JMEPEG (1992) 1:61-66

Effect of Suspended Solids on the Flow-Induced Corrosion of a Modified Al-2.5Mg Alloy in Arabian Gulf Water

Zaki Ahmad and B.J. Abdul Aleem

Suspended solids increase the rate of corrosion and decrease the resistance of a modified Al-2.5Mg alloy to pitting in Arabian Gulf water. It has been shown by electrochemical studies that the pitting potential of the alloy shifts to more negative values in the presence of suspended solids. The rate of mass transfer and the limiting current is significantly increased by suspended particles.

1 Introduction

ENGINEERING materials, particularly steels, when subjected to high flow rates are susceptible to erosion/corrosion due to the simultaneous effect of chemical and mechanical processes at the metal surface. Steels are frequently subjected to high flow rates, resulting in an increase in the mass loss rate due to erosion/corrosion. The rate of erosion/corrosion of steel and copper alloys is known to be increased by suspended particles present in the water.

Whereas the effect of velocity on the erosion/corrosion of steel, copper, and aluminum alloys is widely reported in literature, information on the effect of media containing suspended particles on flow-induced corrosion is limited[1-6] and a systematic study is required. Investigations were therefore undertaken to determine the effect of suspended solids, such as silica sand and polystyrene, on flow-induced corrosion of modified Al-2.5Mg alloy in Arabian Gulf water.

1.1 *Experimental Materials*

A modified Al-2.5Mg alloy containing 0.22 wt% chromium was studied because of its promising potential for desalination applications.[7] The composition of this alloy is given in Table 1.

1.2 *Experimental Techniques*

Weight loss measurements were made in smoothly stirred seawater and in seawater flowing at velocities ranging from 0.4 to 2.48 m/sec. All tests were conducted according to ASTM G-1-88[8] in natural seawater obtained from the Arabian Gulf. The composition of the seawater is given in Table 2.

1.3 *Recirculating Loop*

A recirculating loop made from high-density polyvinyl chloride (HDPVC) was used to study the effect of velocity on corrosion (Fig. 1). A continuous circulating system was maintained. The water entered through a control valve and entered specimen chambers (Fig. 2) with varying diameters. The water left the loop through an exit valve and re-entered the circulation tank. The capacity of the centrifugal pump used in the system was 20 m^3/hr. Devices such as a magnetic flow meter, oxygen sensors, temperature recorder, and conductivity meter were installed in the loop. Provision was made to attach electrochemical measurement devices in the loop. All measurements were made in turbulent flow.

1.4 *Specimen Preparation*

Flat specimens measuring 70 by 100 mm, 58 by 100 mm, 48 by 100 mm, and 40 by 100 mm and tubular specimen measuring 16 mm (ID) by 58 mm length were used. All samples were treated separately for 5 min in boiling benzene, ethanol at 35 °C, and 5% acetic acid at 48 °C. The corroded samples were treated with $Cr_2O_3 + H_3PO_4$ at 80 °C to remove corrosion products.

Table 1 Composition of Modified Aluminum Alloy

Element	Composition, wt%
Si	1.01
Fe	0.10
Cu	<0.01
Mn	0.10
Mg	2.48
Cr	0.22
Zn	0.01
Ti	0.003
Al	Bal

Table 2 Analysis of Arabian Gulf Water

Ions	Concentration, mg/liter
Na^+	19186
Ca^{++}	704
Mg^{++}	2400
SO_4^{--}	4894
Cl^-	34080
CO_3^-	18
HCO_3^{--}	189
Total	61471

