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Forced convection corrosion of steel equipments in the water layer present in crude oil

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The present study addresses the relationship between the presence of some salts in crude oil and the corrosion of metallic equipments in the context of the petroleum refining industry. The rate of corrosion of iron in water containing $CaCl_2$ and $MgCl_2$ with concentrations similar to those in the water present in crude oil before desalting was measured by the weight loss technique. The variables investigated were $CaCl_2$ concentration, $MgCl_2$ concentration, operating temperature and angular speed of rotation. It was found that the rate of corrosion increases with increasing $MgCl_2$ and $CaCl_2$ concentrations up to a certain level, after which it remains almost constant. Increasing the angular speed of rotation favors the rate of corrosion. The rate of corrosion was found to increase with temperature according to the Arrhenius equation with activation energy of 8.64 and 5.16 kcal/ mol for $MgCl_2$ and $CaCl_2$ respectively, which denotes that the corrosion of steel in both $MgCl_2$ and $CaCl_2$ solutions is a diffusion-controlled reaction under the operating conditions.

Key Words: Crude oil, desalting, steel corrosion, diffusion-controlled reaction

INTRODUCTION

Crude oil contains water, inorganic salts, suspended solids, and water–soluble salts of trace metals. During the first step of refinery treatment, crude oil is normally desalted to remove species such as chloride which deactivate the refinery catalysts and cause further corrosion of distillation columns [1–4]. Calcium and magnesium chlorides ($CaCl_2$ and $MgCl_2$) are frequently found in crude oil; the presence of these compounds in crude oil can cause several problems in the refining processes.

Hydrochloric acid is not present in crude oil, but it may be produced during distillation by the hydrolysis of chloride salts, particularly magnesium chloride and calcium chloride, that are present in the brine found in crude oils. The presence of hydrochloric acid leads to the so-called acid corrosion that occurs in vapor lines, condensers, coolers, and rundown lines, particularly at points where water accumulates, such as valves in horizontal lines. The corrosive effect of dilute hydrochloric acid at the temperature maintained in the distillation equipment cannot be satisfactorily sustained by common materials.

Steel equipments suffer severe corrosion attack in water containing electrolytes. The rate of corrosion depends, among other factors, upon the concentration of oxygen and the motion of water. Stainless steel undergoes severe damage in water containing chlorides [5], where pitting corrosion and stress corrosion cracking take place.

The aim of the present work was to study the rate of steel corrosion in salt-containing water simulating the water present in crude oil. Crude oil usually contains some water – dissolved salts such as $CaCl_2$ and $MgCl_2$ [6]. Before processing crude oil in the distillation tower, the water should be removed first by a process known as dehydration and desalting [7, 8]. Early water removal from crude oil minimizes corrosion of process equipment such as pumps, heat exchangers, distillation towers and condensers. On the other hand, the equipment used for handling water that has been separated from the oil can suffer from severe corrosion depending upon the salt content of water.

EXPERIMENTAL TECHNIQUE

The experimental set-up used in the present study is shown in Fig.1. It consists of a 2 dm^3 cylindrical glass container of 11.9 cm diameter and 18 cm height. The container was fitted with a variable speed motor. The impeller was an iron rod of 1 cm diameter and 3 cm height. The iron rod was centered on a stainless steel shaft of 0.7 cm

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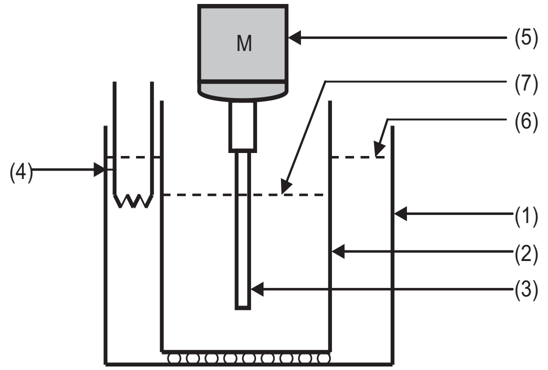

Figure (1): Experimental apparatus. 1- Rectangular water bath; 2- Cylindrical glass container; 3- Iron rod; 4- Thermostat; 5- Variable speed motor; 6- Water level; 7- Electrolyte level.

