A Study of Galvanic Corrosion in Stagnant Ammonium Bisulfide Solution

H. A. Al-Mazeedi, A. Al-Farhan, N. Tanoli, and L. Abraham

Petroleum Research Center, Kuwait Institute for Scientific Research, P.O. Box 24885, 13109, Safat, Kuwait

Correspondence should be addressed to H. A. Al-Mazeedi; hmazidi@kisr.edu.kw

Received 17 October 2018; Revised 25 December 2018; Accepted 31 December 2018; Published 5 February 2019

Guest Editor: Shengxi Li

Copyright © 2019 H. A. Al-Mazeedi et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Galvanic corrosion of carbon steel (CS) coupled to four different alloys, namely, 316 SS, 321 SS, Incoloy 825, and 2205 SS, was studied in deaerated 3.5% ammonium bisulfide solution (ABS) at 60°C by electrochemical techniques under stagnant condition. The electrochemical work included the measurements of the potential of separate alloys as well as the measurement of galvanic potential and galvanic current as a function of time and Evans (polarization) diagrams of coupled metals. The impact of galvanic coupling on the anodic and cathodic reaction rates was determined. It was found that the CS suffered galvanic corrosion when it was coupled to all of the selected alloys but at different rates; so, it is recommended to avoid the galvanic coupling of CS with any of the noble alloys in stagnant deaerated 3.5% ABS at 60°C. Results indicated that the best alloy to be used with the CS in stagnant deaerated 3.5% ABS solution at 60°C is SS2205 since the galvanic couple has the lowest CR with a less negative Ecorr value, indicating that CS corrodes at a lower rate when it is coupled to SS2205 in this environment.

1. Introduction

Galvanic corrosion is an enhanced corrosion between two or more electrically connected different metals originally, where the more active one acts as anode and corrodes, while the less active one is cathode [1, 2]. This will increase the corrosion rate of the anodic metal and reduces that of the cathodic alloy. The active metal is the metal with more negative potential in the electromotive force series of metals, while the noble metal is the metal with less negative potential [3, 4]. The magnitude of the potential difference between dissimilar metals cannot be used to predict the severity of galvanic corrosion, because electrochemical potentials are a function of the thermodynamics and not of the reaction kinetics that may occur. It is the surface kinetics that determines the severity of galvanic corrosion [5, 6].

Ammonium bisulfide (NH₄HS, ABS) corrosion is a well-known problem in the petroleum refining industry. The affected locations and equipment are the stripper overheads of hydrotreater and hydrocracker reactor effluent air coolers (REAC) and the associated piping [7, 8]. There have been numerous reported case histories of severe corrosion problems of carbon steel (CS) and other alloys, and this corrosion has been the cause of several major fires, explosions, and costly unscheduled shutdowns [7, 8]. The CS mostly suffers from general corrosion and erosion-corrosion in stagnant and flowing ammonium bisulfide (ABS) solution, respectively. The extent of this corrosion is increased when the CS is coupled to a more noble metal. Sour ABS solution contains a high concentration of H₂S and contaminants such as chloride, cyanide, and dissolved oxygen. The resulting alkaline sour water solution containing the dissolved ABS salts is highly corrosive [7, 8].

A common practice in refineries to prevent ammonium bisulfide salt blocking the tubes in coolers or heat exchangers is washing them with water, which results in a corrosive ABS that causes uniform corrosion, underdeposit corrosion, and erosion corrosion [9, 10]. This kind of corrosion is named in literature as ammonium bisulfide corrosion, which causes severe corrosion problems in the CS and other alloys leading to leaking and several major fires, explosions, and costly unscheduled shutdowns. The leaking CS tubes are sometimes replaced by other alloys such as: 430 stainless steel (SS), 321 SS, and alloy 800 [9–11]. This replacement of the coolers and
Table 1: Chemical compositions of the alloys (in Wt %).