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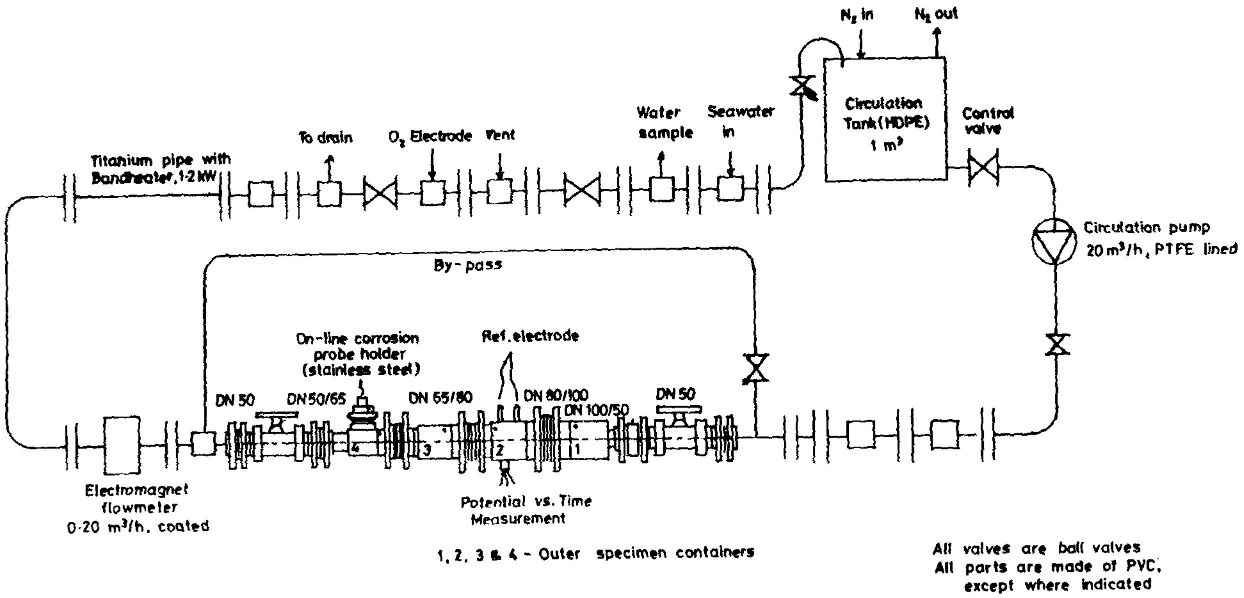

Fig. 1 Schematic of a modified PVC loop for material testing under marine conditions.

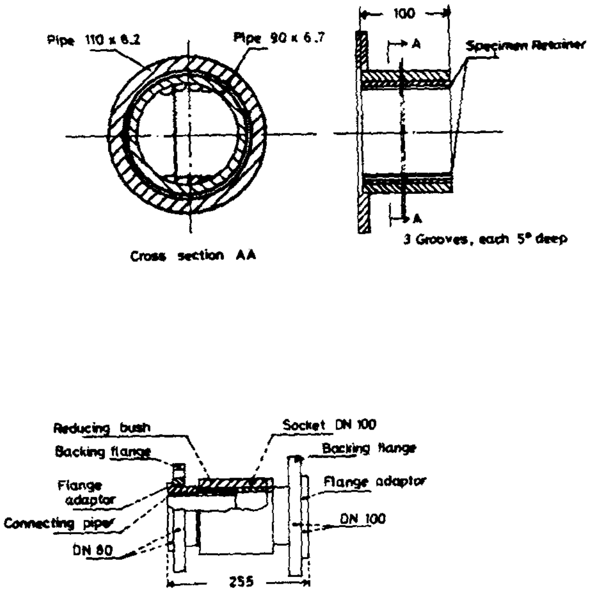

Fig. 2 Detail of specimen containers.

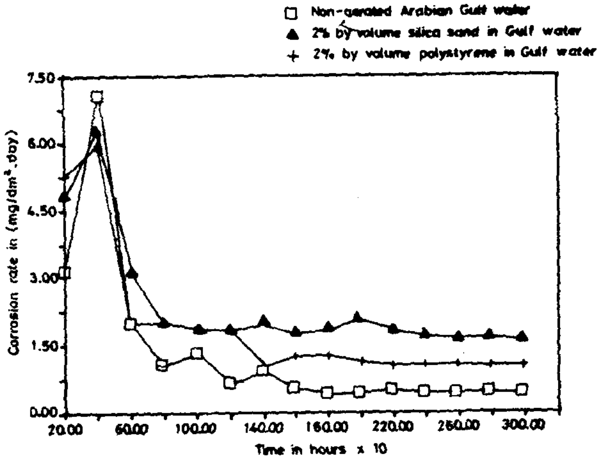

Fig. 3 Variation of corrosion rate with time in nonaerated Arabian Gulf water containing suspended particles.