diameter and 15 cm length at a distance of 4 cm from the vessel bottom. The stainless steel shaft was isolated with epoxy resin. The rotation speed of the motor was controlled by means of a varic and measured by an optical tachometer. Care was taken to avoid vibration and eccentric motion. The cylindrical glass container and its contents were immersed in a rectangular water bath to control the temperature. Before each run, the iron rod was degreased in trichloroethylene, and oxides were mechanically removed with emery paper. The sample (iron rod) was washed under running water, dried with alcohol and ether, and then accurately weighed. 1 dm^3 of fresh $CaCl_2$ or $MgCl_2$ solution was introduced into the cylindrical vessel provided that the iron rod was completely immersed in the solution at various speeds of rotation. Corrosion was allowed to take place for a period of 30 min, after which the iron rod was washed under running water, dried and reweighed. The rate of corrosion was calculated by the formula:

$$r = \frac{\Delta W}{[A * t]} \qquad (1)$$

Where:

r = rate of corrosion in g /cm^2.s, ΔW = weight loss in gram, A = surface area of iron rod in cm^2 and t = time in seconds.

Experiments were carried out over the temperature range 30 - 45°C for $CaCl_2$ and 30 - 40°C for $MgCl_2$. The solution concentration ranged from 0.5 to 10 g/dm^3 for both $CaCl_2$ and $MgCl_2$. The angular speed of rotation ranged from 94.25 to 136.14 and from 107.82 to 281.73 rad/sec for $CaCl_2$ and $MgCl_2$ respectively. All solutions were prepared using A.R. grade chemicals and distilled water.

RESULTS AND DISCUSSION

The effect of $CaCl_2$ and $MgCl_2$ concentrations on the rate of steel corrosion at different angular speeds of rotation is shown in Figs. 2-a and b, respectively. The rate of corrosion increased with increasing $CaCl_2$ and $MgCl_2$ concentrations up to a certain level and remained almost constant with further increase in salt concentration. This may be attributed to the hydrolysis of $CaCl_2$ and $MgCl_2$ [9] according to the following equations:

$$CaCl_2 \text{ and/or } MgCl_2 \rightarrow Ca^{++} \text{ and/or } Mg^{++} + 2\,Cl^- \qquad (2)$$

$$2\,H_2O \rightarrow 2OH^- + 2H^+ \qquad (3)$$

$$2H^+ + 2\,Cl^- \rightarrow 2\,HCl \qquad (4)$$

$$Ca^{++} \text{ and/or } Mg^{++} + 2\,OH^- \rightarrow Ca(OH)_2 \text{ and/or } Mg(OH)_2 \qquad (5)$$

The overall hydrolysis reaction for $CaCl_2$ and $MgCl_2$ is:

$$CaCl_2 \text{ and/ or } MgCl_2 + 2\,H_2O \rightarrow Ca(OH)_2 \text{ and/or } Mg(OH)_2 + 2\,HCl \qquad (6)$$

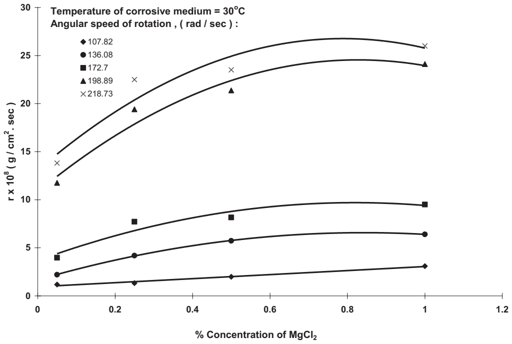

Figure (2-a): Effect of $MgCl_2$ concentration on the rate of corrosion at different angular speed of rotation

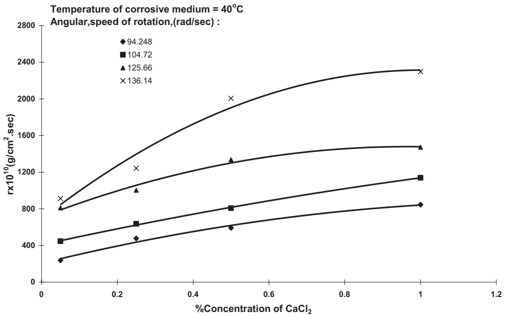

Figure (2-b): Effect of $CaCl_2$ concentration on the rate of corrosion at different angular speed of rotation