| Elements | Carbon Steel | SS 316 | SS 321 | Incoloy 825 | SS 2205 |
|----------|--------------|--------|--------|-------------|---------|
| Fe       | 99.4         | 68.91  | 70.13  | 27.72       | 66.0    |
| Cr       | -            | 16.43  | 18.94  | 20.09       | 22.1    |
| Ni       | -            | 10.27  | 9.08   | 46.09       | 5.6     |
| Mo       | -            | 2.04   | 0.20   | 2.60        | 3.1     |
| Mn       | 0.46         | 1.87   | 1.34   | -           | 2.0     |
| Ti       | -            | -      | 0.31   | 1.06        | -       |
| Cu       | -            | 0.48   | -      | 2.19        | -       |
| Nb       | -            | -      | -      | 0.25        | -       |
| Si       | -            | -      | -      | -           | 1.0     |
| N        | -            | -      | -      | -           | 0.2     |

Heat exchanger tubes (CS with other alloys) might lead to galvanic corrosion in the ABS, as the header box and the tube sheet are still CS and the latter is connected directly to the tubes.

The petroleum refining company, Kuwait National Petroleum Company (KNPC) confirmed that they are interested in a study of the galvanic corrosion of the CS, coupled with five different alloys (316 SS, 321 SS, alloy 2205, and Incoloy 825) in their real solution, that is, 3.5% ABS with whatever contaminants in it, and at 60°C. Galvanic corrosion is expected when the CS tubes in the heat exchangers are upgraded in metallurgy while the header box and the tube sheet are still CS, and when SS ferrules are fitted into CS tubes at inlets and outlets. The main aim of the current study is to assess the galvanic corrosion of CS coupled with different alloys (viz., SS 316, SS 321, Incoloy 825, and SS 2205) in 3.5% ABS solution collected from the petroleum refining company.

2. Experimental Work

The chemical compositions of the tested alloys are shown in Table 1. Specially designed specimen holders, specimens and salt bridges were used for the experiments. Each specimen was cut and machined into bullet-shaped samples with a length of 2 cm and a diameter of 0.8 cm and a surface area of 6 cm², with a thread part at the bottom for electrical connection. Special stoppers were also prepared for holding the counter electrode (CE) in the corrosion cell. The solution used in all of the experiments was 3.5% ABS, which was received from the local petroleum refinery. Chemical analysis of the ABS solution is given in Table 2.

In corrosion tests for uncoupled electrodes (CS, SS 316, SS 321, Incoloy 825, and SS 2205), the specimens were prepared by grinding to 600 grit finish using water cooled abrasive papers. The prepared specimens were screwed to the specimen holder. Saturated calomel electrode (SCE) was used as a reference electrode, and platinum electrode was used as a counter electrode (CE). SCE was placed in a Lugin tube filled with saturated KCl solution. The specimen, the Lugin tube containing the SCE, and the CE were immersed in the 3.5% ABS solution inside the corrosion cell (Figure 1(a)). After setting up the corrosion cell, as shown in Figure 1(a) the entire cell was immersed in a water bath (Figure 1(b)), which was adjusted to 60°C, and then the test cell was deaerated by N₂ gas for 10 min. The experiments were conducted using a software controlled potentiostat, Biologic Model M300.

The corrosion potential of each alloy (CS, SS 316, SS 321, Incoloy 825, and SS 2205) immersed in stagnant ABS was measured versus external SCE under open circuit conditions as a function of time until the quasisteady state was reached. Each test run took five days. Linear polarization measurements (LPR) were taken after reaching the steady state in order to determine the polarization resistance (Rₚ) and the corrosion rate (CR) of each metal. After the experiments were completed, the ABS was analyzed and the specimen’s surface was examined using the digital camera and the scanning electron microscope (SEM). The SEM examinations were performed using a JEOL JSM-IT300. The specimen’s surface was cleaned with deionized water in the ultrasonic bath and then dried with acetone before SEM examination.