1.5 *Electrochemical Measurements*

A potentiodynamic polarization technique was used in accordance with ASTM G61-86. Disc specimens measuring 1.5 cm^2 in diameter were mounted on electrode holders. A polarization cell similar to that described in ASTM G5-1972 was used.

1.6 *Results and Discussions*

The variation of corrosion rate of a modified aluminum alloy (flat-type specimen) with time in smoothly stirred Arabian Gulf water with and without silica sand is shown in Fig. 3. A decrease in the corrosion rate with time is observed. The decrease in the corrosion rate may be attributed to the blocking of cathodic sites by corrosion products that restrict the reduction of oxygen. Once the cathodic reduction ceases, the oxide film reaches an equilibrium thickness. The inner layer of the barrier oxide film on the aluminum alloy becomes more compact with increased exposure time, and hence, it retards further dissolution of the alloy. The buildup of the compact film explains why the corrosion rate of the modified aluminum alloy in smoothly stirred Arabian Gulf water decreases with an increase in exposure time. The strong tendency of the modified Al-2.5Mg alloy to form the compact film may be attributed to the chromium content, which is known to be a strong film former.[9] On addition of 2% silica sand, the corrosion rate of the modified aluminum alloy is increased from 0.5 mg/dm^2 per day (mdd) to 2 mdd after 2000 hr of exposure in Arabian Gulf water at 25 ± 2 °C.

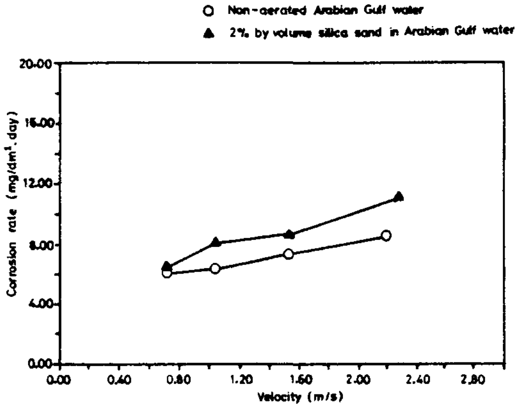

Fig. 4 Variation of corrosion rate with time in dynamic conditions (tubular specimen).

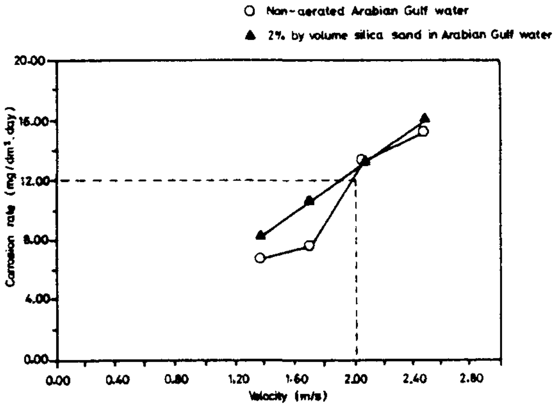

Fig. 5 Variation of corrosion rate with velocity in dynamic conditions (flat plate type specimen).

