CaCO₃ scale prevention by additives in the presence of heavy metal ions

Q. Wang,* H. AlSaiari, F. AlDawood and M. AlDossary

Saudi Aramco, Research and Development Center, Dhahran, 31311, Saudi Arabia *E-mail: <u>giwei.wang@aramco.com</u>

Abstract

Formation of calcium carbonate (CaCO₃) deposition is a common problem during hydrocarbon production process. Effective scale management is important to maintain field productivity and profitability. Use of threshold scale inhibitor has been the most cost effective approach to control CaCO₃ deposition. The performance of scale inhibitors is determined by many factors such as calcium and bicarbonate concentrations, pH, temperature, suspended solids. This article presents the influences of three heavy metal ions, Cu^{2+} , Ni^{2+} , and Zn^{2+} , on the performance of phosphonate and polymeric inhibitors against CaCO₃ precipitation and deposition in synthetic oilfield brine. It is shown that even at 2 to 5 mg/L, heavy metal ions can have a significant impact on phosphonate inhibitors. The inhibition efficiency of tri-phosphonate is improved by Cu²⁺ ions but reduced by Zn²⁺ ions, and the performance of penta-phosphonate is enhanced by Cu²⁺ and Zn²⁺ ions and deteriorated by Ni²⁺ ions. Polymeric inhibitor is less affected by these heavy metal ions and no antagonistic effect is observed. The results presented herein are important in the development of cost-effective CaCO₃ prevention programs and development of new mitigation methods.

Keywords: oilfield scale, calcium carbonate, scale inhibitor, heavy metal ions.

Received: October 28, 2015. Published: December 22, 2015. doi: <u>10.17675/2305-6894-2016-5-1-2</u>

Introduction

The formation of calcium carbonate (CaCO₃) precipitates is a persistent problem in many industrial systems using or processing water, such as boiler, cooling tower, heat exchange, desalination membrane, and oil and gas production facility [1-3]. The deposition of such precipitates on equipment surface, often referred as fouling or scaling, can have a significant impact on the operation of these units, ranging from reduced process efficiency, to increased maintenance cost and total system shutdown. CaCO₃ scaling occurs when water becomes supersaturated, *i.e.*, the product of ion activities, $[Ca^{2+}] \times [CO_3^{2-}]$, exceeds the solubility product (K_{sp}) of CaCO₃ mineral. This could be achieved by changes in water composition or physical conditions. Water evaporation in open cooling system can raise dissolved ion concentrations above solubility limit. Temperature increase in water heater can reduce solubility below scaling ion concentrations. In oilfield operations, CaCO₃ precipitation is largely resulted from pressure drop. As the produced water flowing from

reservoir to wellhead and then to surface processing facilities, pressure is continuously decreased. Dissolved carbon dioxide (CO₂) gas evolves from the water phase to the gas phase under reduced pressure. Then part of the bicarbonate ions (HCO_3^-) converts into carbonate ions (CO_3^{2-}):

$$2 \operatorname{HCO}_{3}^{-} \to \operatorname{CO}_{3}^{2-} + \operatorname{H}_{2}\operatorname{O} + \operatorname{CO}_{2(\operatorname{gas})} \uparrow$$
(1)

Once the ion activities product of calcium and carbonate surpasses K_{sp} , the carbonate ions react readily with dissolved calcium to initiate the scaling process, as expressed by the following equation:

$$2 \operatorname{HCO}_{3}^{-} + \operatorname{Ca}^{2^{+}} \to \operatorname{CaCO}_{3(\operatorname{scale})} \downarrow + \operatorname{H}_{2}\operatorname{O} + \operatorname{CO}_{2(\operatorname{gas})} \uparrow$$
(2)

The use of scale inhibitor is a common practice in industry and often the most cost effective strategy for scale mitigation. With appropriate inhibitor type, CaCO₃ scale can be prevented with very low concentrations of inhibitor product, even at ppm (parts per million) levels. The performance of scale inhibitor is affected by many factors, such as scaling ion concentrations, pH value, total dissolved solids, temperature, and the presence of suspended solids and other treatment chemicals [4, 5]. Small amounts of heavy metal ions, such as ferrous and ferric ions, can also change the efficiency of scale inhibitor [6, 7]. Besides iron, other heavy metal ions also often exist in water naturally [8, 9]. They come from the partial dissolution of minerals in reservoir rocks by aquifer and connate water over geological time. Such reaction can yield high concentrations in oilfield brine under high pressure and high temperature conditions [10, 11]. In addition, heavy metal ions can also be added intentionally as a part of chemical treatment programs. In cooling water treatment, Zn²⁺ is an important component for the synergistic effect with other corrosion inhibitors to provide good protection to carbon steel [12]. Moreover, heavy metal ions have been suggested as additive to improve scale inhibitor squeeze treatment of oil producing wells [13].