In galvanic corrosion tests for coupled electrodes (CS versus SS 321, CS versus SS 316, CS versus 825, and CS versus SS 2205), the specimens were ground using 600 SiC papers and inserted in the specimen holder. The reference electrode (SCE) was placed in a Lugin tube filled with saturated KCl solution. The CS specimen was used as a working electrode (WE), while the other metal specimen was used as a counter electrode (CE). The corrosion cell was deaerated by N₂ gas for 10 min. The corrosion potential of the galvanic couple was then measured under the open circuit condition as a function of time until the steady state was attained. Also, the galvanic current (I) versus time was measured using a zero resistance ammeter (ZRA). Each test run took five days. After the quasisteady-state values of current and potential were attained, the polarization measurements were taken using the ZRA with a scan rate of 0.166 mV/s and a scan range of -1V to 1V, and as a result, an Evans diagram (potential versus log of current) was plotted for each galvanic couple at stagnation. After the experiments, the specimens’ surfaces were examined using the SEM and EDS.

3. Results and Discussion

The electrochemical behavior of CS and four different alloys were investigated in the deaerated 3.5% ABS at 60°C under
Table 2: Chemical composition of ABS solution.

| Analytical Item          | Unit  | Result       |
|--------------------------|-------|--------------|
| Sodium (as Na)           | mg/l  | 705.19       |
| Calcium (as Ca)          | mg/l  | 339.69       |
| Magnesium (as Mg)        | mg/l  | 63.56        |
| Potassium (as K)         | mg/l  | 148.85       |
| Strontium (as Sr)        | mg/l  | 0.0005 - 0.01|
| Barium (as Ba)           | mg/l  | 0.001 - 0.01 |
| Iron (as Fe)             | mg/l  | 0.001 - 0.07 |
| Boron (as B)             | mg/l  | 2.33         |
| Lithium (as Li)          | mg/l  | 0.001 - 0.04 |
| Silicon (as Si)          | mg/l  | 49.96        |
| Chloride (as Cl\textsuperscript-\textsuperscript-) | ppm  | 23928.78     |
| Hydrogen Sulfide (H\textsubscript{2}S) | ppm  | 17786.33     |
| Ammonia (NH\textsubscript{3}) | ppm  | 35858.17     |
| NH\textsubscript{4}HS     | ppm   | 2.68         |
| Total dissolved solids (TDS) (calculated) | mg/l | 44443.02     |
| Cyanide                  | ppm   | 2.68         |
| Oil & Grease             | ppm   | 82           |
| Carbonate (as CO\textsubscript{3}\textsuperscript{2-}) alkalinity | mg/l | 13968.14     |
| Bicarbonate (HCO\textsubscript{3}\textsuperscript{-}) alkalinity | mg/l | 6690.48      |
| OH-alkalinity            | mg/l  | 4533.79      |
| Total Alkalinity         | mg/l  | 17555.29     |
| pH at 25°C               | mg/l  | 9.26         |
| Hardness                 | ppm   | 1041.91      |
| Density at 25°C          | g/cm\textsuperscript{3} | 1.00         |

stagnant conditions. The investigation was made on the individual metals as well as on the galvanic couples, which consisted of CS against the four alloys. The data used to support the findings of this study are available from the corresponding author upon request.

3.1. Results for Uncoupled Alloys. The variation of the corrosion potential of each metal immersed in the stagnant deaerated ABS solution was measured under open-circuit conditions as a function of time till the quasi-steady-state values were reached. Figure 2 shows the changes in the corrosion potential for the different metals. The tests were conducted in triplets and the average was taken. The average potential values for all of the tested alloys in stagnant deaerated 3.5% ABS solution at 60°C were plotted versus time. From Figure 2, it can be seen that the steady-state potentials...
Table 3: Parameters measured for the alloys in the ABS solution at 60°C.

| Alloy Type | B (mV) | Equivalent Weight | Area (cm²) | Density (g/cm³) |
|------------|--------|-------------------|------------|-----------------|
| CS         | 4.43   | 27.92             | 6          | 7.85            |
| SS316      | 1.17   | 25.50             | 6          | 7.99            |
| A825       | 1.13   | 25.52             | 6          | 8.14            |
| SS321      | 4.83   | 25.26             | 6          | 8.00            |
| SS2205     | 1.70   | 36.28             | 6          | 7.91            |

Figure 2: Average potential versus time for all tested alloys in stagnant deaerated 3.5% ABS at 60°C.

