**CAAP Quarterly Report 7**

**06/30/2025**

*Project Name: "Bio-Inspired Rational Design of Bio-Based Inhibitors for Mitigating Internal Corrosion in Metal Pipelines"*

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*Prime University: University of Miami*

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*Reporting Period: 04/01/2025-06/30/2025*

**Project Activities for Reporting Period:**

The primary goal of this report was to identify and evaluate eco-friendly green corrosion inhibitors for protecting gas pipelines. To this end, 59 bio-based surfactants were tested in different corrosion media. Their efficiency was evaluated by weight loss analysis. The study utilized 0.5 M HCl, 3.5 % NaCl, and brine solutions as corrosive environments to compare the inhibition efficiencies of the inhibitors in different corrosive media.

## 1. Conducting Weight Loss Tests to Compare the Efficiency of Bio-based Surfactants

### 1.1. Materials and Methods

Fifty-nine commercially available surfactants were used as inhibitors. The test inhibitors are listed in Table 1.

| No | Inhibitor (Bio-based Surfactant) | No | Inhibitor (Bio-based Surfactant) | No | Inhibitor (Bio-based Surfactant) |
|---|---|---|---|---|---|
| 1 | Greenbentin-LM/010 | 20 | L-35 | 39 | Makon NF-5 |
| 2 | Greenbentin-LM/070 | 21 | F-68 | 40 | Makon NF-12 |
| 3 | Hedipin-CFA/100(1) | 22 | F-108 | 41 | Makon UD-5 |
| 4 | Hedipin-PO/045 VL | 23 | F-127 | 42 | Makon TSP-60 |
| 5 | Hedipin-PS/400 G | 24 | Ethylene Glycol | 43 | Makon P104 |
| 6 | Hedipin-R/2000 G | 25 | Triton X-100 | 44 | Toximul 8321 |
| 7 | Hedipin-R/400 H | 26 | Tween 20 | 45 | Toximul 8350 |
| 8 | Hedipin-RH/400 | 27 | Tween 80 | 46 | Bio-Soft N1-9 |

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|---|---|---|---|---|---|
| 9 | Imbentin-AG/124S/110 | 28 | Span 20 | 47 | Bio-Soft N91-6 |
| 10 | Imbentin-AG/168S/110 | 29 | Span 80 | 48 | Bio-Soft TA-2 |
| 11 | Imbentin-AG/168S/250 | 30 | Glucopon 50 G | 49 | Step-Flow 26F |
| 12 | Imbentin-AG/168S/500 | 31 | Glucopon 215 UP | 50 | Tergitol™ 15-S-30 |
| 13 | Imbentin-AG/168S/800 | 32 | Glucopon 225 DK | 51 | Ecosurf™ EH-6 |
| 14 | Imbentin-C/91/025 | 33 | Glucopon 425 N | 52 | Igepal® CA-720 |
| 15 | Imbentin-C/91/060 | 34 | Makon L61 | 53 | Triton™ X-305 solution |
| 16 | Imbentin-T/400 | 35 | Makon L62 | 54 | Pluronic® 10R5 |
| 17 | Imbentin-T/65 | 36 | Makon L101 | 55 | Pluronic® P-123 |
| 18 | 31R1 | 37 | Makon TD-3 | 56 | Tomamine Amphoteric16 |
| 19 | L-31 | 38 | Makon TD-30 | 57 | Adogen® 464 |
| 58 | Kao Findet MB-212 | 59 | Altapur™ Hydro P-240 | | |

A36 steel specimens (McMaster-Carr, US) with the composition of C: 0.19 %, Cr: 0.04 %, Cu: 0.03 %, Mn: 0.76 %, Mo: 0.01 %, Ni: 0.01 %, Si: 0.019 %, P: 0.01 %, S:0.008 %, V: 0.001 % and Fe: remainder were used in all the experimental studies. The specimen dimensions used in the weight loss experiment were 20 mm x 10 mm x 1.5 mm. Unpolished steel specimens were used for this study.

