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EVALUATION OF MICROBIALLY-INDUCED CORROSION (MIC) OF MILD STEEL IN *Aspergillus Niger* CULTURES

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ABSTRACT

Microbially-Induced Corrosion (MIC) of mild steel in *Aspergillus niger* cultures at various temperatures (30, 40, 50 and 60°C) and times (6, 12, 18 and 24 hours) has been investigated. The *Aspergillus niger* mycelia was cultured and its spores harvested from seven (7) days old slants, inoculated by washing the slants with 0.1% sterilized tween 80 into the 250ml Erlenmeyer flasks containing the cultures, and placed on a rotary shaker at 300rpm, pH4.0 and a temperature of 30°C for 120 hours. The corrosion tests were conducted in a thermo-stated water bath containing eight beakers of *Aspergillus niger* cultures and the coupons. There was a general increase in corrosion rate with exposure time; the highest corrosion rate of 245mpy being attained at a temperature of 40°C. Corrosion rates obtained at 50 and 60°C were found to be lower than those at 30 and 40°C. This might be due to the retardation in the growth of the fungi as the temperature was increased. The metabolic activities of the fungi might have produced some organic substrates which, directly or indirectly, were responsible for the observed degradation of the substrate. It was concluded that the rate of fungal growth, temperature and environment (corrodent) are the major factors affecting the corrosion rate of mild steel under the influence of these microorganisms.

Keywords: *coupons, Microbially-Induced Corrosion (MIC), corrosion rate, Aspergillus niger, metabolic activity, tubercles.*

INTRODUCTION

Steel is an alloy consisting mostly of iron, with carbon content ranging between 0.2% and 2.1% by weight depending on the grade (Callister, 2007). It is conservatively divided into four groups; low carbon steel-0.15 to 0.30% carbon, medium carbon steel-0.30% to 0.60% carbon, high carbon steel-0.60 to 0.90% carbon and very high carbon steel-0.90 to 1.5% carbon (Nestor, 2004). Though steel had been produced by various inefficient methods long before renaissance, its use became more common after more efficient production methods were derived in the 17th century, and with the invention of the Bessemer process in the mid-19th century, steel became an inexpensive mass-produced material (Jain, 2004). Steel is one of the most common materials in the world, with more than 1300 million tons produced annually; it is a major component in building, tools, ships, automobile, machines and weapons (Callister, 2007). The steel industry is often considered to be an indicator of economic progress because of the critical role played by steel in infrastructural and overall economic development (Jain, 2004). In 2008, steel was traded as a commodity in the London metal exchange and by the end of the year, due to global economic decline, the steel industry faced a sharp downturn that led to many cut-backs (Uchitelle, 2009).

Corrosion has been identified as severe metal/material degradation through biological, chemical and electrochemical means. Practically all environments (atmosphere, air/moisture, water-fresh and salty, industrial atmosphere-gases, acids and alkalis etc) are corrosive to some extent. Under "favourable", but unwanted circumstances iron and steel corrode when present in these environments (Fontana, 2005; Schweitzer, 2001).

Mild steel finds variety of applications industrially, in mechanical components and

structures such as bridges, buildings, boiler plates, steam engines and automobiles, and also in most chemical industries due to its low cost and ease of availability and fabrication into various reaction vessels, tanks, pipe etc where MIC is predominant (Auwal, 2008; NICA, 2005; Callister, 2007).

Microbial corrosion, also called bacterial corrosion, bio-corrosion, microbiologically influenced corrosion or Microbially-Induced Corrosion (MIC), is a degradation/corrosion promoted, directly or indirectly, by the activities of microorganisms and affects both metallic and non-metallic materials (Fontana, 2005; Rothwell, 2003). The term micro-organisms covers a wide variety of life forms, including bacteria, blue green cyanobacteria, algae, fungi and protozoa (NACE, 1994). Most of these micro-organisms live in the mesophilic range of 20-40°C (69-110°F) which corresponds to the usual temperature range of the earth, and a pH value between 0 and 11 (Fontana, 2005 and Schweitzer, 2001). Microbial species effect corrosion by releasing aggressive materials to the environment (e.g. sulphide), biodegradation of the environment, formation of deposits, stimulating cathodic process and interfering with corrosion inhibitors (Kamalu, 2006). Microbes are predominantly water-based and contain C, O, N, H, P, S, K, Na, Mg, Cl, Fe, etc. If these elements are absent from the environment, the microbes cannot develop their cell structures and flourish (Jones, 1998).