As a result of the above hydrolysis reaction, the solution becomes acidic, and the higher the salt concentration, the higher is the acidity of the solution. The acidity favors the rate of corrosion as a result of:

1. The increase in solution conductivity due to the presence of the highly mobile H^+, which (in accordance with Faraday's law) leads to an increase in the corrosion rate.
2. The presence of relatively high H^+ concentration leads to H_2 evolution at the cathode in addition to oxygen reduction. That means, under the present conditions, O_2 reduction takes place at the cathode simultaneously with H_2 evolution, according to the following reactions [2,3,4]:

Anodic area: $$Fe \rightarrow Fe^{2+} + 2e^- \qquad (7)$$

Cathodic area:

$$1/2\ O_2 + H_2O + 2\ e^- \rightarrow 2OH^- \qquad (8)$$

$$2\ H^+ + 2\ e^- \rightarrow H_2 \qquad (9)$$

The fact that the corrosion rate remained almost constant at relatively high $CaCl_2$ or $MgCl_2$ concentrations may be due to balanced opposing effects, e.g., higher salt concentrations suppress the solubility of dissolved O_2 in the solution. This is known as the “salting out” effect [6, 10]. Also, oxygen depletion results in a decrease in the rate of corrosion [11, 12]. Additionally, it is possible that Ca^{++} or Mg^{++} may inhibit the rate of corrosion to some extent by combining with OH^- formed at the cathode to deposit an inert film of $Ca(OH)_2$ or $Mg(OH)_2$ in the cathodic areas, thereby decreasing the effective area exposed, with a consequent decrease in the rate of steel corrosion [6,10,13]. It seems that the above retarding effects balanced the enhancing effect arising from the increase in solution conductivity at high $CaCl_2$ or $MgCl_2$ concentrations.

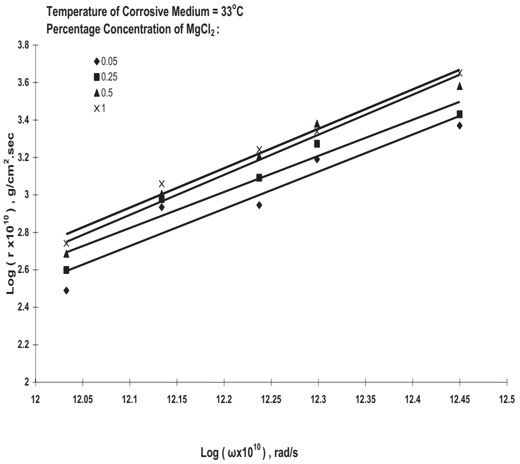

Figure (3-a): Effect of angular speed of rotation on the rate of corrosion at different $MgCl_2$ concentration

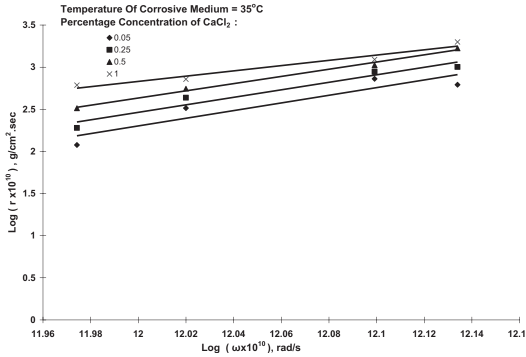

Figure (3-b): Effect of angular speed of rotation on the rate of corrosion at different $CaCl_2$ concentration

The data shown in Figs. 3-a and b fit the following two relations for $CaCl_2$ and $MgCl_2$, respectively:

$$r = a_1 \omega^{18.13} \qquad (10)$$

$$r = a_2 \omega^{11.82}$$

Where:

ω is the angular speed of rotation in rad/s, a_1 and a_2 are constants.