Figure 3: Average corrosion rates versus time for all the tested alloys in stagnant deaerated 3.5% ABS at 60°C.

From the visual observation, it was noticed that all of the tested alloys in 3.5% ABS in stagnant condition were shiny and not corroded, even SS321. On the other hand, the CS samples had a surface film that was orange in color, reflecting slight corrosion (Figure 4). This observation was identical with the SEM results that showed clean uncorroded surfaces for all of the tested alloys, except for the CS, which was slightly corroded in some places.

From the visual observation, it was noticed that all of the tested alloys in 3.5% ABS in stagnant condition were shiny and not corroded, even SS321. On the other hand, the CS samples had a surface film that was orange in color, reflecting slight corrosion (Figure 4). This observation was identical with the SEM results that showed clean uncorroded surfaces for all of the tested alloys, except for the CS, which was slightly corroded in some places.

3.2. Results for Coupled Alloys. Alloys under study (SS316, SS2205, SS2205, SS2205, and SS321) were coupled with CS in separate experiments in stagnant, deaerated 3.5% ABS at 60°C. The experiments were conducted in triplicate for accuracy. For each couple, potential (E) versus time was measured till the quasi-steady state was reached, and current (I) versus time was measured using a ZRA. For each couple, the average results of E versus time were calculated. Then, the average potential values for all galvanic couples were plotted in a comparative graph (Figure 5).

From the graph, it can be seen that the potential versus time for the galvanic couples in general started from almost the same potential value and had almost the same trend but with different values of potential and time except for the CS versus SS321 couple. In CS coupled to SS316 and SS2205, their potential started from -0.555 V, increased further, and then fluctuated about the same average value of potential for the first 7 h and then sharply increased to a more noble value, reaching a quasi-steady-state value of -0.53 V. The behavior
of the galvanic couple CS/SS 2205 had a similar trend but
with a slower rate where the potential started from -0.555
V, increased further, and then fluctuated about the same
average value of potential for the first 10 h and then sharply
increased to a more noble value, reaching a quasi-steady-
state value of -0.5475 V. The potential for the CS versus
SS321 couple started from -0.555 V and then fluctuated about
the same average value of the potential for the first 2 h.
Then, the value increased sharply to a more noble value,
reaching a steady-state value of -0.5425 V between 10 and
20 h, and then rose to another quasi-steady-state value of
-0.53 V.

After the steady-state values of current and potential
were attained, the polarization measurements were measured
using the ZRA, and as a result, Evans diagrams (potential
versus log of current) were plotted. For each couple, the aver-
gages were calculated, and a comparative graph for all coupled
alloys was plotted (Figure 6). The results show that the best
alloy to be coupled to CS under stagnant condition is SS 2205
since it provides the lowest $I_{corr}$, while the other galvanic
couples provide higher $I_{corr}$ values with more negative $E_{corr}$ values
indicating that CS corrodes at a higher rate when it is coupled
to them. Finally, the quantitative relationship connecting
the principal controlling factors of electrochemical corrosion
was determined through studying the kinetics of the anodic
and the cathodic reactions. According to Tomashov [12], the
ratios $dE_c/di_a$ and $dE_c/di_a$ represent the true polarization of
the cathode and the anode, respectively, at a given current
density ($i$). The reciprocal derivative, $d_i/dE_i$, is a measure of
the actual electrode reaction rate and is called the effective
electrode process. Based on the aforementioned ratios, the
different polarization parameters were calculated, namely,
percentage of anodic and cathodic control (the kinetics of the
cathodic and the anodic reactions), and the results are given
in Table 4.