MIC gives appearance of pitting and may occur in metallic materials used for various industrial applications such as chemical processing, nuclear power generation, underground pipeline, metalworking, onshore and offshore oil and gas plants, water treatment, sewage handling, highway maintenance and aviation (Shreir *et al*., 2000).

Fungi are members of a large group of eukaryotic organisms that include microorganisms such as yeasts, molds, as well as the more familiar mushrooms (Cavalier, 2008). These organisms are classified as a kingdom and present a great deal of problems to biologists; they exhibit both plant and animal characteristics even though modern genetic studies have shown that fungi are more closely related to animals than to plants (Allen, 2007).

Fungi, together with bacteria, are important decomposers and have fundamental roles in nutrient cycling and exchange (Blackwell, 2004). They have long been used as direct source of food, such as mushroom and truffles, as a leavening agent for bread, and in fermentation of various food products such as wine, beer, and soy sauce (Dean *et al.*, 2005). Since the1940s, fungi have been used for the production of antibiotics, and more recently various enzymes produced by fungi are used industrially (Dinovi *et al.*, 2006).

Most metals and their alloys (including stainless steel, aluminum, and copper alloys) are attacked by certain microorganisms. Polymers, hessian, and concrete are also not immune to this form of damage. Corrosion damage to aircraft fuel tanks is one of the well-known problems associated with fungi. Fungi tend to produce corrosive products as part of their metabolisms; it is these by-products that are responsible for corrosive attack. Furthermore, fungi can trap other materials, leading to fouling and associated corrosion problems (Roberge, 1999). Because of the nature of this corrosion which gives the appearances of microscopic pits on the material(s), it is a source of concern to every corrosion engineer, hence the need for carrying out this research work on the evaluation of Microbially-Induced Corrosion (MIC) of mild steel in *Aspergillus niger* cultures.

EXPERIMENTAL

The as-received mild steel (chemical composition: 0.19%C, 0.35%Si, 0.70%Mn, 0.03%P, 0.04%S, and balance 97.61%Fe) was machined and sectioned to the desired corrosion test coupons with dimensions 11.7mm by 30mm. The coupons were ground and polished with different grades of emery/grit papers (220-800 grades), cleansed in carbon tetrachloride (CCl_4) solvent to degrease them, dried, weighed and stored in a desiccator to prevent interactions with contaminants and atmospheric moisture.

Growing and preparation of *Aspergillus niger* in submerged culture for extraction

Prior to growing *Aspergillus niger*, the glassware and media used were sterilized by autoclaving at 121°C for 15minutes. Growing the *Aspergillus* mycelia was done as described by Nestor (2004) using a media containing 10g glucose, 1.65g Ammonium Sulfate, 0.67g Ammonium Chloride, 0.1g Magnesium Sulfate (hydrated), 2.5g KH_2PO_4, 1.5g Sodium hydrogen Phosphate, 0.03g Sodium Sulfate, 0.08g Potassium Sulfate and 0.1g Magnesium chloride in one liter of distilled water. Appropriate quantity of Potassium dichromate (0.075mg) was added to the media and then sterilized. Fresh media was aliquoted into sterile 250ml Erlenmeyer flasks. Spores of *Aspergillus niger* were harvested from 7days old culture slants and inoculated by washing the slants with 0.1% sterilized tween80 into the 250ml Erlenmeyer flasks containing the medium. The fungus was grown in these flasks on a rotary shaker at 300rpm, pH4.0 and temperature of 30°C for 120 hours.