Three different corrosive media were prepared as follows:

1. **0.5 M HCl solution**: The electrolyte solution of 0.5 M HCl was prepared by diluting 37 % analytical-grade HCl (Sigma-Aldrich) with deionized water.
2. **3.5 % NaCl solution:** The solution was prepared by dissolving 35 g of NaCl in deionized water to obtain a 1 L solution.
3. **Brine solution:** The solution was prepared by dissolving 17.31 g of NaCl, 0.78 g of CaCl, 2.71 g of MgCl, 0.54 g of $Na_2SO_4$, and 1.83 g of $NaHCO_3$ in deionized water to obtain a 1 L solution. The initial pH of the prepared solution was measured to be 7.42. Before initiating the weight loss test, carbon dioxide ($CO_2$) gas was dissolved into the brine solution, and the pH was adjusted to fall within the range of 4.5 to 5.0. During the experiment, the dissolution of $CO_2$ gas into the solution continued.

The bio-based surfactant inhibitors were dissolved separately in the 0.5 M HCl solution, the 3.5 % NaCl solution, and the $CO_2$-injected brine solution to achieve concentrations of 0.05 %.

### 1.2. Weight Loss Measurements

Weight loss measurements were conducted to evaluate and compare the corrosion behavior and inhibition efficiencies of bio-based surfactant inhibitors on A36 steel specimens exposed to different corrosive environments, namely a 0.5 M HCl solution, a 3.5% NaCl solution, and a $CO_2$-injected brine solution. These assessments provided quantitative insights into the extent of material degradation, enabling the investigation of how varying environmental conditions impact corrosion rates. By analyzing weight loss over a defined period, the effectiveness of bio-based surfactants as corrosion inhibitors across multiple aggressive media was determined, contributing to a deeper understanding of their performance and the durability of A36 steel under diverse exposure scenarios.

First, A36 steel specimens (20 mm x 10 mm x 1.5 mm) were immersed in corrosive solutions in the absence and presence of bio-based surfactant inhibitors for 7 days of measurements. After the immersion period, the steel specimens were rinsed with deionized water and acetone, dried in air, and reweighed. The weight loss was calculated as the difference between the weight of the specimens before and after 7 days of immersion.

Three replicates were used for each test. The average relative mass loss of the A36 steel specimens was determined from three individual measurements. All the measurements were taken at room temperature. The corrosion rate (CR) and inhibition efficiency (IE) were calculated by the following equations:

$$CR\ (mmy) = \frac{KW}{\rho A t} \tag{1}$$

where $W$ is the weight loss (in g), $\rho$ is the density (gcm$^{-3}$), $A$ is the exposed area of the specimen (cm$^2$), and $t$ is the exposure time (h). $K$ is a constant that can be varied to calculate the corrosion rate in various units. For the case of mm/year for CR calculation, $K$ is equal to $8.75 \times 10^4$.

$$IE_{WL}(\%) = \frac{CR_0 - CR_i}{CR_0} \times 100 \tag{2}$$

where $CR_0$ and $CR_i$ are the corrosion rates of A36 steel in the absence and presence of inhibitors, respectively.

## 2. Results and Discussion

### 2.1. Weight Loss Measurements

#### 2.1.1. Weight Loss Measurements in 0.5 M HCl Solution

The corrosion behavior of A36 steel in 0.5 M HCl solution, both in the absence and presence of 0.05% bio-based surfactant inhibitors, was investigated through weight loss measurements over a 7-day immersion period, with the results presented in Table 2. For all tested inhibitors, the presence of a 0.05% concentration resulted in enhanced inhibition efficiency, indicating effective adsorption of the inhibitor molecules onto the A36 steel surface and the subsequent formation of a protective barrier against corrosion. This adsorption enhances surface coverage and facilitates the formation of a protective barrier against the corrosive medium. Among the tested surfactants, Adogen 464 exhibited the highest inhibition efficiency, reaching 95.28% under the specified conditions.

**Table 2:** The weight loss parameters obtained for A36 steel specimens in 0.5 M HCl solution without and with the 0.05 % bio-based surfactant inhibitors.

