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Elucidating the Influence of Calcium Ion Concentration on Corrosion Inhibitor Performance

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ABSTRACT

CO₂ corrosion is one of the most common problems faced during oil and gas production, although steel pipes offer a long-term economical use in CO₂ corrosive environments with the application of carefully selected corrosion inhibitors. Inhibitor efficiency is affected by many variables, including temperature, pressure, flow velocity, pH, and composition of produced water. The impact of brine composition on corrosion inhibitor performance is elucidated in this work; more specifically, the question of whether high salinity or high Ca²⁺ concentration has a greater impact on corrosion inhibitor performance is answered. Corrosion inhibition performance of various inhibitors, including quaternary amines and alkyl pyridine quat, were evaluated with brines of varying Ca²⁺ concentration (0 to 20,000 mg/L) and salinity [57,000 to 250,000 total dissolve solids (TDS)]. The corrosion inhibition was studied *in situ* by linear polarization resistance (LPR), using a UNS G10180⁽¹⁾ (carbon steel). The goal of this study is to help improve corrosion inhibitor design for high calcium containing brines.

Key words: CO₂ corrosion, corrosion inhibitors, quat, ECBQ, pyridine, APQ, calcium ion, TDS

INTRODUCTION

The oil and gas industry uses corrosion inhibitors (CIs) as a cost effective method to mitigate corrosion.¹ A corrosion inhibitor is a chemical substance, which when added to a corrosive system, significantly decreases the corrosion rate of a metal exposed to that environment.² Most of the

⁽¹⁾ Unified Numbering System for Metals and Alloys (UNS). UNS numbers are listed in Metals & Alloys in the Unified Numbering System, 10th ed. (Warrendale, PA: SAE International and West Conshohocken, PA: ASTM International, 2004).

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knowledge about corrosion inhibitors for specific environments was acquired by laboratory testing in which field conditions were simulated and the inhibition efficiency of different corrosion inhibitors were measured.^{3,4} Corrosion inhibitors are often complex formulations and consist of many individual components. A corrosion inhibitor usually contains one or more active chemicals (raw materials) and can also contain surfactants, such as synergists, solvents, dispersants, demulsifiers, and defoamers. There are many physical conditions: brine chemistry, temperature, gas/liquid velocity, pH, and TDS that can affect corrosion inhibitor performance. Other production chemicals present in the system could also affect inhibitor performance. Researchers found that the key factors that affect the inhibitor performance are shear stress, temperature, predicted corrosion rate, and TDS.⁵

During this study, attention was given to TDS and different levels of Ca^{2+} ions in brine. Brine TDS encountered within the oil and gas industry vary significantly from one field to another. Some fields produce formation water with higher TDS: in the Middle East (250,000 ppm) and the USA (300,000 ppm) whilst seawater TDS is roughly 40,000 ppm.⁶⁻⁸ The Ca^{2+} ion concentration in brines varies significantly too, it could be as low as ≈ 8 ppm and exceeding 20,000 ppm.^{9,10}

The goal of this work is to help increase the understanding of the effect of Ca^{2+} ions in brines with different TDS on the performance of a couple of individual inhibitor compounds with respect to their ability to control general corrosion rates.

The focus of the paper is directed toward assessing inhibitor efficiency in terms of reducing general corrosion but not localized corrosion. To assess the effectiveness of the inhibitor against localized corrosion, the test durations would need to be significantly longer than those discussed in this paper.

EXPERIMENTAL PROCEDURE

Experiments discussed were conducted in ambient pressure bubble cells, which are primarily used for basic screening of corrosion inhibitors and are normally followed by more complex test methods that simulate field representative conditions. A three-electrode set up (working, counter, and reference electrodes) and a potentiostat were used to conduct electrochemical measurements. Working and reference electrodes were made from carbon steel, polished to 600 grit, and counter was made from UNS N10276 nickel-molybdenum-chromium alloy. The surface ratio of working electrode to counter electrode is 1:1. The rotational speed of the magnetic stirrer (cylindrical: 30 x 6 mm) was set at 200 rpm. LPR measurements were performed every 30 minutes by polarizing the working electrode ± 15 mV from the open circuit potential (OCP) at a scan rate of 0.4 mV/s. The Tafel parameters of 120 mV/dec for both anodic and cathodic reactions were assumed and used for conversion of polarization resistance to corrosion rate. Samples were pre-corroded for two hours before the addition of corrosion inhibitor. All testing was conducted at 50 °C and atmospheric pressure in CO_2 saturated synthetic brines summarized in Table 1. Brine composition and test parameters were selected using ScaleSoftPitzer SSP2013⁽²⁾ to avoid calcium carbonate formation. Within this research, the brines with three different TDS (57k, 150k and 250k) were tested. Almost all cation/anion concentrations except sodium, calcium and chloride ions were fixed. Variation of the Na^+ and Ca^{2+} ion concentration allowed adjustment of the ionic strength whilst maintaining the same TDS. Consequently, the impact of various concentration of Ca^{2+} ions in brines with the same TDS on general corrosion was measured.

