonate-scale inhibition. It can be seen from **Fig. 6** that RSI-2 appears to provide nearly complete inhibition at 12 ppm in the presence of citrate, whereas BHPMP and HDTMP still failed at 24 ppm when combined with citrate.

Conclusions
Under calcium carbonate scaling conditions, a reduction in the performance of the selected inhibitors was observed in the presence of dissolved iron under both static bottle and dynamic tube-blocking tests. However, relatively small reductions in performance of the two new modified phosphonate inhibitors were recorded under test conditions.

Similarly, BHPMP and HDTMP completely failed to control calcium sulfate scale buildup in the presence of 100 ppm Fe²⁺, whereas the new modified phosphonate products provided effective inhibition at a moderately enhanced MIC.

It is evident that the inhibition efficiency of RSI-1 and RSI-2 is enhanced through the addition of citrate. The mechanism of the
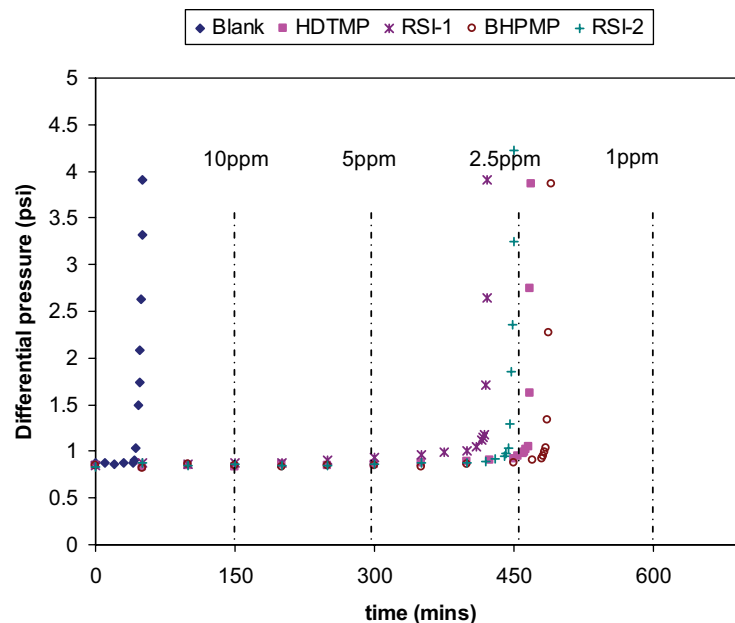
Fig. 4—The performance of selected inhibitors in the dynamic tube-blocking tests in the absence of Fe^{2+}.
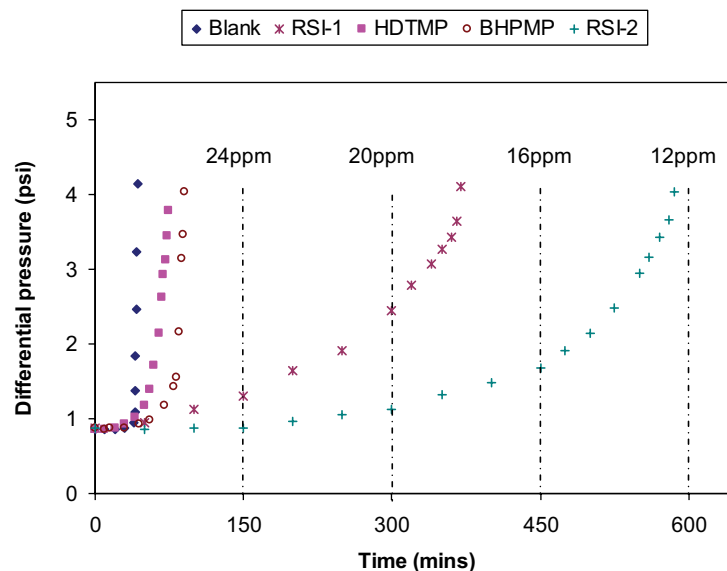

Fig. 5—The performance of selected inhibitors in the dynamic tube-blocking tests in the presence of 100 ppm Fe^{2+}.

synergistic effect of citrate with the modified phosphonate inhibitors remains largely unknown.

This paper identified the detrimental effects that minimal quantities of dissolved iron may have upon the performance of scale inhibitors applied in high-TDS waters such as the Marcellus. As a result of this study, new products were developed that provide protection against calcium carbonate and iron carbonate scales in this environment. Further work is planned to adsorb these new products onto inert, proppant-sized, solid particles that can be applied in conjunction with a fracture treatment. Combining these treatments will save the operator time and possibly expense, as well as extend scale-inhibition lifetime.

Acknowledgments

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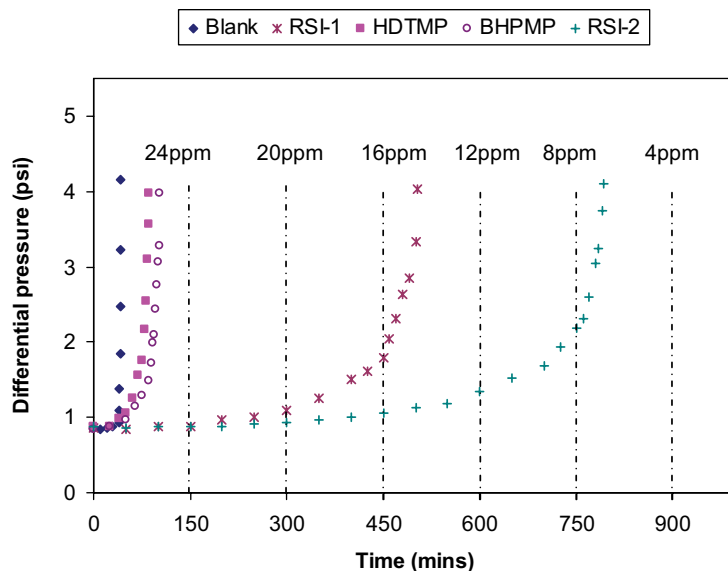
Fig. 6—The effect of citrate addition on the performance of selected inhibitors in the dynamic tube-blocking test in the presence of 100 ppm Fe^{2+} (inhibitor/citrate=2 wt/wt).

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