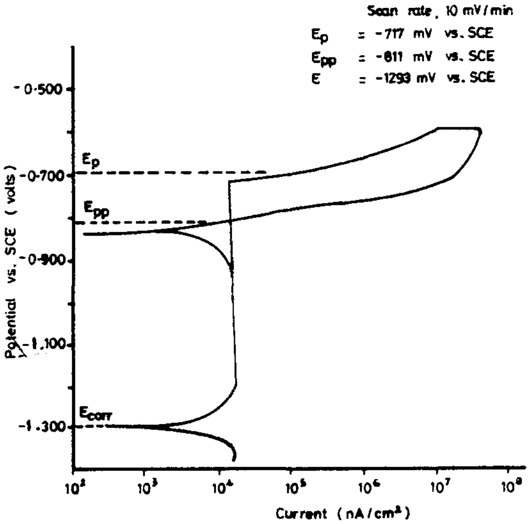

Fig. 6 Hysteresis loop for aluminum alloy in Arabian Gulf water containing 2% by volume silica sand as suspended particles (static condition).

Table 3 Variation of Sherwood Number with Reynolds Number in Arabian Gulf Water without Suspended Particles

Velocity, m/sec	Reynolds number (Re)	Sherwood number (Sh)
2.48	2.12×10^4	35.35
2.10	1.77×10^4	31.18
1.70	1.45×10^4	17.89
1.40	1.10×10^4	15.90

Table 4 Variation of Sherwood Number with Reynolds Number in Arabian Gulf Water Containing Suspended Particles

Velocity, m/sec	Reynolds number (Re)	Sherwood number (Sh)
2.48	2.12×10^4	37.14
2.10	1.77×10^4	30.51
1.70	1.45×10^4	24.68
1.40	1.10×10^4	19.13

The effect of velocity with and without solid particles on the tubular and flat specimens is shown in Fig. 4 and 5. The rate of corrosion of tubular specimens shows a significant increase compared to flat specimens. The effect of flow geometry is therefore predominant, and it appears to act synergistically with velocity on the protective oxide layer. The corrosion rate of the modified aluminum alloy shows a linear increase with seawater containing silica sand. However, the relationship between the corrosion rate and velocity is not observed to be linear in seawater not containing silica sand. The increase in the corrosion rate of the modified aluminum alloy in seawater containing suspended particles can be attributed to the breakdown of the passive layer by high kinetic energy particles. The intensity of corrosion is therefore directly related to the hydrodynamics of film.

1.7 *Mass Transfer Measurements*

Mass transfer measurements were made to determine the effect of suspended particles on flow-induced corrosion. Such measurements have been made mainly to predict the effect of flow regime on corrosion.[10] The Sherwood number has been used to express the magnitude of corrosion. It is correlated with the Reynolds (Re) and Schmidt (Sc) numbers as:

$$\mathrm{Sh} = K\,\mathrm{Re}^x \mathrm{Sc}^y$$

where K is a constant, x varies between 0.3 to 1, and $y = 3$.

In the above mass transfer correlation,

$$\mathrm{Re} = \frac{Vd}{\nu}$$

and

$$\mathrm{Sc} = \frac{\nu}{D}$$

Table 5 Comparison of Pitting Potential and Protection Potential in Arabian Gulf Water

Velocity, m/sec	E_{corr}, mV$_{SCE}$	Pitting potential (E_p), mV$_{SCE}$	Protection potential (E_{pp}), mV$_{SCE}$	$\Delta E = E_p - E_{pp}$, mV$_{SCE}$
2.48	−1113	−730	−835	105
2.10	−1146	−720	−821	101
1.70	−1201	−710	−808	98

Note: Values were obtained by the potentiodynamic method (dynamic conditions) in Gulf Water at 25 °C with a pH of 7.8 ± 0.1.

Table 6 Comparison of Pitting Potential and Protection Potential in Arabian Gulf Water Containing 2 vol% Silica Sand as Suspended Particles

Velocity, m/sec	E_{corr}, mV$_{SCE}$	Pitting potential (E_p), mV$_{SCE}$	Protection potential (E_{pp}), mV$_{SCE}$	$\Delta E = E_p - E_{pp}$, mV$_{SCE}$
2.48	−1107	−743	−858	115
2.10	−1134	−740	−848	108
1.70	−1187	−725	−835	105

Note: Values were obtained by the potentiodynamic method (dynamic conditions) in Gulf Water at 25 °C with a pH of 7.8 ± 0.1.