Scale inhibitor squeeze treatment involves the injection of a large quantity of diluted scale inhibitor and other fluids into reservoir [1]. Part of the injected scale inhibitor is retained by reservoir rocks via adsorption and/or precipitation reactions. When production is resumed, the retained scale inhibitor is slowly released into the produced water, via desorption and/or dissolution mechanism, at concentration above a threshold value which is sufficient to prevent scale formation. Once the inhibitor concentration falls below this threshold value, the squeeze life is reached and a new treatment will be required. The squeeze life is determined by the retention/release behavior of scale inhibitor and its inhibition efficiency toward the specific scale. Apparently, long squeeze life would be expected if the majority of injected scale inhibitor is retained by reservoir and if the scale formation is inhibited by inhibitor with low threshold value. Different approaches have been suggested. Adding calcium ions into the treatment fluid has been applied to improve the scale inhibitor retention [14, 15]. Recent laboratory studies demonstrated that some

heavy metal ions were more effective than Ca^{2+} ions by forming low solubility precipitates with injected scale inhibitors [13, 16]. The squeeze life can be further prolonged if the added metal ions can improve the scale inhibitor performance. On the other hand, the treatment life may not be increased, or even be shortened, if the added metal ion deteriorates the inhibitor performance.

The negative impact of Fe^{2+} ions on scale inhibitor performance was well documented [17, 18]. In contrast, Zn^{2+} ions showed synergistic effect to barium sulfate scale inhibition [16, 19]. The influence of heavy metal ions, other than Fe^{2+} ions, on CaCO₃ scale inhibitors have not yet been studied. Such knowledge is imperative for the selection of appropriate scale inhibitor product and the development of cost-effective treatment programs. The objective of this work is to study the impact of three heavy metal ions, Cu^{2+} , Ni^{2+} , and Zn^{2+} , on the performance of CaCO₃ scale inhibitors. Evaluation tests were performed with static precipitation and dynamic deposition methods to examine the different aspects of inhibition behaviors.

Materials and Methods

Test Brine and Scale Inhibitor

Synthetic brine was used in all tests. Brine composition used in this study was based on the oilfield water produced from a shallow limestone reservoir. It contained 12820 mg/L sodium, 539 mg/L potassium, 2752 mg/L calcium, 1052 mg/L magnesium, 83 mg/L strontium, 1254 mg/L sulfate, 500 mg/L bicarbonate, and 27000 mg/L chloride. Synthetic brines were prepared with deionized water (18 m Ω ·cm) and reagent grade chemicals: sodium chloride (Fisher, 99.8%), potassium chloride (JT Baker, 99.8%), calcium chloride dihydrate (Sigma-Aldrich, $\geq 99\%$), magnesium chloride hexahydrate (Fisher, 99.1%), strontium chloride hexahydrate (JT Baker, 100.1%), cupric chloride (Sigma-Aldrich, \geq 99.9%), nickel chloride hexahydrate (Sigma-Aldrich, \geq 98%), zinc chloride (Sigma-Aldrich, $\geq 98\%$), sodium bicarbonate (Fisher, 100.0%) and sodium sulfate (JT Baker, 99.5%). Cation and anion brines were prepared separately, with anion brine containing bicarbonate and sulfate ions and cation brine containing divalent metal and potassium ions. Sodium chloride was divided equally into the two brines. The prepared brines were filtered through 0.45 µm filter paper and degassed under vacuum for overnight before use. For anion brine bicarbonate salt (NaHCO₃) was added after degassing treatment to minimize pH change due to the loss of dissolved carbon dioxide (CO₂) gas. Desired brine composition was achieved by mixing equal volumes of cation and anion brines.

Three types of inhibitor chemistries were studied in this work: tri-phosphonate (amino tri[methylene phosphonic acid], MW = 299), penta-phosphonate (diethylenetriamine penta [methylene phosphonic acid], MW = 573) and homopolymer (polyacrylate, MW = 4000). Their molecular structures are listed in Figure 1. They represent the most commonly used CaCO₃ scale inhibitors in the oil field. All scale inhibitor stock solutions (1000 mg/L) were adjusted to pH 4.0 with 0.1 M NaOH.



c). Poly(acrylic acid).

