

Investigation of Field Failure of a Zinc Phosphate Coated UNS G61500 Disc Spring Steel Exposed to a Hydraulic Fluid Using Electrochemical Methods

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ABSTRACT

The malfunction of a hydraulic system on an offshore production platform was traced to environmentally assisted cracking (EAC) of a zinc phosphate conversion coated UNS G61500⁽¹⁾ disk spring steel. The hydraulic fluid in the affected equipment (Fluid B) was an aqueous ethylene glycol (EG) with a brand-specific proprietary inhibitor package and it caused EAC of the equipment at approximately 50°C. Other hydraulic systems (Fluid C) using a different inhibitor package had not experienced any similar failures as of the incident field investigation.

Hydrogen embrittlement (HE) was considered as one possible cause of the observed cracking. In this work, multiple electrochemical tests were conducted to characterize the electrochemical behaviors of the conversion coated disk spring steel in a benchmark EG hydraulic fluid without additives added, Fluid B, and Fluid C.

It is found, in 50°C-Fluid B, the hydrogen evolution reaction (HER) threshold potential for the disc spring steel was determined as $-0.7 V_{sce}$, more positive than that obtained ($-1 V_{sce}$) from 50°C-Fluid C, suggesting HER on the steel immersed in Fluid B was more feasible than in Fluid C. The well-coated steel in Fluid B showed open circuit potential (OCP) higher than the respective HER threshold potential ($-0.7 V_{sce}$) at 50 °C, indicating the HER and the related HE of the steel may not occur. However, If the conversion coating degraded and lost corrosion protective property, the OCP could drop below the HER potential and possibly induce HE.

Keywords: Environmentally assisted cracking, hydrogen embrittlement, hydrogen evolution reaction potential, zinc phosphate conversion coating, high-strength low-alloy (HSLA) disk spring steel

INTRODUCTION

The malfunction of a hydraulic system on an offshore production platform was traced to environmentally assisted cracking (EAC) of UNS G61500 disk spring steel coated with a zinc phosphate ($Zn_3(PO_4)_2$)

⁽¹⁾ Unified Numbering System for Metals and Alloys (UNS)

conversion coating. The hydraulic fluid (Fluid B) in the affected equipment was an aqueous ethylene glycol (EG) with a brand-specific proprietary inhibitor package and it caused cracking of the equipment at approximately 50°C. Other hydraulic systems (Fluid C) on the same platform using a different commercial aqueous EG solution had not experienced similar failures as of the incident field investigation.

Hydrogen embrittlement (HE) was considered as one possible cause of the EAC. An electrochemical study was conducted to characterize the electrochemical properties of the zinc phosphate conversion coating on the disk spring exposed to three different hydraulic fluids, which are:

- Fluid A – A benchmark aqueous fluid containing 46% EG without additives added,
- Fluid B – A commercial hydraulic fluid that results in the cracking of the conversion-coated disk spring, and
- Fluid C – A commercial hydraulic fluid used on the same offshore platform with no history of field failure of the conversion-coated disk springs.

Specific electrochemical conditions must be present for the hydrogen charging precursor step of HE, specifically the OCP of the phosphate conversion-coated steel must be cathodic to (negative to) the hydrogen evolution reaction (HER) threshold potential in order for hydrogen ions to be reduced to atomic hydrogen on metal surface, which then diffuse into the steel to cause HE.

The objectives of the study were to assess:

- The effects of the two aqueous EG hydraulic fluids on the phosphate conversion-coated disk spring steel, and
- Determine whether the specific electrochemical conditions for HE may have been present in the cracked disk spring steel.

EXPERIMENTAL PROCEDURE

Materials

Working electrodes (WEs) used in the work were machined from a conversion coated UNS G61500 disk spring steel. The WEs were rectangular steel prisms nominally 0.25-inch (6.3-mm) square by 3.5 inches (90 mm) long, coated on two opposing faces with zinc phosphate conversion coating less than 100 µm thick. All exposed machined surfaces were masked with a proprietary baked fluoropolymer coating such that only the conversion-coated surfaces were exposed to the test solution. The conversion coatings were polished from a few of these electrodes to characterize the cathodic polarization behavior of uncoated substrate steel.

