

Water-soluble inhibitor on microbiologically influenced corrosion in diesel pipeline

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Abstract

The effect of water-soluble corrosion inhibitor on the growth of bacteria and its corrosion inhibition efficiency were investigated. Corrosion inhibition efficiency was studied by rotating cage test and flow loop techniques. The nature of biodegradation of corrosion inhibitor was also analyzed by using Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR) and Gas chromatography and mass spectrometer (GC-MS). The bacterial isolates (*Serratia marcescens* ACE2, *Bacillus cereus* ACE4) have the capacity to degrade the aromatic and aliphatic hydrocarbon present in the corrosion inhibitor. The degraded products of corrosion inhibitor and bacterial activity determine the electrochemical behaviour of API 5LX steel. The influence of bacterial activity on degradation of corrosion inhibitor and its influence on corrosion of API 5LX have been evaluated by employing weight loss techniques and electrochemical studies. The main finding of this paper is that the water-soluble corrosion inhibitor is consumed by the microbial action, which contributes to the decrease in inhibitor efficiency. The present study also emphasis the importance of evaluation of water-soluble corrosion inhibitor in stagnant model (flow loop test) and discusses the demerits of the water-soluble corrosion inhibitors in petroleum product pipeline.

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1. Introduction

The possible effect of corrosion inhibitor on bacteria is of considerable interest to people involved in oil and gas production and transmission pipelines. It is possible that corrosion inhibitors will have biocidal effects on bacteria [1]. Organic film-forming inhibitors used in the oil and gas industry are generally of the cationic/anionic type and include imidazolines, primary amines, diamines, amino-amines, oxyalkylated amines, fatty acids, dimmer-trimer acids, naphthaneic acid, phosphate esters and dodecyl benzene sulphonic acids. Their mechanism of action is to form a persistent monolayer film adsorbed at the metal/solution interface. It is well known that bacteria can oxidize a wide variety of chemicals and use them as nutrient source and enhance the proliferation of bacteria [2–4]. However aerobic bacteria and fungi participate in the corrosion process [5–7]. The microorganisms influence the corrosion by altering

the chemistry at the interface between the metal and the bulk fluid [8,9]. Thus, the alteration of the molecule of the inhibitor caused by microbial degradation during their use, can affect their specific performance on corrosion inhibition [10]. Microbial degradation of simple heterocyclic inhibitor of the type morpholine (C_4H_9NO) has been recently reported by Poupin et al. [11]. Bento et al. [12] and Muthukumar et al. [13] have reported that the understanding of the microbial species involved in microbial corrosion and their interactions with metal surfaces. The degradation involved an enzymatic attack at the C–N position, followed by ring cleavage to produce glycolic acid [11]. Dominguez et al. [14] (1998) reported the loss in efficiency of organic corrosion inhibitors in the presence of *Pseudomonas fluorescens* isolated from injection water system used in off-shore oil production.

Recently Maruthamuthu et al. [15] and Rajasekar et al. [4] have noticed the degradation of corrosion inhibitors and their effect on the corrosion process in a petroleum product transporting pipeline at northwest, India. In petroleum product pipelines, it would be better to know if the water-soluble corrosion inhibitor is acting as a nutrient source or as biocide or indeed whether what

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its effect at all. In the present study, a laboratory experiment was designed to evaluate the degradation of corrosion inhibitor by employing dominating individual species (*Serratia marcescens* ACE2, *Bacillus cereus* ACE4) and their role on corrosion process in petroleum products.

2. Materials and methods

2.1. Background information of the study

A cross-country pipeline in India, transports petroleum products such as kerosene, petrol and diesel. This pipeline has intermittent petroleum product delivery cum pressure booting stations at different locations. Severe corrosion and microfouling problems have been faced in the pipeline even though corrosion inhibitor was added. About 200–400 kg of muck (corrosion product) was received from a 200 km stretch of the pipeline within 30 days [15]. The corrosion product was pushed out of the pipeline by pigs (cylindrical device that moves with the flow of oil and cleans the pipeline interior) while cleaning the pipeline. The corrosion product samples were collected in sterile containers for microbial enumeration and identification. In the present study, commercially available water-soluble corrosion inhibitor used in petroleum transporting pipeline was evaluated to find out the nature of degradation, which was used in petroleum pipeline. The water-soluble corrosion inhibitor contains carboxylic acid and ester based compounds.