Generic Corrosion Inhibitors

Corrosion testing was performed with an epichlorohydrin bis-quat (ECBQ) and an alkyl pyridine benzyl chloride quat (APQ) raw material. Two different corrosion inhibitor blends were tested, a quat-based corrosion inhibitor (referred to as “ECBQ CI” in the text below) and a pyridine-based corrosion inhibitor (referred to as “APQ CI” in the text following). Sulfur- containing compound (thiosulphate) used as

⁽²⁾ Trade name

synergists and ethoxylated tallow amine used as dispersant aid were added to the corrosion inhibitors blends.

Solubility Test

Solubility of the individual blends in the various saline waters was subject to direct, visual evaluation. ECBQ CI and APQ CI blend solubility was investigated at room temperature $\approx 20^{\circ}\text{C}$. The corrosion inhibitor concentrations tested included 10, 100, 1000 ppmv, and 1 %. After samples were dosed with corrosion inhibitor, they were shaken 10 times, and left for 24 hours.

Table 1: Synthetic brine compositions used in tests

Name	57k TDS no Ca^{2+}	57k TDS with 200 Ca^{2+}	57k TDS with 2k Ca^{2+}	57k TDS with 20k Ca^{2+}
Ion	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Na^{+}	21,887	21,669	19,708	100
K^{+}	100	100	100	100
Mg^{2+}	200	200	200	200
Ca^{2+}	0	200	2,000	20,000
$[\text{HCO}_3]^{-}$	100	100	100	100
$[\text{SO}_4]^{2-}$	100	100	100	100
Cl^{-}	34,294	34,312	34,472	36,080
pH measured	4.98 ± 0.1	4.95 ± 0.1	4.96 ± 0.1	4.71 ± 0.1
pH from SSP ⁽²⁾	4.67	4.67	4.67	4.67
TDS	56,681	56,681	56,680	56,680
Ionic strength (mol/L)	0.99	1.00	1.10	2.04
Name	150k TDS no Ca^{2+}	150kTDS with 200 Ca^{2+}	150k TDS with 2k Ca^{2+}	150k TDS with 20k Ca^{2+}
Ion	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Na^{+}	58,596	58,379	56,418	36,810
K^{+}	100	100	100	100
Mg^{2+}	200	200	200	200
Ca^{2+}	0	200	2,000	20,000
$[\text{HCO}_3]^{-}$	100	100	100	100
$[\text{SO}_4]^{2-}$	100	100	100	100
Cl^{-}	90,903	90,923	91,083	92,691
pH measured	4.83 ± 0.1	4.86 ± 0.1	4.82 ± 0.1	4.64 ± 0.1
pH from SSP ⁽²⁾	4.58	4.58	4.59	4.63
TDS	149,999	150,002	150,001	150,001
Ionic strength (mol/L)	2.59	2.60	2.69	3.64
Name	250k TDS no Ca^{2+}	250k TDS with 200 Ca^{2+}	250k TDS with 2k Ca^{2+}	250k TDS with 20k Ca^{2+}
Ion	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Na^{+}	97,934	97,716	95,755	76,147
K^{+}	100	100	100	100
Mg^{2+}	200	200	200	200
Ca^{2+}	0	200	2,000	20,000
$[\text{HCO}_3]^{-}$	100	100	100	100
$[\text{SO}_4]^{2-}$	100	100	100	100
Cl^{-}	151,567	151,584	151,745	153,353
pH measured	4.80 ± 0.1	4.81 ± 0.1	4.80 ± 0.1	4.60 ± 0.1
pH from SSP ⁽²⁾	4.55	4.55	4.56	4.62
TDS	250,001	250,000	250,000	250,000
Ionic strength (mol/L)	4.30	4.31	4.40	5.34

