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The impact of Ferrous Iron (II) on Scale Inhibitors Performance in the Field – Is it a Problem?

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ABSTRACT

The general perception in the oil and gas industry is that the presence of ferrous iron in produced water can have adverse effects to the performance of scale inhibitors in controlling the build-up of calcium carbonate (CaCO_3) and barium sulfate (BaSO_4) scales. However, the exact causes of its impact to scale inhibition are not clearly understood as previous studies appear to be influenced by the type of tests and the procedures adopted.

This paper presents some aspects of two case studies on the behavior of several iron tolerant scale inhibitor chemistries in water containing different levels of iron (II) ion. Laboratory assessments of the performance of the inhibitors were based on anaerobic static jar studies, Scanning Electron Microscopy (SEM)/Energy Dispersive X-Ray Spectroscopy (EDXS) analysis and Dynamic Scale Loop (DSL) tests on both calcium carbonate and barium sulphate. Discussion is made to elucidate the mechanisms involved during scale inhibition when in the presence of different levels of iron (II) ion.

Key words: Calcium carbonate; barium sulfate, iron (II), scale inhibitors, efficiency, minimum inhibitor concentration

INTRODUCTION

Mineral scale formation and deposition (e.g., CaCO_3 , BaSO_4) can lead to unacceptable safety risks and the increase of operational costs¹⁻². The build-up of scale deposit layers can compromise the performance, malfunctioning and/or operational safety of process equipment (e.g. heat exchangers, subsurface safety valves, pumps, tubing, etc.). Such failures can result in system downtime, reduced revenue, increased maintenance and operational costs. With the above reasons, the standard

industrial practice adopted by many operators is to apply chemical solutions to ensure flow assurance, which are considered to be the most cost-effective approach and the preferred route to prevent and mitigate most of flow assurance and piping integrity problems³⁻⁴.

An effective scale inhibitor plays a very important role in maintaining flow assurance integrity in oil and gas production systems. In recent years, oil and gas exploration and production are taking place in more arduous environment and remote locations, with which the industry has been faced with many new challenges, including unconventional resources, deeper formations, higher temperature, higher pressure, higher content of scale forming ions, protection of the environment and reduction in total cost of operation etc. Innovative techniques and solutions have been developed to address the operational issues. Appropriate chemical selections and applications form part of the elements in meeting these challenges⁴⁻⁵.

Scale inhibitors are generally applied to delay, reduce, or prevent the formation of inorganic scale deposits. The laboratory qualification test work typically covers the selection of a scale inhibitor and the determination of the minimum inhibitor concentration (MIC) for the specific scale of interest. Different scale inhibitor chemistries have been used through continuous chemical injection and/or periodic batch squeeze treatments⁵⁻⁷.

Ferrous iron (II) ion may be naturally present in reservoir formation water or in produced water due to the corrosion of carbon steel equipment handling the produced fluids. Under appropriate thermodynamic and anaerobic conditions, iron (II) ions can undergo precipitation with carbonate ions to form iron carbonate (i.e., siderite) or react with sulfide ions in sour systems to form iron sulfide, both of these are typical corrosion products whose prevention and mitigation has been extensively studied⁸⁻⁹. Under certain conditions, ferrous iron (II) may also be oxidized to ferric iron (III) which then precipitates in the form of either ferric hydroxide or hydroxyl form of ferric oxide particles. Deposition of such corrosion products may cause upsets in the production system and impair with the functionality of the scale inhibitors¹⁰⁻¹⁵.

It was reported in some studies¹⁴⁻²¹ that the presence of ferrous iron (II) in produced water may have a detrimental impact on the performance of scale inhibitors. However, it is still unclear why certain scale inhibitor chemistries previously thought to be iron sensitive are able to offer good performance in the presence of ferrous (II) ions.

For example, Yuan and Stoppelenburg¹⁴ noticed an increase in the scale inhibition efficiency against BaSO_4 in tests with the presence of iron (II) whilst Graham and Dyer¹⁶ recorded a reduction in scale inhibitor efficiency in their studies. Furthermore, in CaCO_3 deposition studies it has been noted that in presence of dissolved iron (II) under anaerobic conditions, there seems to be a delay in the onset of nucleation with increase in iron (II) concentrations, thus resulting in longer induction times for scale formation^{16, 21}. In these studies, the longer scaling blanks during CaCO_3 deposition in presence of iron (II) have been attributed to a drop in the pH *in-situ*, which slowed down the precipitation kinetics for CaCO_3 . Furthermore, once FeCO_3 is formed, there is an increase in the local pH that fasten the kinetic deposition rate of CaCO_3 in the dynamic tube blocking rigs.

Different scale inhibitor candidates were selected for assessing their performance, both in absence and/or presence of iron (II) via standard static jar tests and dynamic scale loop (DSL) methods. During the anaerobic tests, the two-part synthetic brines were bubbled with oxygen-free-nitrogen (OFN) gas before and during the experiment to prevent from any oxygen ingress that could lead to the oxidation of iron (II) ions.

Furthermore, Wada et al.²⁵ reported the works on studying the effects of seven divalent cations on calcium carbonate morphology and kinetics. The results suggested that the incorporation of ions such as iron (II) may form a neutral complex, inhibiting the CaCO_3 growth and enabling morphological changes in CaCO_3 appearance at early stages.