| No | Inhibitor | IE (%) | No | Inhibitor | IE (%) |
|---|---|---|---|---|---|
| 1 | Greenbentin-LM/010 | 56.43 | 31 | Glucopon 215 UP | 33.39 |
| 2 | Greenbentin-LM/070 (MB) | 81.76 | 32 | Glucopon 225 DK | 48.69 |
| 3 | Hedipin-CFA/100(1) | 85.59 | 33 | Glucopon 425 N | 68.37 |
| 4 | Hedipin-PO/045 VL | 67.38 | 34 | Makon L61 | 82.19 |
| 5 | Hedipin-PS/400 G (MB) | 74.05 | 35 | Makon L62 | 81.87 |
| 6 | Hedipin-R/2000 G | 80.73 | 36 | Makon L101 | 83.87 |
| 7 | Hedipin-R/400 H | 84.10 | 37 | Makon TD-3 | 88.97 |
| 8 | Hedipin-RH/400 | 73.06 | 38 | Makon TD-30 | 82.65 |
| 9 | Imbentin-AG/124S/110 90% (MB) | 77.65 | 39 | Makon NF-5 | 90.48 |
| 10 | Imbentin-AG/168S/110 | 74.77 | 40 | Makon NF-12 | 93.62 |
| 11 | Imbentin-AG/168S/250 | 80.04 | 41 | Makon UD-5 | 88.23 |
| 12 | Imbentin-AG/168S/500-AA | 73.56 | 42 | Makon TSP-60 | 77.64 |
| 13 | Imbentin-AG/168S/800 (1) (MB) | 79.58 | 43 | Makon P104 | 82.57 |
| 14 | Imbentin-C/91/025 | 79.70 | 44 | Toximul 8321 | 82.40 |
| 15 | Imbentin-C/91/060 | 84.71 | 45 | Toximul 8350 | 82.95 |
| 16 | Imbentin-T/400 | 81.90 | 46 | Bio-soft N1-9 | 83.40 |
| 17 | Imbentin-T/65 | 73.64 | 47 | Bio-soft N91-6 | 88.06 |
| 18 | 31R1 | 78.91 | 48 | Bio-soft TA-2 | 91.98 |
| 19 | L-31 | 80.76 | 49 | Step-flow 26F | 82.38 |

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|---|---|---|---|---|---|
| 20 | L-35 | 80.45 | 50 | Tergitol™ 15-S-30 | 85.55 |
| 21 | F-68 | 77.21 | 51 | Ecosurf™ EH-6 | 89.39 |
| 22 | F-108 | 81.19 | 52 | Igepal® CA-720 | 87.61 |
| 23 | F-127 | 81.63 | 53 | Triton™ X-305 solution | 82.56 |
| 24 | Ethylene Glycol | 11.45 | 54 | Pluronic® 10R5 | 83.02 |
| 25 | Triton X-100 | 83.49 | 55 | Pluronic® P-123 | 79.69 |
| 26 | Tween 20 | 85.49 | 56 | Tomamine Amphoteric 16 | 86.40 |
| 27 | Tween 80 | 86.26 | 57 | Adogen® 464 | 95.28 |
| 28 | Span 20 | 39.37 | 58 | Kao Findet MB-212 | 88.53 |
| 29 | Span 80 | 30.51 | 59 | Altapur™ Hydro P-240 | 47.16 |
| 30 | Glucopon 50 G | 49.31 | | | |

In acidic environments, iron dissolution as well as hydrogen evolution occur [2]. Visual observations showed that the hydrogen evolution decreased (i.e., an increase in the inhibition effect of inhibitors) upon the addition of the inhibitor. Therefore, the corrosion rate of A36 steel specimens decreased in the presence of the inhibitors. This could be attributed to the corrosion inhibition mechanism of inhibitors, which can be identified with the adsorption of the molecules of inhibitors at the steel/aggressive solution interface [3].

### 2.1.2. Weight Loss Measurements in 3.5 % NaCl Solution

The corrosion behavior of A36 steel in 3.5% NaCl solution was evaluated through weight loss measurements in both the absence and presence of 0.05% bio-based surfactant inhibitors. The results, summarized in Table 3, show that certain surfactants significantly improved corrosion protection, as evidenced by higher inhibition efficiencies. Among the tested inhibitors, Hedipin-RH/400 exhibited the highest inhibition efficiency, reaching 64.9% at the specified concentration in 3.5% NaCl solution.