2.2. Microorganism

The strains *S. marcescens* ACE2 and *B. cereus* ACE4 [4] were used in this study were isolated from oil transporting pipeline of oil refineries in northwest India (the nucleotide sequences data has been deposited in GenBank under the sequence numbers DQ092416 and AY912105).

2.3. Composition of growth medium

The medium used for detecting the corrosion inhibitor degrading process by ACE4 was Bushnell–Hass broth (magnesium sulphate, 0.20 gm/l; calcium chloride, 0.02 gm/l; monopotassium phosphate, 1 gm/l; di-potassium phosphate, 1 gm/l; ammonium nitrate, 1 gm/l; ferric chloride, 0.05 gm/l, Hi-Media, Mumbai) and Bushnell–Hass agar. Three sets of erlenmeyer flasks were used for the inhibitor degradation studies using the selected bacterial strains.

2.4. Biodegradation of corrosion inhibitor and their characterization

Two sets of Erlenmeyer flasks containing 100 ml of the BH broth, 400 ppm of water-soluble corrosion inhibitor with ACE2 and ACE4 were inoculated. An uninoculated control flask was incubated parallelly to monitor abiotic losses of the corrosion inhibitors substrate. The flasks were incubated at 30 °C for 30 days in an orbital shaker (150 rpm). At the end of the 30 days of incubation period, the residual corrosion inhibitor for each

system of the entire flask was extracted with an equal volume of dichloromethane. Evaporation of solvent was carried out in a hot water bath at 40 °C. About 1 µl of the resultant solution was analyzed by Fourier transform infrared spectroscopy (FT-IR) and ^1H nuclear magnetic resonance spectroscopy (NMR). FT-IR spectrum (Nicolet Nexus 470) which was taken in the mid IR region of 400–4000 cm^{-1} with 16-scan speed. The samples were mixed with spectroscopically pure KBr in the ratio of 1:100 and the pellets were fixed in the sample holder, and the analysis was carried out. Infrared peaks localized at 2960 and 2925 cm^{-1} were used to calculate the CH_2/CH_3 ratio (absorbance) and functional group of both aliphatic and aromatic components present in water-soluble corrosion inhibitor. ^1H NMR (Bruker, 300 MHz) analysis was used to detect the protons of the nuclei in the diesel compound. The sample of diesel was dissolved using deuterated chloroform solvent. Tetramethyl silane (TMS) was used as a reference standard. The 1 µl of the resultant corrosion inhibitor solution was analyzed by Thermo Finnigan gas chromatography/mass spectrometry (trace MS equipped with a RTX-5 capillary column (30 m long $\times$ 0.25 mm internal diameter) and high purity nitrogen as carrier gas. The oven was programmed between 80 and 250 °C at a heating temperature of 10 °C/min. The GC retention data of the inhibitor correspond to structural assignments done after NIST library search with a database and by mass spectra interpretation.

2.5. Inhibitor efficiency test

2.5.1. Rotating cage test

Corrosion inhibition efficiency was studied by rotating cage test [16, ASTM G170]. API 5LX grade steel (C, 0.29 max; S, 0.05 max; P, 0.04 max; Mn, 1.25 max) coupons of size 2.5 cm $\times$ 2.5 cm were mechanically polished to mirror finish and then degreased using trichloro ethylene. Four coupons supported by polytetra fluoro ethylene (PTFE) disks were mounted at 55 mm apart on the rotatory rod. Holes were drilled in the top and bottom PTFE plates of the cage in order to increase the turbulence on the inside surface of the coupon. The rotatory rod runs at 200 rpm, which corresponds to a linear velocity of 0.53 m/s. In the present study, 500 ml of diesel with 2% water containing 120 ppm chloride as system I (control); 500 ml of diesel with 2% water containing 120 ppm chloride and 2 ml of mixed cultures of ACE2 and ACE4 as control system II; 500 ml of diesel with 2% water containing 120 ppm chloride and 100 ppm of corrosion inhibitor as system III; while 500 ml diesel with 2% of water containing 120 ppm chloride, 100 ppm of corrosion inhibitor inoculated with 2 ml of mixed cultures of ACE2 and ACE4 were used as the experimental system IV.

2.5.2. Flow loop test—for simulating the stratification of water in pipe flow

In order to simulate this sort up condition, a flow loop set-up was fabricated [16]. The flow loop system consists of a reservoir that maintains the solution under test, a pump with piping and bypass valve that controls the solution flow. Flow loop model has been made in the laboratory for creating stagnant water in the pipeline for simulating the field conditions.

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