Figure 1. Molecular structure of scale inhibitors.

Test Method

Both static and dynamic test methods were used in this study. Both methods are widely used in oilfield industries to evaluate inhibitor performance, although they assess different aspects of scale formation and prevention. The static test is used to measure the inhibitor efficiency to limit scale precipitation in bulk solution, while the dynamic test is to study the inhibitor effectiveness to prevent scale adhesion on tubing wall under flowing conditions.

In the static precipitation tests, sample preparations were carried out at room temperature (~22°C). The test bottle was first filled with 50 mL anion brine and then dosed with pre-calculated amount of inhibitor. After adding 50 mL cation brine, the test bottle was quickly capped, sealed, shaken to mix thoroughly and placed into the pre-heated oven (71°C). Control sample, which replaced cation brine with DI water, and blank sample, which contained no inhibitor, were also prepared. After 3 and 24 hours of test durations, ~15 mL solid-free brine was withdrawn from the test bottle for bicarbonate (HCO₃⁻) measurement. The exact weight of brine sample was measured to the second decimal (0.01 g). The HCO₃⁻ content in sample was determined by titrating with 0.020 N sulfuric acid standard solution to the end point of pH 4.3. The HCO₃⁻ concentration was calculated from sample weight and titrant volume. The pH meter was calibrated with pH 7.00 and 4.01 standard solutions.

 HCO_3^- concentration was used as the indicator to measure the inhibitor performance, instead of Ca²⁺ as often used [20]. This was because the changes in HCO_3^- concentration in this study were much easier to be determined. The test brine contained much higher Ca²⁺ (68.8 mM) than HCO_3^- (8.2 mM). Assuring that 50% of HCO_3^- ions were consumed due to CaCO₃ precipitation, decrease in Ca²⁺ concentration would be less than 3% in the test sample, based on the stoichiometry relationship shown in Eq. (2). Percent inhibition attained was then calculated using the following equation:

Inhibition% =
$$\frac{(\text{HCO}_{3}^{-})_{\text{Sample}} - (\text{HCO}_{3}^{-})_{\text{Blank}}}{(\text{HCO}_{3}^{-})_{\text{Control}} - (\text{HCO}_{3}^{-})_{\text{Blank}}} \times 100$$
(3)

The influences of heavy metal ions on inhibitor performance were assessed by the changes in the calculated inhibition percent.

At the end of 24-hour test, brine was filtrated through a 0.45 μ m filter. The retained precipitates were washed with DI water to remove residual dissolved salts and dried at 40°C overnight for environmental scanning electron microscope (ESEM) and energy-dispersive X-ray spectroscopy (EDS) analyses. Backscattered images were acquired at 15 kV, 0.15 Torr water vapor pressure and working distance of about 10 mm.

In the dynamic deposition tests, the rate of scale formation was measured in a flowing system. The method operated under the principle that scale buildup on the interior surface of a small capillary increases the pressure drop across the capillary. A schematic drawing of test setup is shown in Figure 2. The system consisted of three HPLC pumps (A, B, and C). They were used for cation brine (pump A), anion brine (pump B) and inhibited anion brine (pump C). Change in inhibitor concentration during test runs was achieved by adjusting the flow rates of pump B and C. The combined flow rates of these two pumps were kept at 5 ml/min, as the same to cation pump A. Brines from pump B and C were mixed prior to a preheating coil. Then preheated cation and anion brines were comingled in a mixing chamber in front of the scaling coil (Monel alloy, 1 mm ID, 1 m in length). Differential pressure (ΔP) across the scaling coil was continuously monitored and recorded, along with mixing chamber temperature and back pressure. The formation of CaCO₃ deposit was indicated by an increase in ΔP due to a reduced cross-section area. The deposition induction period was defined as the amount of time elapsed between the beginning of test run to the onset of ΔP showing speeded increase, and scaling time was determined as the time elapsed to ΔP increase reaching 1 psi. The improvement in inhibitor efficiency by heavy metal ion was indicated by extending induction period and scaling time; vice versa, the deterioration of inhibitor performance would accelerate the scale deposition by shortening induction period and scaling time. Blank runs, which were free of heavy metal ion and inhibitor, were conducted prior to each test with inhibitors and/or heavy metal ions to ensure repeatable blank scaling time. The blank scaling time was used to determine the test duration for inhibitors. During the evaluation test, the inhibitor concentration was kept at constant for a

duration equivalent to ~3 times of blank scaling time and then, if ΔP increase was less than 1 psi, was reduced stepwise (1 mg/L) to the lower level. At the end of each run, scaling coil was cleaned with 10% acetic acid for 30 minutes followed with DI water for at least 2 hours to remove CaCO₃ blockage and residual inhibitor.