**Table 3:** The weight loss parameters obtained for A36 steel specimens in 3.5 % NaCl solution without and with the 0.05 % bio-based surfactant inhibitors.

| No | Inhibitor | IE (%) | No | Inhibitor | IE (%) |
|---|---|---|---|---|---|
| 1 | Greenbentin-LM/010 | 13.56 | 31 | Glucopon 215 UP | 22.73 |
| 2 | Greenbentin-LM/070 (MB) | 13.08 | 32 | Glucopon 225 DK | -30.33 |

| | | | | | |
|---|---|---|---|---|---|
| 3 | Hedipin-CFA/100(1) | 43.17 | 33 | Glucopon 425 N | 3.16 |
| 4 | Hedipin-PO/045 VL | 20.35 | 34 | Makon L61 | 0.68 |
| 5 | Hedipin-PS/400 G (MB) | 60.79 | 35 | Makon L62 | 19.61 |
| 6 | Hedipin-R/2000 G | 61.22 | 36 | Makon L101 | 12.55 |
| 7 | Hedipin-R/400 H | 64.90 | 37 | Makon TD-3 | -23.30 |
| 8 | Hedipin-RH/400 | 20.96 | 38 | Makon TD-30 | 12.94 |
| 9 | Imbentin-AG/124S/110 90% (MB) | 7.90 | 39 | Makon NF-5 | -6.22 |
| 10 | Imbentin-AG/168S/110 | 35.51 | 40 | Makon NF-12 | 9.27 |
| 11 | Imbentin-AG/168S/250 | 58.17 | 41 | Makon UD-5 | -20.11 |
| 12 | Imbentin-AG/168S/500-AA | 59.96 | 42 | Makon TSP-60 | 2.39 |
| 13 | Imbentin-AG/168S/800 (1) (MB) | 45.01 | 43 | Makon P104 | 5.46 |
| 14 | Imbentin-C/91/025 | 6.79 | 44 | Toximul 8321 | 2.13 |
| 15 | Imbentin-C/91/060 | 8.25 | 45 | Toximul 8350 | -17.90 |
| 16 | Imbentin-T/400 | 42.45 | 46 | Bio-soft N1-9 | 4.58 |
| 17 | Imbentin-T/65 | 49.03 | 47 | Bio-soft N91-6 | 3.02 |
| 18 | 31R1 | -28.64 | 48 | Bio-soft TA-2 | -12.83 |
| 19 | L-31 | -35.92 | 49 | Step-flow 26F | 33.89 |
| 20 | L-35 | -2.83 | 50 | Tergitol™ 15-S-30 | -5.20 |
| 21 | F-68 | 6.61 | 51 | Ecosurf™ EH-6 | -30.90 |
| 22 | F-108 | -26.41 | 52 | Igepal® CA-720 | -16.14 |
| 23 | F-127 | 15.13 | 53 | Triton™ X-305 solution | 1.12 |
| 24 | Ethylene Glycol | -9.18 | 54 | Pluronic® 10R5 | -11.00 |
| 25 | Triton X-100 | 7.28 | 55 | Pluronic® P-123 | 4.15 |
| 26 | Tween 20 | -29.59 | 56 | Tomamine Amphoteric 16 | 29.98 |

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|---|---|---|---|---|---|
| 27 | Tween 80 | 15.29 | 57 | Adogen® 464 | -23.05 |
| 28 | Span 20 | 22.73 | 58 | Kao Findet MB-212 | 43.61 |
| 29 | Span 80 | 14.70 | 59 | Altapur™ Hydro P-240 | 15.90 |
| 30 | Glucopon 50 G | 9.45 | | | |

The corrosion behavior of metals varies significantly between HCl and NaCl solutions due to differences in their chemical conditions. HCl, a strong acid, dissociates completely in aqueous solutions, providing a high concentration of hydrogen ions ($H^+$), accelerating the anodic dissolution of metals. In contrast, NaCl is a neutral salt that dissociates into sodium ($Na^+$) and chloride ($Cl^-$) ions, with the chloride ions primarily contributing to localized corrosion, such as pitting. Studies have shown that metals exhibit higher corrosion rates in HCl compared to NaCl solutions [4]. This increased rate in HCl is attributed to its strong acidic nature, which leads to more aggressive uniform corrosion. Conversely, in NaCl solutions, corrosion tends to be less severe but can result in localized forms such as pitting.