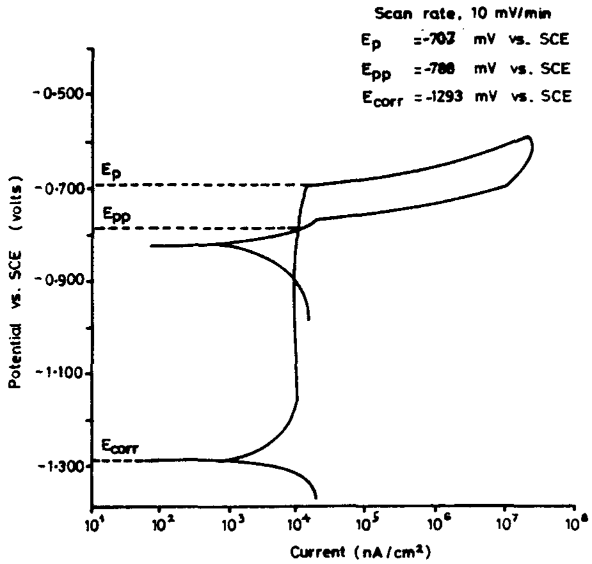

Fig. 7 Hysteresis loop for aluminum alloy in Arabian Gulf water (static condition).

where D is diffusivity (m^2s^{-1}), V is velocity (ms^{-1}), d is the characteristic length of a specimen (m), and v is viscosity (m^2s^{-1}).

Several correlations have been developed for different geometry and flow conditions. However, the following are generally used because of their wide applicability:

$Sh = 0.02\ Re^{0.8}Sc^{0.33}$ Chilton and Colburn[11]

$Sh = 0.0096\ Re^{0.913}Sc^{0.346}$ Harriot and Hamilton[12]

The experimental values of Re and Sh are shown in Tables 3 and 4. High Re and Sh values are obtained in seawater containing suspended particles. The Sherwood number (Sh) is directly related to the mass transfer coefficient (K), and it describes the rate at which species are transported from the bulk solution to the electrolyte/metal interface. An increase in Sherwood number, therefore, indicates an increase in the rate of corrosion. In the absence of suspended particles, as the velocity is increased from 1.40 to 2.48 m/sec, the Sherwood number is increased from 15.90 to 35.35. On adding suspended particles, the Sherwood number increases from 19.13 to 37.14, with the same increase in velocity. Suspended particles increase the rate of corrosion appreciably at a velocity of 1.70 m/sec, as shown by an increase in the Sherwood number from 17.89 to 24.68 (Tables 3 and 4).

1.8 *Electrochemical Studies*

The reaction of aluminum in water is represented by:

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$$

The rate-limiting step is the dissolution of the oxide film, which is pH dependent:

$$Al_2O_3 + 6H^+ \rightarrow Al^{+++} + 3H_2O$$

$$Al_2O_3 + 6OH^- \rightarrow 2AlO_3 + H_2O$$

Pitting takes place by breakdown of the passive surface in the presence of oxygen. The onset of pitting is shown by a break in the anodic polarization curve, accompanied by a sudden rise in current density. The cathodic reaction is largely responsible for corrosion, as the diffusion of oxygen to the metal/electrolyte interface is the rate-controlling step. The anodic and cathodic polarization curves for the aluminum alloy in seawater with and without the presence of suspended solids are shown in Fig. 6 and 7. Under static conditions, the effect of suspended particles on the pitting potential is not significant; however, under dynamic conditions, the pitting potential (E_P) tends to shift to more negative values. At higher flow velocities, the effect of suspended particles becomes more pronounced as compared to lower velocities. At a velocity of 2.48 m/sec, the pitting potential shifts from −730 mV$_{SCE}$ to −743 mV$_{SCE}$ on adding 2% silica sand, as shown in Table 5. The more active potentials obtained at higher