Corrosion testing

Thermo-stated water bath was filled with water up to a reasonable level above the heating element to take care of the probability of water level falling below the heating element due to evaporation (especially at 50 and 60°C). It was then switched on and set to the desired temperature. Continuous stirring was exercised to obtain and maintain homogeneity throughout the bath until the desired temperature was achieved; by setting with a thermostat and monitoring the temperature of the water bath using a thermocouple.

Eight beakers containing the *Aspergillus niger* cultures and the corrosion test coupons were placed in the thermo-stated water bath and the temperature was first maintained at 30°C (assumed to be room temperature). The samples were removed individually at intervals of six hours after which they were washed with brush, rinsed in water, dried and re-weighed.

The final weights (W_f) were recorded and the weight losses computed using equation (1).

$$\Delta W = W_i - W_f \quad (1)$$

ΔW is the mass loss (g)

W_i is the initial mass of the coupon (g)

W_f is the final mass of the coupon (g)

In each case, also, the Corrosion Penetration Rate (CPR), in mpy, was calculated using equation (2) below:

$$\text{CPR} = \frac{534\Delta W}{\rho A t} \quad (2)$$

ΔW, $\boldsymbol{\rho}$, A, and t are specified in units of milligrams, grams per cubic centimeter, square inches, and hours, respectively (Callister, 2007).

The same procedures were adopted in obtaining the corrosion rates at 40, 50 and 60°C**.**

RESULTS AND DISCUSSION

The effect of *Aspergillus niger* culture on the corrosion rate of mild steel.

Visual observations revealed blackening of the coupons immersed in the cultures of the fungi (*Aspergillus niger*). This could be due to the production of Hydrogen which further reacted with metabolite sulphur from the fungi to form Hydrogen Sulphide at different rates and/or concentration. This might have also led to the blackening of the metal samples due to the formation of Iron sulphide (FeS) which is cathodic to the steel as reported by Kamalu (2005). According to the classic mechanism for MIC of steel & iron proposed by Von Wolzogen Kuhr in 1934, the fungi might be the consumers of hydrogen through the action of their hydrogenase enzymes and thus "depolarize" the cathode thus accelerating corrosion (Scully, 1997). This is also corroborated by the fact that the rate limiting step in corrosion is the dissociation of hydrogen from the cathodic sites as established by Tang *et al.* (2003).

The action of these fungi could be likened to that of the sulphate reducing bacteria (SRB) and thus the classic mechanism of anaerobic corrosion could be used to elucidate it, viz:

$$4Fe + SO_4^{2-} + 4H_2O \longrightarrow 3Fe(OH)_2 + FeS + 2OH^- \quad (3)$$

$$FeS + 2HCl \longrightarrow H_2S + FeCl_2 \quad (4)$$

$$H_2S + Fe + H_2O \longrightarrow FeS + 4H^+ \quad (5)$$

This is cathodic depolarization, achieved through the metabolic oxidation of Hydrogen by the SRB as reported by Scully (1997). FeS had relatively low Hydrogen evolution overvoltage/over potential, hence galvanic effect between iron sulphide and the substrate prevails, thus accelerating the corrosion of the substrate. This is also contained in an earlier report by Schennan and Vance (1997).

Corrosive by-products, such as organic acids, are also associated with these organisms.

Furthermore, they produce nutrients that support bacteria and fungi. It was also observed that the corrosion rate varied from one medium to another. This might likely be as a result of the fungal growth, leading to the formation of tubercles on the surfaces of the coupons/substrates. These tubercles are activated fungi whose metabolic activities considerably result in corroding the substrates (coupons), hence the resultant weight losses and consequent increase in corrosion rates. This might likely result in shifting the corrosion potential to a more positive value as reported by Kamalu (2005).

Effect of exposure time and temperature on the corrosion rates of mild steel

Generally, corrosion rates of most materials increase with time. In this case, as the exposure time of the coupons to the corrosive media was increased, corrosion rates were found to increase in the time interval of 6-12 hours, as evidenced in Figure 1.