The increase in the rate of corrosion (r) may be due to the fact that the reaction is diffusion-controlled. The diffusion-controlled nature of the reaction was confirmed by the following three facts:

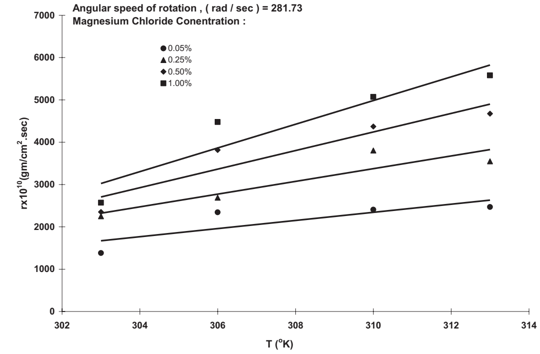

Figure (4-a): Effect of corrosive medium temperature on the steel corrosion at different $MgCl_2$ concentration

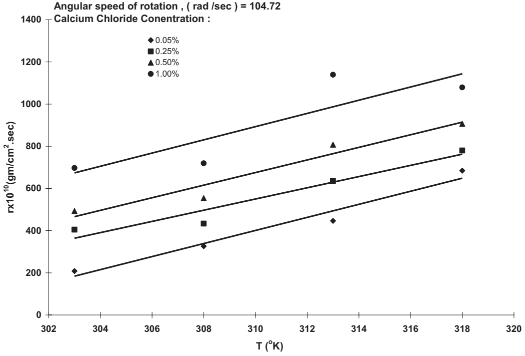

Figure (4-b): Effect of corrosive medium temperature on the steel corrosion at different $CaCl_2$ concentration

a) The corrosion rate systematically increases upon increasing the angular speed of rotation. The higher angular speed of rotation reduces the diffusion layer thickness (cf. Fig. 7) which favours the rate of transfer of dissolved oxygen from the solution bulk to the metal surface with a consequent increase in the rate of steel corrosion.

(b) The H_2 bubbles evolved at the cathodic areas may generate turbulence in the diffusion layer with a consequent increase in the rate of corrosion.

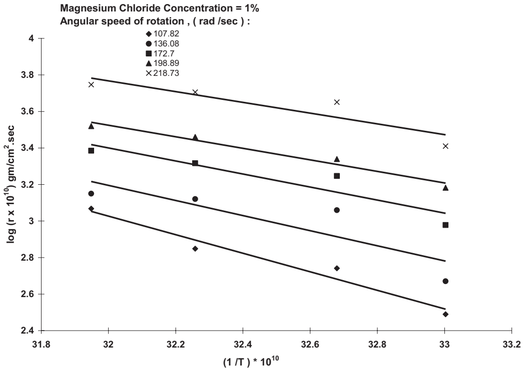

Figure (5-a): Arrhenius plot of the experimental results at different $MgCl_2$ concentration

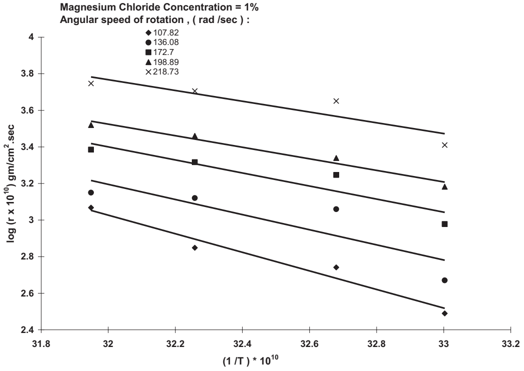

Figure (5-b): Arrhenius plot of the experimental results at different $CaCl_2$ concentration

Figs. 4-a and b show the effect of temperature on the rate of steel corrosion at different concentrations of $CaCl_2$ and $MgCl_2$, respectively. Increasing the temperature of the corrosive medium increases the rate of corrosion. This may be ascribed to the increased reaction rate, which might be assisted by the reduced viscosity of the solution, with a consequent increase in the O_2 diffusivity according to the Stocks-Einstein equation [14]:

$$\frac{D\mu}{T} = \mathrm{C} \qquad (12)$$

Where:

D = the diffusion coefficient in cm^2 /s, μ = the solution viscosity in g/cm.s, and C is a constant.

In order to better understand the mechanism of steel corrosion in $CaCl_2$ and $MgCl_2$ solutions, the activation energy was determined by plotting log (r) versus (1/T) according to Arrhenius equation (cf. Figs. 5-a and b):

$$r = A\exp(\frac{-E}{RT}) \qquad (13)$$

Where:

A = pre-exponential factor or frequency factor, R = gas constant = 1.9854×10^{-3} kcal/mol.K and E = activation energy, kcal/mol.