Despite the investigations¹⁴⁻²⁶, no consensus has been reached as to how iron may interact with different scale types and/or the inhibition mechanisms. In order to elucidate these fundamental questions, this paper presents different case studies for assessing the behavior of BaSO₄ and CaCO₃ scale formation and inhibition in absence and presence of iron (II); using the standard static jar tests and dynamic scale loop methods.

EXPERIMENTAL PROCEDURE

Brine Preparation

Experiments were carried out using synthetic brines based on the water chemistry of each field. Two-part synthetic brines were prepared by dissolving Analar Grade salts into de-ionized water and mixed into an equal volume at the start of the test to give the full composition shown in Table 1. The equimolar two-part synthetic brines (i.e., cations and anions water) have been pH adjusted using buffer solutions.

Table 1: Formation Water Composition for Fields A and B

Ions	A	B
	Quantity (mg/L)	Quantity (mg/L)
Bicarbonate	1119	195
Sulphate	1484	20
Chloride	22700	26400
Sodium	13557	13900
Potassium	481	490
Magnesium	731	430
Calcium	517	1620
Strontium	30	190
Barium	47	125
Iron (II)	20	8
pH	6.3	7.0

Various candidate scale inhibitors were pre-selected for assessing their performance, both in absence or presence of iron (II) via standard static jar tests and dynamic scale loop (DSL) methods. With the anaerobic tests, the two-part synthetic brines were bubbled with oxygen-free-nitrogen (OFN) gas before and during the experiment to prevent oxygen contamination that could lead to the oxidation of iron (II) ions.

Field A brine represents a North Sea case in which the maximum scaling tendency with respect to BaSO₄ is at 50% seawater breakthrough (i.e., contains 50% formation water and 50% seawater). Due to environmental restrictions, a new downhole scale inhibitor needed to be re-assessed for MIC and its iron-tolerance.

Field B brine represents another North Sea case in which there was a need for reassessing the potential for iron (II) affecting the scale inhibitor selection for CaCO₃ inhibition.

Aerobic Static Jar Tests

The static jar test is a well-known standard screening technique adopted in the oil and gas industry to assess the performance of different candidate scale inhibitor chemistries under static conditions. The general procedure consisted in preparing a series of bottles containing a scaling blank, a control sample and several dosed inhibited bottles. These bottles were sealed and placed in an oven at test temperature for a 24-hour period. At the end of the experiment, visual observations and aliquot

samples were taken from each of the bottles to determine the concentration of scale ions formed over time via Inductively Coupled Plasma (ICP) analysis. Once samples have been analyzed via ICP, the variations in the content of calcium and barium ions were used for determining the efficiency of the candidate scale inhibitors with respect to the original calcium and barium concentrations using the following equation:

$$\%Efficiency = \left[\frac{(C_I - C_B)}{(C_0 - C_B)} \times 100 \right] \quad (1)$$

Where,

- C_I Average concentration of cations in a sample (i.e., inhibitor present)
- C_0 Average concentration of cations in unscaled sample (control)
- C_B Average concentration of cations in scale sample (i.e., no inhibitor present – blank)

The pass criteria for the standard static jar test is determined as being the lowest dose rate that showed efficiencies greater or equal than 80 % or the lowest dose that remained a clear, bright liquid and showed no signs of precipitates. All tests were done in duplicates.

Anaerobic Static Jar Tests

The anaerobic static jar method followed identical steps to the standard jar technique mentioned above, with the exception that these tests were performed under an oxygen-free environment.

Prior to the start of the experiment, deaeration of the synthetic anionic and cationic waters was made by sparging with nitrogen gas for at least 4 hours. A 1000-ppm iron (II) stock solution was also prepared using $\text{FeCl}_4 \cdot 4\text{H}_2\text{O}$ into de-ionized water. This iron (II) stock solution was used for dosing ferrous iron (II) into the testing brines. With the exception of the scaling blank and control, all other samples were dosed with the candidate scale inhibitors and aliquots from the bottle were collected at the end of the experiment to assess the scale inhibitor performance using Equation 1. All tests were done in duplicates.

In addition, the deposition behavior of the test fluid on metal surface was evaluated by placing a stainless steel metal coupon in each static bottle under anaerobic conditions. This was designed to mimic the scale formation taking place in the dynamic scale loop rig in presence of iron (II) ions.

Scanning Electron Microscope (SEM) with Energy Dispersive X-Ray Spectroscopy (EDXS)

The SEM/EDXS equipment was used to characterize and identify the chemical nature and morphology of small-scale crystals present in brine samples used in the static jar tests. Pictures of scale crystals were taken over a 20 μm -200 μm range, EDXS was performed with a full elemental composition analysis to detect the scale elements present in each of the samples.

Dynamic Scale Loop (DSL) Tests

The dynamic scale loop consists of equipment with precise and programmable pumps, which pump individual anionic and cationic synthetic brines to a mixing chamber connected to a coil placed inside an oven set to the required test temperature. The coil used is made of stainless steel alloy 316L (UNS S31600), 1 m long with 1/16" OD. Upon mixing of anionic and cationic brines, the scale deposition starts taking place in the loop; the differential pressure across the coil is measured; an increase in ΔP is an indication of blockage caused by scale deposition over time.

This technique is well known in the industry for assessing the blank scaling time of brines and the inhibition performance of scale inhibitors for their ability to prevent the adherence of scale deposits to the metal surface. The anaerobic DSL tests were conducted in a similar manner with continuous