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Understanding Multi-component Corrosion Inhibitor Adsorption Kinetics

Introduction and Background

The cost of corrosion worldwide is estimated at $2.5 trillion, $276 billion of which is associated with the degradation of metallic materials. The Energy sector is significantly affected by metallic corrosion, mainly as a result of the numerous extreme and demanding environments and operating conditions encountered across a spectrum of processes.

One of the most prevalent degradation mechanisms observed in the Energy sector is internal CO_2 corrosion of carbon steel pipelines, a process found in geothermal, carbon capture and storage (CO_2 transport/injection), CO_2 sequestration, landfill gas, and oil and gas production and transportation, to name a few.

Carbon steel remains one of the most popular construction materials for pipelines as a result of its favourable mechanical properties and low cost. The most cost effective method for corrosion control of carbon steel in CO_2 environments is the application of corrosion inhibitors. These inhibitors are typically surfactant molecules which adsorb onto the steel surface, creating a dynamic physical barrier to protect the steel pipeline integrity. The high efficiency (performance) of these inhibitors is therefore paramount to the safe and reliable operation of carbon steel systems.

Despite corrosion inhibitors being deployed worldwide for decades, particularly in the oil and gas industry, there remains little understanding of how commercially available multi-component inhibitor packages both function and perform. From a research perspective, many of the fundamental studies of corrosion inhibitor performance focus on the response of a single active component system. However, most commercial corrosion inhibitor consist of 3 to 5 active surfactant molecules often forming a homologous series.

Project Scope

The goal of this program is to extend the current industry understanding of the kinetics of corrosion inhibitor adsorption and their performance from the current single component to multi-component systems. The project will combine elements of experimental, theoretical, and numerical analysis exploration, as well as introduce new concepts not covered in the Engineering Programme, such as electrochemical methods, chemical analysis, implementation of design of experiments and non-linear analysis of experimental data.

The elements of the program are described below.

Element 1 – Surfactant Adsorption study of Single Component

- Develop an understanding of the adsorption of surfactant molecules at surfaces

- Experimentally record adsorption kinetics of a single inhibitor component onto carbon steel in laboratory studies using electrochemical techniques
- Model Langmuir kinetics for the single component (Blanchard/Woollam)
- Theoretical extension of kinetics models from single component to competitive multi-component using supporting data from the literature
- Use the electrochemical techniques developed in Element 2 to measure the single component and multi-component equilibrium thermodynamic and kinetic adsorption isotherms

Element 2 – Implementation of Electrochemical Techniques to Measure Corrosion Rate

- Develop and understanding of electrochemistry and electrochemical techniques (specifically the linear polarisation resistance technique)
- Understand the CO2 system and use electrochemical measurement to record corrosion rate of carbon steel vs time and hence, observe inhibitor adsorption kinetics with time
- Experimentally record adsorption kinetics of a second single inhibitor component onto carbon steel in laboratory studies using electrochemical techniques
    - Simple NaCl/CO2 (1 bar) system adjusting pH with bicarbonate to pH 4/5/6

Element 3 – Physical Properties of Surfactants

- Develop and equilibrium model for the CO_2-NaCl-H_2O system to understand and validate the experimental system
- Understand physical properties of surfactants
- Review literature for C12 – C16 carboxylic acids, notably Zhu and Free
- Measure the properties of surfactants using a range of analytical techniques
    - Micelle measurements using surface tension
    - Partitioning (oil-water) using spectrometry
- Use the electrochemical methods developed elsewhere, measure the change in corrosion inhibitor performance upon the introduction of a second liquid phase simulating oil phase (toluene)

Element 4 – Non-linear Data Analysis/Fitting and Interpretation

- Develop an understanding on non-linear techniques to analyse experimental data and fit non-linear models (typically non-linear least squares fit but other approaches are available)
- Develop specific numerical techniques to analyse the adsorption data generated in Element 1 (determine to best adsorption kinetic model) and ultimately develop and apply techniques to competitive multi-component adsorption,
    - Non-linear least squares fit
    - Approximations at the extremes (Blanchard)
- Develop techniques for analysis of multi-component competitive adsorption
- The data/results from Elements 1, 2, and 3 will be input into this element

- The Element will also be expected to not just fit non-linear model but also develop the statistical methods to assess the confidence/error range in the derived parameters
- Note, there are two forms on non-linear fit required, analysis of the electrochemical response curve (especially if Tafel plots used) and then the analysis of the resultant inhibitor curves

Element 5 – Corrosion Inhibitor Performance Optimization

- The three members of the carboxylic acid homologous series are C_{12}, C_{14}, and C_{16} which will be used singerly and together to measure the CMC and corrosion inhibitor performance
- In order to assess optimal performance an experimental ternary design is required to cover the compositional range 0 to 100% for each component to drive the experimental work program
- Based on the results of the measured CMC, an optimal composition can be estimated, maximizing the CMC and hence maximizing the concentration of inhibitor in solution (mixture design and performance surface analysis – see paper by Cornell)
- Similarly, the corrosion test matrix will need to be designed to measure the performance of the single components and mixtures
- Analysis of the performance surface will yield an optimal corrosion inhibitor concentration to maximize corrosion inhibitor performance based on composition
- Based on the analysis of the corrosion performance surface, calculate the optimal corrosion inhibitor composition
- Test/measure the performance of the optimal composition – how does this compare to the optimal CMC composition and the statistical confidence in the optimal composition.