Table 4 shows that the couple CS/Incoloy 825 had the
highest $I_{corr}$ (and CR) and the most negative $E_{corr}$, which
means that in stagnant deaerated 3.5% ABS solution at 60° C,
the CS sample corroded at the highest rate when it was
coupled to Incoloy 825. On the other hand, the lowest $I_{corr}$
and CR was found for CS/SS 2205 couple. Also, it was noticed
that for all the couples, the anodic control was higher than the
cathodic control indicating that the corrosion of CS was the
dominant factor in the galvanic couples in stagnant deaerated

---

**Figure 4:** Cleaned alloy specimens after testing in stagnant 3.5% ABS at 60°C.

**Figure 5:** Average potential versus time for all galvanic couples in stagnant deaerated 3.5% ABS at 60°C.

**Figure 6:** Evans diagrams for all galvanic couples in stagnant deaerated 3.5% ABS at 60°C.
Table 4: Percentages of anodic and cathodic control for stagnant solution.

| Couples   | $E_a$ (Anodic) CS (V) | $E_c$ Cathodic (Other alloys) | $E_m = E_{corr}$ (V) | $I_{corr}$ (μA) | CR (mpy) | $\Delta E_c = E_c - E_m$ (V) | Degree of Cathodic Control (%) | $\Delta E_A = E_m - E_a$ (V) | Degree of Anodic Control (%) |
|-----------|-----------------------|------------------------------|-----------------------|------------------|----------|-------------------------------|-------------------------------|-------------------------------|------------------------------|
| CS / SS2205 | -0.5147               | -0.5541                     | -0.5347              | 5.71             | 0.44     | 0.0194                        | 49.15                         | 0.0200                        | 50.85                         |
| CS / SS316   | -0.5155               | -0.5555                     | -0.5358              | 6.97             | 0.54     | 0.097                        | 49.16                         | 0.0203                        | 50.84                         |
| CS / SS321   | -0.5190               | -0.5595                     | -0.5398              | 6.80             | 0.52     | 0.097                        | 48.70                         | 0.0208                        | 51.30                         |
| CS / 825     | -0.5241               | -0.5644                     | -0.5449              | 9.70             | 0.75     | 0.095                        | 48.29                         | 0.0208                        | 51.71                         |
3.5% ABS at 60°C. Also this table shows that the CS suffered galvanic corrosion when it was coupled to all of the selected alloys.

From the visual observation, it was noticed that all of the tested alloys in 3.5% ABS at stagnant conditions were shiny and did not suffer corrosion, except the CS specimens, which were corroded (Figure 7). This observation was identical with the SEM results that showed clean specimen surfaces, without any noticeable corrosion for all of the tested alloys, except for the CS alloy, which was severely corroded (Figure 8). In fact CS specimens showed deeper attack at isolated locations. From all the above results, it is recommended to avoid the galvanic coupling of CS with any of the noble alloys in deaerated 3.5% ABS at 60°C. Inhibitors can also be used for reducing the galvanic corrosion in case avoiding the coupling is not possible. In general, galvanic corrosion can be prevented by employing different methods such as using inhibitors or coatings or coupling to a third metal that acts as an anode to both original alloys. Also, galvanic corrosion can be minimized by selecting a combination of metals close to each other in the galvanic series, avoiding the use of a small anode area and a large cathode area, changing the environment, and breaking the conductive path between the coupled alloys [13, 14].

4. Conclusions

(i) The results show that the best alloy to be used with the CS in stagnant deaerated 3.5% ABS at 60°C is SS 2205 since it has the lowest $I_{corr}$ and, consequently, the lowest CR with a less negative $E_{corr}$ value, indicating that the CS corrodes at a lower rate when it is coupled to SS 2205 in this environment.