Figure 2. Schematic drawing of dynamic test setup.

Results

Test results with two methods showed a good agreement. Results from both sets of tests demonstrated that the scale inhibitor performance could be significantly affected by trace amount of heavy metal ions.

Effects on the inhibition of CaCO₃ precipitation

Static tests were performed with 1, 2 and 5 mg/L of inhibitor concentrations with and without 2 mg/L of heavy metal ions. Tests were repeated three times to confirm the findings. Results from these separated runs showed high consistency. More importantly, each heavy metal ion displayed the same impact on the inhibitor performance in every run. Results presented below were the averaged values from these three runs. Complete inhibition was achieved in all samples with 5 mg/L of inhibitors.

Test results for tri-phosphonate inhibitor are summarized in Figure 3. It is clear that the Zn^{2+} reduced the inhibitor efficiency. At 1 mg/L inhibitor, 2 mg/L Zn^{2+} decreased the inhibition efficiency from 62% to 25% in 3-hour tests and from 20% to less than 10% in the 24-hour tests. The inhibition percent at 2 mg/L of inhibitor was 95% in the 3-hour tests and 81% in the 24-hour tests. With the presence of 2 mg/L Zn^{2+} , its performance was decreased to less than 80% and 15%, respectively.

Unlike Zn^{2+} , Cu^{2+} showed positive effect to the performance of tri-phosphonate inhibitor, although the impact was insignificant. In the 3-hour tests, the inhibition percent increased from 62% to 77% at 1 mg/L and from 95% to complete inhibition at 2 mg/L, respectively. A similar trend was also observed in the 24-hour tests at 2 mg/L inhibitor concentration. The inhibition percent was improved to above 90%. Ni²⁺ ions had little

effect on the tri-phosphonate inhibitor. The inhibition percent was almost the same for tests with and without Ni^{2+} ions.



Figure 3. Static test results showing the influence of heavy metal ions on tri-phosphonate inhibitor performance.

These heavy metal ions showed very different behaviors to penta-phosphonate inhibitor (Figure 4). Both Cu^{2+} and Zn^{2+} improved the inhibitor performance. In the 3-hour tests, the inhibition percent was increased from 43% to over 60% for 1 mg/L inhibitor and from < 80% to 100% at 2 mg/L inhibitor. In the 24-hour tests, the inhibition percent was increased from < 15% to >20% by Cu^{2+} to 30% by Zn^{2+} in samples with 1 mg/L inhibitor and from 41% to 69% by Cu^{2+} and to 83% by Zn^{2+} with 2 mg/L inhibitor.



Figure 4. Static test results showing the influence of heavy metal ions on penta-phosphonate inhibitor performance.

The performance of pente-phosphonate was deteriorated by Ni^{2+} as observed in all samples. At 1 mg/L inhibitor concentration, the inhibition percent was decreased from 43% to 20% in the 3-hour tests. More significant changes were observed in the tests with 2 mg/L inhibitor. The inhibition percent was reduced to 58% from 77% in the 3-hour tests and form 41% to <20% in the 24-hour tests.

Compared to phosphonates, polyacrylate inhibitor was less affected by these three heavy metal ions (Figure 5). Its inhibition% showed slight improvement in the presence of Zn^{2+} . In the 3-hour tests, its inhibition% at 1 mg/L was increased from 58% to 64% and from 90% to 97% at 2 mg/L. Cu²⁺ also showed some positive effect in the 3-hour test at 1 mg/L inhibitor concentration where the inhibition percent was increased from 58% to 70%. No noticeable changes in performance were observed in samples with Ni²⁺.



Figure 5. Static test results showing the influence of heavy metal ions on polymeric inhibitor performance.

In the absence of scale inhibitor, the heavy metal ions alone showed little influence on $CaCO_3$ precipitation. The differences in bicarbonate concentrations were less than 5% for samples with and without heavy metal ions.