Two gallons of each of the two commercial hydraulic fluids (Fluid B and Fluid C) were used in the study. A benchmark 46% EG fluid (Fluid A) was prepared from reagent grade ethylene glycol and distilled water.

Testing Methodology

All electrochemical tests were performed using a GAMRY G750⁽²⁾ potentiostat connected to multiple 1-L glass electrochemical kettles via an ECM8™ multiplexer. ⁽³⁾

Before testing, each cell was charged with 900 mL of the respective Fluid (A, B, or C). The fluid was deaerated by purging overnight with ultrahigh purity (UHP) nitrogen while the cell was being chilled or heated to the target temperature.

⁽²⁾⁻⁽³⁾ Gamry Instruments

Once the target temperature was obtained, a coated or bare WE, a counter electrode (carbon rod), and a saturated calomel reference electrode (SCE) installed in a luggin capillary probe apparatus were inserted into each cell through a nitrogen blanket. The cell was purged continuously with UHP nitrogen through the duration of the test run.

The following electrochemical experiments were conducted.

- 7-day OCP vs time surveys. OCP of the conversion-coated steel was recorded at five-minute intervals for 7 days.¹ These surveys were completed in all three hydraulic fluids at 0 °C, 20 °C, 50 °C, and 70 °C,
- Cathodic Potentiodynamic Polarization (CPP) scans. The tests were conducted on conversion-coated steel WEs immersed in all three hydraulic fluids and scanned from OCP to $-1.6 V_{SCE}$ at a rate of -0.167 mV/sec following about 1–2 hours hold to obtain the OCPs.² Since the field EAC occurred at 50 °C in Fluid B, the tests were only performed at 20 °C and 50 °C, where 20 °C tests were used as control.
- CPP scans of bare disk spring steel in Fluid B at 20 °C and 50 °C, and
- Coating degradation-over-time study in which conversion-coated steel electrodes were “aged” in Fluid B at 50°C for 1 hour, 1 day, and 4 days before the execution of CPP scans.

In addition to the above electrochemical experiments, X-ray diffraction (XRD) was performed on deposits from the conversion-coated OCP-vs.-time electrodes to identify the major corrosion products.

RESULTS AND DISCUSSIONS

OCP-Time Survey from Conversion-Coated Steel Electrodes

Post-Exposure Visual Appearance. Figure 1 shows the visual appearance of the zinc phosphate conversion coated electrodes after 7-day exposures at four different temperatures.

- Fluid A. Red-yellowish corrosion products were observed on the specimens after exposure at 20 °C, 50 °C, and 70 °C. while only a slight visible change in appearance was observed after exposure at 0°C.
- Fluid B. No change in the appearance of the conversion coating was observed at any temperature.
- Fluid C. No change in the appearance of the conversion coating was observed at any temperature.

OCP-vs.-Time Plots. The OCP-vs.-Time plots from the four temperatures in the three fluids are shown in Figure 2, while the data extracted from these plots are summarized in Table 1.

- Fluid A.
 - At 0 °C, the OCP of the coated steel was stable at $-0.30 V_{SCE}$ by the end of Day 1.
 - At 20 °C, the OCP of the coated steel was decreasing steadily at 0.02 V/day by the conclusion of elapsed Day 3, reaching $-0.45 V_{SCE}$ by the end of Day 7.
 - At 50 °C, the OCP of the coated steel was decreasing steadily at 0.03 V/day by the conclusion of elapsed Day 3, reaching $-0.60 V_{SCE}$ by the completion of Day 7.
 - At 70 °C, the OCP of the conversion-coated steel was stable at $-0.60 V_{SCE}$ by the conclusion of Day 1.
- Fluid B. The OCPs at 0 °C, 20 °C, and 50 °C stabilized at -0.12 to $-0.13 V_{SCE}$ by the end of elapsed Day 1. The OCP at 70 °C stabilized at $-0.18 V_{SCE}$ by the end of elapsed Day 2.
- Fluid C.
 - At 0 °C, the OCP of the conversion-coated steel was stable at $-0.30 V_{SCE}$ by the conclusion of elapsed Day 2.