(ii) For all the couples, the anodic control is higher than the cathodic control, indicating that the corrosion of CS is the dominant factor in the reaction of the metallic couples in the stagnant and deaerated 3.5% ABS solution at 60°C.

(iii) A study on galvanic corrosion was conducted for all of the couples (CS/SS 321, CS/SS 316, CS/SS 2205, and CS/825) in stagnant and deaerated 3.5% ABS at 60°C. It was found that the CS suffered galvanic corrosion when it was coupled to all of the selected alloys.
Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

Acknowledgments
The authors would like to acknowledge the financial support extended to this project by the Kuwait Institute for Scientific Research (KISR) and the Kuwait National Petroleum Company (KNPC). The authors would like to extend their gratitude to the water laboratory team in KISR for analyzing the ammonium bisulfide solution.

References
[1] R. Baboian and S. Begum, “Corrosion, Galvanic Encyclopedia, Reference Module in Materials Science and Materials Engineering,” in Encyclopedia of Materials: Science and Technology, p. 1689, 2016.
[2] D. Franco, “Volta and the 'Pile,'” in Electrochemistry Encyclopedia, Case Western Reserve University, 2012, https://web.archive.org/web/2012-07-16/http://electrochem.cwru.edu/encycl/art-v01-volta.htm.
[3] S. H. E. Far and A. Davoodi, “Galvanic corrosion behavior of plain carbon steel-B4C composite in 3.5% NaCl solution with electrochemical noise,” Journal of Central South University, vol. 24, no. 1, 2017.
[4] B. O. Hasan, “Galvanic corrosion of carbon steel-brass couple in chloride containing water and the effect of different parameters,” Journal of Petroleum Science and Engineering, vol. 124, pp. 137–145, 2014.
[5] X. Cheng, Y. Wang, C. Dong, and X. Li, “The beneficial galvanic effect of the constituent phases in 2205 duplex stainless steel on the passive films formed in a 3.5% NaCl solution,” Corrosion Science, vol. 134, pp. 122–130, 2018.
[6] R. C. Woollam, A. Huggins, C. Mendez, J. R. Vera, and W. H. Durnie, “Localized corrosion due to galvanic coupling between FeS covered and uncovered areas: Another oilfield myth?” in CORROSION/2013, Paper No. 02715, National Association of Corrosion Engineers, Houston, TX, USA, 2013.
[7] R. J. Horvath, V. V. Lagad, S. Srinivasan, and R. D. Kane, “Prediction and assessment of ammonium bisulfide corrosion under refinery sour water service conditions - Part 2,” in
[8] H. Iwawaki and K. Toba, “Corrosion behavior of steels in concentrated \( \text{NH}_4\text{HS} \) environments,” in CORROSION/2007, Paper No. 7576, National Association of Corrosion Engineers, Houston, TX, USA, 2007.

[9] API 932-A, A Study of Corrosion Control in Hydroprocess Reactor Effluent Air Cooler Systems, American Petroleum Institute Publishing Services, Washington, DC, USA, 1st edition, 2002.

[10] API 932-B, Design, Materials, Fabrication, Operation, and Inspection Guidelines for Corrosion Control in Hydroprocessing Reactor Effluent Air Cooler (REAC) Systems, American Petroleum Institute Publishing Services, Washington, DC, USA, 1st edition, 2004.

[11] A. M. Alvarez and C. A. Robertson, “Materials and design considerations in high pressure HDS effluent coolers,” Materials Performance, vol. 12, no. 5, pp. 16–21, 1973.

[12] N. D. Tomashov, Theory of Corrosion and Protection of Metals - The Science of Corrosion, Macmillan, New York, 1966.

[13] M. G. Fontana, Corrosion Engineering, McGraw-Hill Book Company, Singapore, 3rd edition, 1987.

[14] D. A. Jones, Principles and Prevention of Corrosion, Macmillan Publishing Company, Singapore, 2nd edition, 1992.