Effects on the prevention of CaCO₃ deposition

Test runs without heavy metal ions and scale inhibitor were conducted initially to determine the blank scaling times. No ΔP changes were observed for 90 min. duration in the repeated runs. Then HCO₃⁻ concentration was raised from 500 mg/L to 1000 mg/L to accelerate the scaling process. Blank scaling times were shortened to around 30 min (Figure 6). Based on these results, the test duration for inhibitor was set at 90 min. The inhibitor concentration was started at 8 mg/L and decreased by 1 mg/L after every 90 min

until the ΔP increase across scaling coil exceeded 1 psi. Heavy metal ion concentration was kept constant in each run, with 0, 2, and 5 mg/L for Ni²⁺ and Zn²⁺ and 0 and 2 mg/L for Cu²⁺. The cation brine with 5 mg/L Cu²⁺ turned pale blue with time, possibly due to the formation of Cu(OH)₂ colloidal particles.



Figure 6. Dynamic test results for solution without heavy metal ions and inhibitors.

Tests with heavy metal ions only showed little difference from the blank runs, suggesting they had negligible effect on $CaCO_3$ deposition under this test conditions. The scaling time fell within a narrow range of 28 to 33 min. Results from selected runs are presented in Figure 7.



Figure 7. Dynamic test results for solutions containing heavy metal ions.

Test results with scale inhibitors are displayed in Figures 7–12. In the absence of heavy metal ions, tri-phosphonate inhibitor was effective till concentration reduced to 4 mg/L (Figure 8). ΔP started to increase rapidly at 360 min. and passed 1 psi at 409 min. Little changes were observed when 2 mg/L Ni²⁺ ions was added, as ΔP reached to 1 psi at 400 min. Delay in CaCO₃ deposition, although not significant, was observed with 2 mg/L Cu²⁺. The deposition induction period was increased to 392 min and scaling time was also extended to 430 min. In test runs with 2 mg/L Zn²⁺ the CaCO₃ deposition became faster than inhibitor alone. The deposition induction period and scaling time were decreased to 260 and 347 min, respectively. Similar results were observed in runs with 5 mg/L heavy metal ions (Figure 9). With 5 mg/L Zn²⁺ ions, the deposition induction period was further reduced to 260 min and the scaling time was changed to less than 320 min. At 5 mg/L, Ni²⁺ ions showed positive influence on tri-phosphonate performance, indicated by delaying both induction period and scaling time ~40 min.



Figure 8. Dynamic test results showing the influence of heavy metal ions (2 mg/L) on triphosphonate inhibitor performance.

Penta-phosphonate itself showed much less effectiveness than the tri-phosphonate inhibitor (Figure 10). It failed at 8 mg/L concentration in the repeated runs (<90 min). 2 mg/L Ni²⁺ reduced the scaling time further to 70 min. The same was found in test with 5 mg/L Ni²⁺ (Figure 11). Both Cu²⁺ and Zn²⁺ significantly improved its performance. The inhibitor was still effective at 6 mg/L in the presence of Cu²⁺ and Zn²⁺. The deposition induction period and scaling time were prolonged from 45 and 87 min to 255 and 324 min by 2 mg/L Cu²⁺, 257 and 296 min by 2 mg/L Zn²⁺, and to 295 and 353 min by 5 mg/L Zn²⁺ ions.



Figure 9. Dynamic test results showing the influence of heavy metal ions (5 mg/L) on triphosphonate inhibitor performance.



Figure 10. Dynamic test results showing the influence of heavy metal ions (2 mg/L) on pentaphosphonate inhibitor performance.

The performance of polymer inhibitor was not affected by Ni^{2+} ions. 2 mg/L Cu^{2+} and Zn^{2+} showed marginal positive influence as the scaling times were slightly delayed, but all runs failed at inhibitor concentration of 5 mg/L (Figure 12). A notable delay in CaCO₃ deposition was observed at 5 mg/L of Zn^{2+} . The deposition induction period and scaling

time were extended from 267 and 300 min to 320 and 425 min, respectively (Figure 13), and the polymer inhibitor was sufficient at 5 mg/L to prevent $CaCO_3$ deposition under test conditions.



Figure 11. Dynamic test results showing the influence of heavy metal ions (5 mg/L) on pentaphosphonate inhibitor performance.



Figure 12. Dynamic test results showing the influence of heavy metal ions (2 mg/L) with polymer inhibitor performance.