Studies have shown that the effectiveness of inhibitors and their mechanism of inhibition depend on multiple factors, including the presence of corrosive ions, the chemical structure of the inhibitor, the number of adsorption sites available on the metal surface, and other related parameters. Moreover, it is stated in most studies that organic inhibitors are highly effective in acidic environments, as they strongly adsorb onto the metal surface, forming a protective barrier that mitigates corrosion [5,6]. However, their performance in saline environments, such as a 3.5% NaCl solution, is often limited due to the aggressive nature of chloride ions ($Cl^-$), which can penetrate and destabilize the inhibitor film, leading to localized corrosion, particularly pitting corrosion [7]. This could explain, based on the obtained data from Table 2 and Table 3, why certain inhibitors exhibited a positive effect in HCl, significantly reducing the corrosion rate, while in NaCl, they demonstrated a negative impact, leading to an increase in the corrosion rate.

### 2.1.3. Weight Loss Measurements in $CO_2$-injected Brine Solution

The corrosion performance of A36 steel in a $CO_2$-injected brine environment was assessed through weight loss measurements, both in the absence and presence of selected bio-based surfactant inhibitors. Table 4 presents the results obtained after 7 days of immersion.

The control sample, exposed to the uninhibited $CO_2$-injected brine solution, exhibited a corrosion rate (CR) of 0.008 mm/year. The introduction of bio-based surfactants, namely Pluronic L35 and Pluronic 10R5, led to a notable reduction in the corrosion rate. Specifically, Pluronic L35 reduced the CR to 0.004 mm/year, corresponding to an inhibition efficiency (IE) of 43.5%, while Pluronic 10R5 achieved a CR of 0.005 mm/year with an IE of 37.7%.

These findings suggest that both surfactants are capable of forming protective layers on the steel surface, thereby mitigating the corrosive effects of the $CO_2$-saturated environment. The relatively higher efficiency observed with Pluronic L35 may be attributed to its molecular architecture and adsorption affinity, which likely enhance its ability to inhibit aggressive species from interacting with the metal surface. Overall, the results underscore the potential of bio-based surfactants as environmentally friendly inhibitors in $CO_2$-rich corrosive media.

**Table 4:** The weight loss parameters obtained for A36 steel specimens in $CO_2$-injected brine solution without and with the 0.05 % bio-based surfactant inhibitors.

| No | Inhibitor | CR (mm/year) | IE (%) |
|---|---|---|---|
| 1 | Control ($CO_2$-injected Brine Solution) | 0.008 | - |
| 2 | Pluronic L35 | 0.004 | 43.5 |
| 3 | Pluronic 10R5 | 0.005 | 37.7 |

## 3. Conclusions

The effect of bio-based surfactant inhibitors was investigated using weight loss analysis. The obtained results showed that most of the used inhibitors showed exceptional inhibition efficiency for A36 steel in tested corrosive solutions. The mechanism for the inhibition could be explained by the adsorption of the inhibitor molecules on the metal surface by their functional groups. The adsorbed molecules of inhibitors formed a complex film on the metal and effectively blocked the steel surface from being attacked by the corrosive media.

**Project Financial Activities Incurred during the Reporting Period:**

One Graduate Research Assistant (GRA) at the University of Miami.

Materials and Supplies

Advanced Materials Characterization User Fee

**Project Activities with Cost Share Partners:**

N/A

**Project Activities with External Partners:**

A collaboration with industry partners has been initiated to investigate the practical application of bio-based corrosion inhibitors. This partnership brings valuable industry perspectives into the experimental design, ensuring the research addresses real-world challenges and needs. By engaging closely with industry stakeholders, the research methods will be fine-tuned to enhance their practical relevance, ultimately supporting the effective implementation of these innovative corrosion prevention solutions.

**Potential Project Risks:**

N/A

**Future Project Work:**

- Future research will focus on the evaluation of different types of corrosion inhibitors, including proteins, synthesized molecules, and commercially available formulations, under varying corrosive environments.
- Comprehensive electrochemical and surface analyses will be carried out on selected representative surfactants categorized into distinct groups based on their shared physicochemical characteristics. These groups will be established to enable a more systematic investigation of structure–activity relationships. The selected surfactants will be subjected to in-depth evaluation to elucidate the correlation between their molecular structures and observed inhibition efficiencies.

**Potential Impacts to Pipeline Safety:**

The results of this research have the potential to make a substantial contribution to the advancement of corrosion inhibition technologies aimed at mitigating internal corrosion in oil and gas pipelines.

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