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HALIDE BRINES ON DUPLEX 2205: A CORROSION AND COMPATIBILITY INVESTIGATION

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ABSTRACT

The effect of chlorides on metal corrosion has been known for a long time, and continues to be extensively studied in order to adopt the best practices with regard to mitigation. The dominant type of corrosion in the presence of chlorides is pitting corrosion.

Bromides on the other hand have not been extensively studied, and – after being proposed for a well-start up application for flexible pipes in offshore Trinidad – a general literature review was conducted to assess their compatibility against 2205 duplex stainless steel.

In this review, a general understanding of pitting corrosion is presented, along with some mechanisms found in the literature. Additionally, the influence of inclusions, and alloying elements is highlighted, as well as the particular section on the effect of different halides (bromide vs chlorides). It is commonly understood that chlorides are more severe than bromides, however the literature survey showed that this is not applicable in all cases.

A 5-day screening test was devised to compare the effect of the two halides individually, and a mixed solution containing both of chloride ($CaCl_2$) and bromide (NaBr). This paper will cover how this investigation was undertaken and present its findings, including how the combination of chlorides and bromides can also alter the aggressiveness of the environment.

Keywords: Pitting, corrosion, bromides, chlorides, halides, compatibility, brines

1. INTRODUCTION

One of the main causes of concern regarding metallic pipelines is corrosion, which can be mitigated by modifying the metal's immediate environment. Brines (concentrated salt solutions) are typical downhole well-start up chemicals.

Chlorides are the most commonly studied; these aggressive anions can initiate breakdown of the stainless steel passive layer, and subsequently cause localised corrosion. This generally occurs in three stages: passivity breakdown, an incubation stage, and a growth stage/re-passivation stage. The corrosive extent of other halides are not as widely studied. As such, when bromides were proposed for a well start-up application in offshore Trinidad, the literature was surveyed to assess bromide compatibility against the 2205 duplex stainless steel used for flexible pipe carcass, and how they compare to chlorides.

A NACE-published study [1] makes mention of reports of increased aggressiveness in the presence of a combination of bromides and chlorides, but their own investigation found that bromides were more aggressive. A second NACE study [2] concluded that it is chlorides that are more potent, calculating that 3.5 times as much bromide (compared to chloride) is necessary for an equivalent reduction in duplex's breakdown potential.

In light of this conflicting literature, and the change in ion concentration and pH that will arise as a result of changing salt type and density, a test was commissioned to better understand the extent of corrosion of 2205 duplex in this environment and the implications this has on design.

2. MATERIALS AND METHODS

The procedure followed for this test is standard practice for the Baker Hughes Drilling & Completion Fluids lab near Aberdeen. It is intended as a screening test, and does not utilize the large-volume cells that corrosion labs typically offer. The formulation of the brines used for the tests are shown in Figure 1 below.

The test involves weighing the samples, suspending them inside the 316L ageing cell (lined with PTFE), introducing the test solution, sealing and pressurising with N_2. The test was done at 70˚C for 5 days, then the cell was cooled in a water bath. The test solution was assessed for any visual changes, and the corrosion coupons were examined, cleaned, and weighed. Upon retrieving the

samples from the lab, they have been inserted in an ultrasonic bath prior to sectioning and microscopy.

Figure 1: Brine formulations for each test

12.1ppg NaBr brine formulation

Water g/l	NaBr g/l
835.3	616.30

11.9ppg $CaCl_2$/CaBr brine formulation

11.6 ppg $CaCl_2$ Brine, bbls	14.2 ppg CaBr Brine, bbls	94-97% $CaCl_2$, lbs
0.914	0.077	9.1

10.74ppg $CaCl_2$ brine formulation

Water g/l	94-97% $CaCl_2$ g/l
884.1	392.61

3. RESULTS AND DISCUSSION

Test 1 (NaBr) showed some features of localised corrosion, in which the corrosion products seemed to precipitate around the corroded areas, but there was no associated depth. Other areas showed deeper pits, and some discolouration. Test 3 ($CaCl_2$) showed severe corrosion, numerous hemispherical pits at the sample edge and deposited corrosion products surrounding them. No features were found in the bulk of the material. The samples exposed to the mixed-brine solution in Test 2 showed aggressive pit morphologies, testifying to the detriment of the mixed-halide regime. The morphologies observed can be a considerable risk for through-thickness pinhole corrosion in 2205 rigid pipelines.

Although the pitting observed in each test is not insignificant, it is extremely localised, explaining why over 99% of the pre-test sample weight was retained at the end of the test.

4. CONCLUSION

2205 duplex samples exposed to chlorides, bromides, and a mixture of both were inspected for corrosion. All three samples displayed features of pitting, some shallow and others with an associated depth. Discolouration and deposition of corrosion product was also observed. A purely comparative assessment of pit depth is argued to not be representative of the extent of attack; pitting location and morphology need to be considered in parallel. These findings are relevant to metallic pipelines, and indicate that care should be taken when considering the safe duration of exposure of 2205 duplex to concentrated mixed brine solutions. It is in particular recommended that studies should be commissioned to understand the effect from lesser-studied halides such as bromides, especially in combination with chlorides; it should not be assumed that test data using chloride brines will adequately represent these scenarios.

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