- At 20 °C, the OCP of the conversion-coated steel was decreasing steadily at 0.02 V/day by the conclusion of Day 3, reaching $-0.45 V_{SCE}$ by the conclusion of elapsed Day 7.
- At 50 °C, the OCP of the conversion-coated steel was decreasing steadily at 0.03 V/day by the conclusion of elapsed Day 3, reaching $-0.60 V_{SCE}$ by the end of elapsed Day 7.
- At 70 °C, the OCP of the conversion-coated steel was stable at $-0.60 V_{SCE}$ by the conclusion of elapsed Day 1.

CPP Scan Results from Conversion-Coated Steel Electrodes

The plots of the CPP scans for the conversion-coated electrodes are shown in Figure 3 while the data extracted from these plots are summarized in Table 2.

In Fluid A, typical cathodic currents were obtained in the CPP scans at both 20 °C and 50 °C over the entire scan range from the OCP to $-1.6 V_{SCE}$. At equal potentials, the currents obtained at 50 °C were greater than at 20 °C. The low electrolyte conductivity retarded the kinetics of the HER, and no well-defined HER potential was obtained at both temperatures.

In Fluid B, at 20 °C, the current in the CPP curve from the OCP to $-1.6 V_{SCE}$ was cathodic over the entire scanned potential range, with an HER potential of $-0.85 V_{SCE}$.

At 50 °C, the current was cathodic from the OCP to $-0.55 V_{SCE}$, anodic to $-0.66 V_{SCE}$, and cathodic again from $-0.66 V_{SCE}$ to $-1.60 V_{SCE}$, creating an anodic loop between $-0.55 V_{SCE}$ and $-0.66 V_{SCE}$, as shown in Figure 3. anodic loops occurring cathodic to the OCP generally reflect oxidation of a dissolved substance in the fluid. According to the sponsor of the test program, the substance could be an oxygen scavenger dissolved in Fluid B. The HER potential was $-0.85 V_{SCE}$ at 20 °C and $-0.70 V_{SCE}$ at 50 °C.

In Fluid C, cathodic currents were obtained during the CPP scan at 20 °C and 50 °C. Since the inhibitor package did not include the oxygen scavenger dissolved in Fluid B, the anodic loops were not observed between $-0.55 V_{SCE}$ and $-0.66 V_{SCE}$. The HER potentials obtained at 20 °C and 50 °C were at approximately $-1.0 V_{SCE}$ and $-0.95 V_{SCE}$, respectively, negative to the values obtained in Fluid B.

CPP Scan Results from a Bare Steel Electrode in Fluid B

To further investigate the failure mechanism of the UNS G61500 disk spring steel exposed to Fluid B, the zinc phosphate conversion coating was polished off and the electrochemical behaviors of the bare electrodes were studied at 20 °C and 50 °C through the CPP method, the results of which are shown in Figure 4.

At 20 °C, it was not surprising to observe that the OCP ($-0.28 V_{SCE}$) of the bare steel electrode more negative than that obtained on the conversion-coated electrode ($-0.12 V_{SCE}$). The CPP curve for the bare steel electrode exhibited an anodic loop between $-0.51 V_{SCE}$ and $-0.75 V_{SCE}$. However, no anodic loop was shown on the coated electrode in the fluid (Figure 3), suggesting the conversion coating somewhat blocked the fluid from reaching the metal substrate surface at this temperature.

At 50 °C, the OCP of the bare steel substrate was determined as $-0.81 V_{SCE}$, more negative than HER potential ($-0.7 V_{SCE}$) obtained from the coated electrode, suggesting that hydrogen evolution reaction could occur on the steel substrate and result in HE if the conversion coating lost physical barrier property and exposed the steel to the fluid at the temperature. Additionally, the anodic loop manifested in the CPP curve from conversion-coated steel is not visible in Figure 4 because these phenomena occur above the OCP of the bare steel electrode.

Coating Degradation Over Time Study