In order to influence either the initiation or the rate of corrosion in the field, microorganisms usually become intimately associated with the corroding surface.

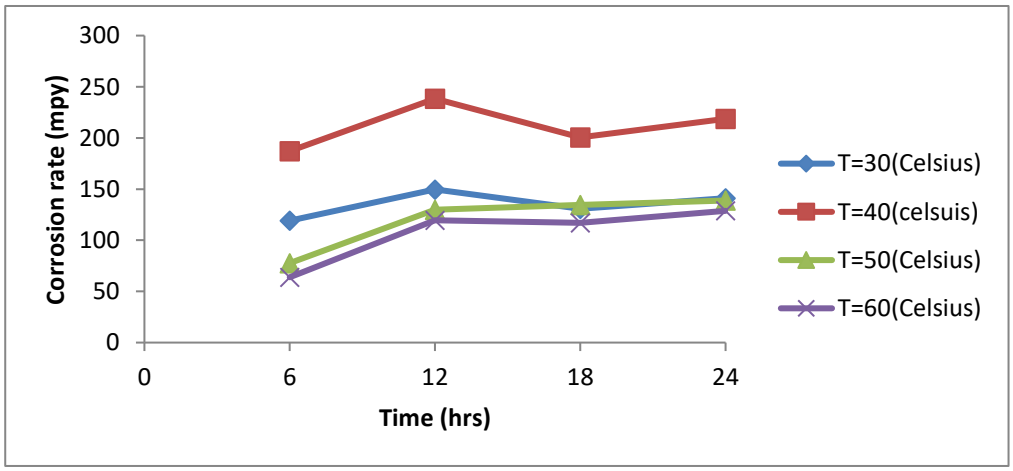
Figure 1: Variation of corrosion rate of fungi (Aspergillus niger) solution at var

In most cases, they become attached to the metal surface in the form of either a thin, distributed film or a discrete island as reported by Roberge (1999). It can be seen that there was an initial increase of corrosion rate of the mild steel coupons with time at 30°C and 40°C.

This could be attributed to the fact that at lower temperatures, near room temperature, the fungi (*Aspergillus niger*) were able to grow and thrive, secreting metabolites(tubercles) at a faster rate, due to resultant increase in the metabolic activities of the fungi

The corrosive nature of these metabolites might be responsible for causing high susceptibility of the substrates to corrosion, as corroborated by Pope *et al.* (1989) in an earlier research.

The corrosion rates decreased as the exposure time was increased from 12 to 24 hours. This was probably due to the fact that as the exposure time was increased, competition for micronutrients especially oxygen, became high such that some of the *Aspergillus niger* species could not compete favourably, hence they perish. When this occurs, overall decrease in metabolic activities would be observed, resulting in lower activities of these microorganisms and less secretion of the corrosive tubercles/metabolites. This has also been reported by Roberge (1999). The highest corrosion rate of 245mpy, observed at 40°C,



was due to the fact that most of these microorganisms live in the mesophilic range of 20-40°C, which corresponds to the usual temperature range of the earth, and a pH range of 0-11, as reported by Fontana (2005) and Schweitzer (2001). At temperatures of 50°C and 60°C, the corrosion rates were observed to be relatively lower than those obtained at 30 and 40°C. This might likely be due to decreased activities of the microorganisms, resulting in low metabolic activities/secretion of metabolites; 50°C and 60°C are beyond the mesophilic range. This is in agreement with a report by Pope *et al*. (1989).

CONCLUSION

Based on the results obtained from this research, it could be concluded that:-

1. Microbially-Induced Corrosion (MIC) of mild steel is a function of the fungal growth, which is time and temperature dependent.
2. The metabolism of the *Aspergillus niger* produced an organic acid at different rates and/or in different concentration, resulting in corroding the substrates (coupons) and also blackening them due to the formation of Iron sulphide (FeS).
3. The fungi (*Aspergillus niger*) thrived in mesophilic range (20-40°C), hence corrosion became more pronounced.

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