RESULTS

Effect of Calcium Ions on General Corrosion Rate

The impact of various concentrations of the Ca^{2+} ions in brines with 57k, 150k, and 250k TDS on general corrosion was evaluated and results are shown in Figure 1, 2, and 3. It is clear from Figure 1, 2, and 3 that the corrosion rate in brine containing 20k Ca^{2+} ions in all TDS concentrations (57k, 150k and 250k) is higher. A summary of corrosion rates is presented in Table 2. Presumably, this difference is caused by the pH or ionic strength difference of brine containing 20k Ca^{2+} ions (57k, 150k and 250k TDS) compared to brines containing 0 to 2k mg/L Ca^{2+} in different TDS. The pH values measured before the start of the test and calculated ionic strength can be found in Table 1.

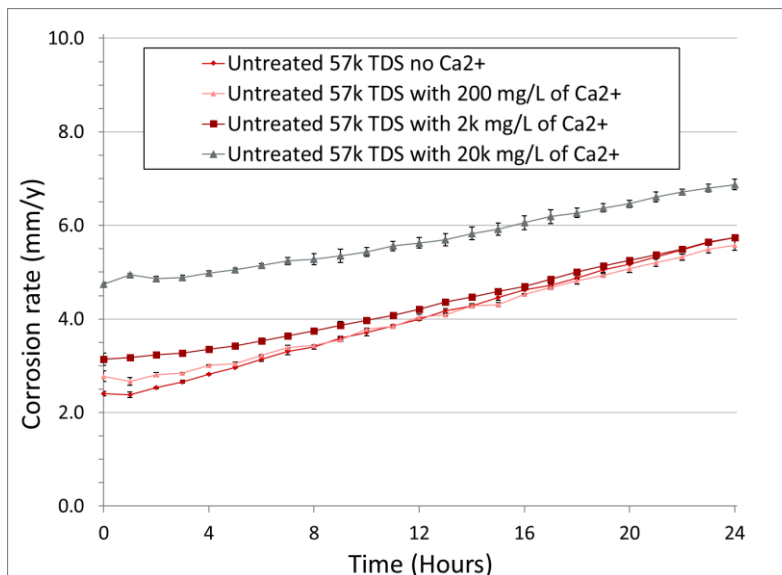


Figure 1: Effect of varying Ca^{2+} ion concentrations from 0 to 20k mg/L in brines with a 57k TDS: LPR measured corrosion rate over time

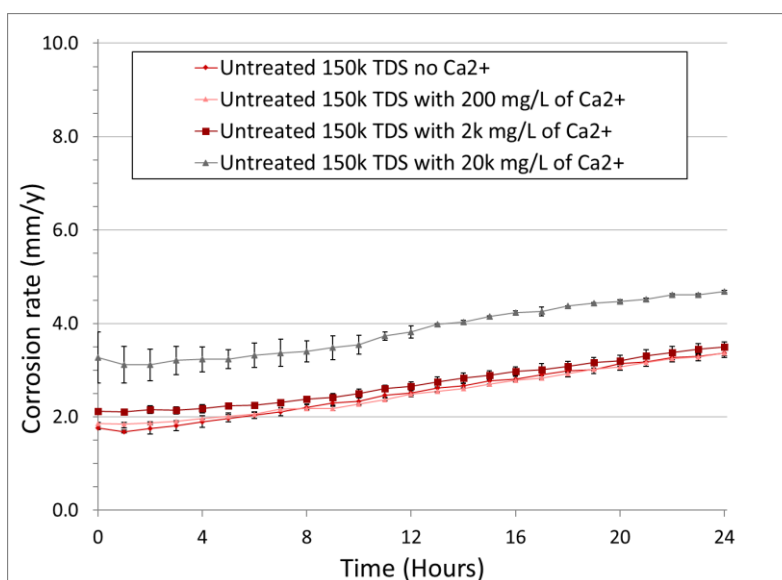


Figure 2: Effect of varying Ca^{2+} ion concentrations from 0 to 20k mg/L in brines with a 150k TDS: LPR measured corrosion rate over time