It was found that the activation energy was 5.16 and 8.46 kcal/ mol for $CaCl_2$ and $MgCl_2$, respectively. The low value of the activation energy (< 10 kcal/mol) lends support to the diffusion – controlled mechanism of the reaction under the present conditions [15-17]. This is in agreement with the previous studies [6, 10, and 13].

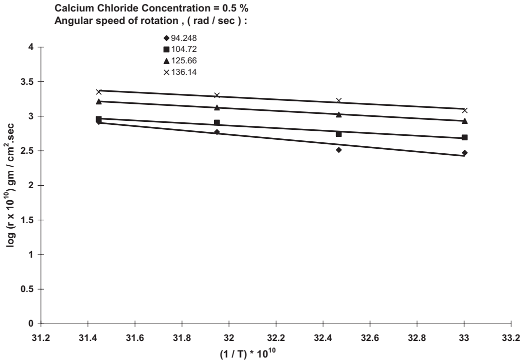

Figure (6): Comparison between the effect of temperature on the rate of steel corrosion at constant (ω) and constant concentration of $CaCl_2$ and $MgCl_2$

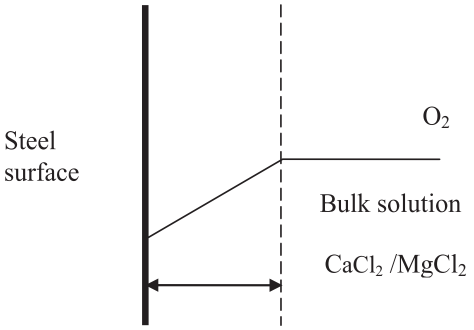

Figure (7): Diffusion layer through which O_2 diffuses from the solution bulk to the steel surface.

Fig. 6 shows a comparison between the effects of temperature on the rate of steel corrosion in $CaCl_2$ and $MgCl_2$ solutions at a constant angular speed of rotation (ω = 136.1 rad/s) and constant salt concentration (0.5 %). It was found that the $CaCl_2$ solution is a more corrosive medium than the $MgCl_2$ solution.

CONCLUSIONS

The effect of the different variables on the rate of steel corrosion in aqueous solutions of $CaCl_2$ or $MgCl_2$ can be summarized as follows:

- The rate of steel corrosion increased upon increasing $CaCl_2$ and/or $MgCl_2$ concentrations up to a certain level and remained almost constant with further increase in salt concentration.
- The corrosion rate was found to increase with increasing speed of agitation and temperature of the corrosive medium.
- The mechanistic study of the present corrosion process revealed that the process is diffusion-controlled.
- The rate of steel corrosion in aqueous solutions of $CaCl_2$ is higher than that in $MgCl_2$ solutions under the same conditions.
- Steel equipments sustain severe corrosion in oil refinery wastewater, especially in the presence of high $MgCl_2$ and $CaCl_2$ content.
- Sufficient precautions such as cathodic protection should be taken to protect these equipments.

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ПРИНУДИТЕЛНА КОНВЕКЦИОННА КОРОЗИЯ НА СТОМАНЕНИ СЪОРЪЖЕНИЯ ВЪВ ВОДНИЯ СЛОЙ В СУРОВ ПЕТРОЛ

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(Резюме)

Настоящото проучване разглежда връзката между наличието на някои соли в суровия петрол и на корозията на метални съоръжения в контекста на петролната промишленост. Скоростта на корозия на желязо във вода, съдържаща $CaCl_2$ и $MgCl_2$ с концентрации, подобни на тези във водата, присъстваща в суровия петрол, преди обезсоляване е измерена чрез загубата на тегло. Изследваните променливи са концентрацията на $CaCl_2$, концентрацията на $MgCl_2$, работната температура и ъгловата скорост на въртене. Установено е, че скоростта на корозия нараства с увеличаване на концентрациите на $MgCl_2$ и $CaCl_2$ до определено ниво, след което остава почти постоянна. Увеличаването на ъгловата скорост на въртене благоприятства скоростта на корозия. Установено е, че скоростта на корозия се увеличава с температурата, в съответствие с уравнението на Арениус с активираща енергия от 8,64 и 5,16 ккал/мол съответно за $MgCl_2$ и $CaCl_2$, което означава, че корозията на стомана в двата разтвора на MgCl2 и на CaCl2 е дифузионно контролирана реакция при условията на работа.