Figure 13. Dynamic test results showing the influence of heavy metal ions (5 mg/L) with polymer inhibitor performance.

Effects on CaCO₃ morphologies

CaCO₃ particles formed in this study were predominately prismatic aragonites. Small amounts (<5%) of rhombic calcites were also observed in the blank samples. The aragonite crystals were mainly in the form of branched columns (20–30 μ m in length) radiating from a center point. The precipitates formed in the blank run had well defined and smooth surfaces (Figure 14). Heavy metal ions showed little effects on the aragonite size and shape, except the column faces became rough in some crystals. This was most noticeable with Zn²⁺ ions (Figure 15).



Figure 14. CaCO₃ crystals formed in blank solution showing smooth surfaces.



Figure 15. CaCO₃ crystals formed in solution with 2 mg/L Zn^{2+} ions.

The aragonite crystals formed in the presence of inhibitors were much larger in size (Figure 16). Most aragonite columns were 50 to 200 μ m in length. Such change may suggest that the CaCO₃ nucleation rate was retarded and fewer crystals were formed. With low number of crystals, there were more reactants available for crystals to grow. All crystals had smooth surface, as in the blank sample, but the columns became slightly curved. The most visible changes were the column tops evolved from flat to jagged and pointed. No significant change was observed with the addition of heavy metal ions, except when Zn²⁺ was added with tri-phosphonate inhibitor. In this case, the crystals were smaller (50 to 100 µm) and their column tops became much less irregular (Figure 17).

No heavy metal elements were detected in aragonites by EDS analysis. This may imply that these metal ions were not incorporated into the $CaCO_3$ crystals. It is also possible that their contents in the precipitates were below the detection limits.



a. Tri-phosphonate.



b. Penta-phosphonate.



c. Polyacrylate.

Figure 16. Aragonite crystals formed in solutions containing 2 mg/L of inhibitors.



Figure 17. Aragonite crystals formed in solution with 2 mg/L of tri-phosphonate and Zn^{2+} ions.

Discussions

Previous studies have shown that trace amounts of Cu²⁺, Zn²⁺ and Ni²⁺ can effectively interfere with the CaCO₃ formation process. Kitano et al. [21] reported that the presence of trace amount of Zn^{2+} (0.5–5 mg/L) in solution inhibited very strongly the transformation of aragonite to calcite at 25°C. Meyer [22] showed that the calcite growth rate at 20°C could be halved by 0.1 μ mol/L Zn²⁺ ions and 6 μ mol/L Ni²⁺, and reduced 80% by 0.2 μ mol/L Zn²⁺ and 10 µmol/L Ni²⁺, respectively. Wada et al. [23] examined the effects of different divalent cations on the nucleation, growth and transformation of CaCO3 polymorphs and found that the presence of Cu^{2+} , Ni^{2+} and Zn^{2+} favored the formation of aragonite. Abouali et al. [24] noticed the complete inhibition of CaCO₃ scale precipitation by 0.6 mg/L Cu²⁺ ions or 0.05 mg/L Zn²⁺. Zeppenfeld et al. [25] observed a significant increase of CaCO₃ nucleation induction period and about 90% inhibition efficiency attained by Cu²⁺ contents of >2 mg/L. Moreover, Pernot *et al.* [26] indicated that the number of CaCO₃ crystals was increased in solution containing 0.5 and 5 mg/L Zn^{2+} and suggested that zinc ions might act as an accelerator of heterogeneous nucleation in the bulk solution instead of on the surface. Such effect may lead to a decreased risk of CaCO₃ scale deposition. In addition, Lisitsin et al. [27] showed that a Zn^{2+} concentration in the order of 2 mg/L was able to exert a marked suppression effect on both CaCO₃ bulk precipitation and scaling of reverse osmosis (RO) membrane surface.

The results in this study did not show any noticeable changes on the rates of CaCO₃ precipitation and deposition by these metal ions. Such discerption could be attributed largely to the test conditions. Most of the previous studied were conducted at temperatures around 25°C and in low to moderate supersaturated solutions. The CaCO₃ crystals formed in these studies would be mainly calcite. It is possible that the three heavy metal ions have a stronger effect to interfere with calcite than aragonite crystals, as indicated by the disappearance of calcite precipitate in solutions with 2 mg/L of heavy metal ions. Coetzee et al. [28] have shown that the Zn^{2+} ions encouraged CaCO₃ crystallization in aragonite form, even under conditions favoring calcite formation. The carbonates of these heavy metal ions have only calcite crystal form. They may tend to incorporate into calcite lattices, consequently, exerts a more significant influence on calcite formation than to aragonite. Such effect has been well documented for magnesium ions [29, 30]. The inhibition effects are suggested due to slow dehydration of these ions prior to incorporation or increased solubility of calcite solid-solution. Besides, the solution used in this study was highly supersaturated with respect to aragonite. The driving force for aragonite precipitation, combined with the elevated temperature, could be too great for the trace amount of heavy metal ions to have any noticeable influence.

The supersaturation (Ω) can be calculated using Eq. (4):

$$\Omega_{\text{Aragonite}} = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_{3}^{2-}}}{K_{\text{sp,Aragonite}}}$$

$$= \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{HCO}_{3}}}{K_{\text{sp,Aragonite}}} \cdot \frac{10^{\text{pH}}}{K_{1}}$$

$$= \frac{(\text{Ca}^{2+}) \cdot \gamma_{\text{Ca}^{2+}} \cdot (\text{HCO}_{3}^{-}) \cdot \gamma_{\text{HCO}_{3}^{2-}}}{K_{\text{sp,Aragonite}}} \cdot \frac{10^{\text{pH}}}{K_{1}}$$
(4)

In Eq. (4), a_i represents ion activity; () denotes ion concentration; K_1 is the first ionization constant of carbonic acid and γ_i is activity coefficient; $K_{sp,Aragonite}$ is the aragonite thermodynamic solubility constant and it equals to $10^{-8.765}$ at 71°C [31].

K_{sp.Aragonite}

Activity coefficients for calcium and bicarbonate ions, $\gamma_{Ca^{2+}}$ and $\gamma_{HCO_{2}^{2-}}$, are determined from the Pitzer equations, which takes into accounts of both long-range electrostatic effects considered in the Debye-Hückel equation and short-range interactions in the high concentrated solutions [32].

The calculation results show that the supersaturation was, respectively, 39 and 103 for static (HCO₃⁻ 500 mg/L, pH 6.89) and dynamic (HCO₃⁻ 1000 mg/L, pH 7.01) test, which were much higher than these in the previous studies ($\Omega < 10$) [24–27].

Although negligible impacts on CaCO₃ formation by themselves, these heavy metal ions exhibited considerable influences on the performance of scale inhibitors. It is interesting to note that the influence is inhibitor specific. Cu^{2+} ions showed positive impact on all three inhibitors studied, while its effect was more pronounced for pentaphosphonate. Ni²⁺ ions had little influence on tri-phosphonate and polymeric inhibitors, but decreased the effectiveness of penta-phosphonate. Zn^{2+} ions enhanced the effectiveness of penta-phosphonate; but they deteriorated the performance of tri-phosphonate. These results may suggest that the inhibition of CaCO₃ scale is achieved by the complexes of inhibitor and metal ions, instead of inhibitor molecules themselves. Heavy metal ions pair with inhibitor molecules and form complexes. The interaction between these complexes with the active growth sites on CaCO₃ surface determines the inhibition efficiency. Comparing to phosphonates, poly(acrylic acid) does not form strong complexes with the heavy metal ions and, consequently, its performance is not significantly affected.

Conclusions

The present study describes the impact of heavy metal ions, Cu²⁺, Ni²⁺, and Zn²⁺, on CaCO₃ scale inhibitor performance. Results of static precipitation and dynamic deposition tests show good correlation in the effects of heavy metal ions, indicating that even trace amount of heavy metal ions can have a significant influence on the performance of CaCO₃ scale inhibitors. Heavy metal ions form strong complexes with inhibitor molecules and these complexes determine the inhibition efficiency against $CaCO_3$ scale formation. Synergistic effects are observed between penta-phosphonate inhibitor with zinc and copper ions. Copper ions also improve the performance of tri-phonsphonate inhibitor. Nickel ions have negligible influence to tri-phosphonate, but interfere with penta-phosphonate inhibitor. Similarly, zinc ions deteriorated the performance of tri-phonsphonate. These three heavy metal ions have no adverse effect to polymeric inhibitor and their influences are insignificant. Findings from this study suggest that the influence of heavy metal ions, even at low concentrations, should be considered in the selection of inhibitor products for CaCO₃ scale prevention.

Acknowledgments

The authors wish to acknowledge Saudi Aramco for granting permission to publish this article.

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