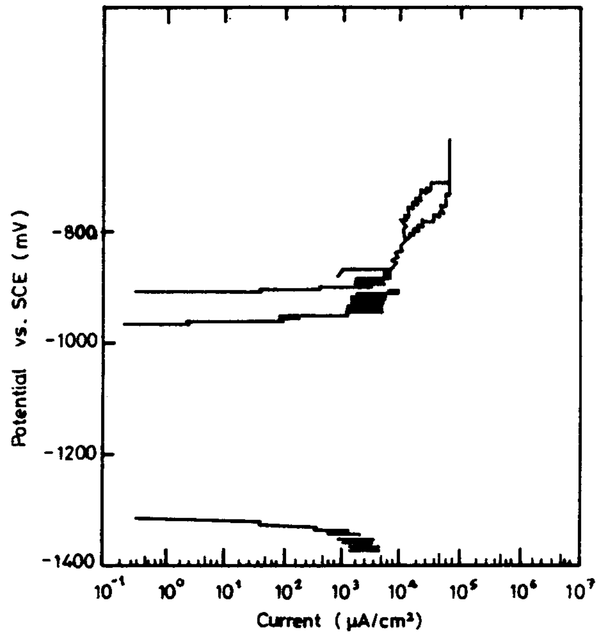

Fig. 8 Hysteresis loop for aluminum alloy in Arabian Gulf water in dynamic condition (velocity 2.48 m/sec).

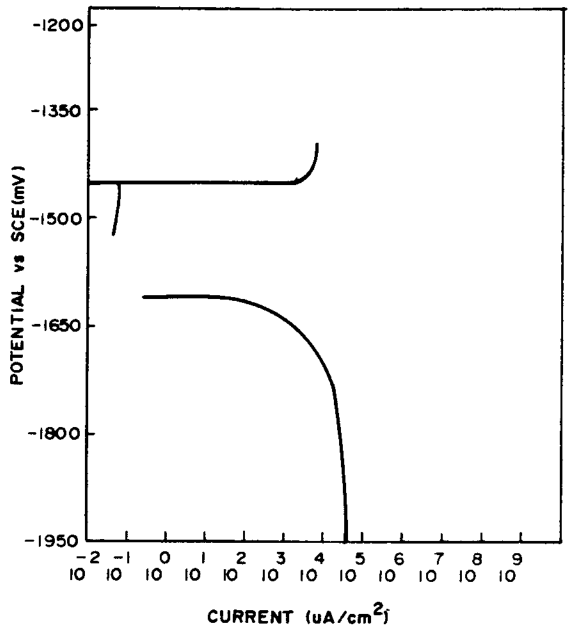

Fig. 9 Cathodic polarization curve of aluminum alloy in Arabian Gulf water containing 2% by volume silica sand as suspended particles in dynamic condition (velocity 2.10 m/sec).

velocities in the presence of suspended particles signify a higher rate of pitting propagation. The width of hysteresis curve shown in Fig. 8, indicated by $\Delta E = E_p - E_{pp}$, also suggests an increased rate of pitting propagation.

1.9 *Cathodic Polarization and Limiting Current*

Generally, in alkaline solutions, the reaction rate is controlled by the diffusion of OH^- ions to the electrode surface. The limiting current density (i_L) increases with an increase in the velocity. It has been observed that the magnitude of limiting current density of the modified aluminum alloy increases further with addition of suspended solids in seawater.[13] Limiting current densities at different velocities were obtained experimentally by cathodic polarization of the modified alloy. The values of limiting current densities are shown in Table 7. A typical cathodic polarization curve of modified aluminum alloy in Arabian Gulf water containing 2% by volume silica sand as suspended particles is shown in Fig. 9.

The limiting current density increases as the velocity increases, as shown by Table 7. For instance, i_L increases from 10 mA/cm^2 at 1.40 m/sec to 30 mA/cm^2 at 2.48 m/sec. On adding solid particles, i_L is further increased to 50 mA/cm^2 at 2.48 m/sec. The increase in the limiting current has been attributed to increased turbulence on the boundary surface due to impingement of particles.[5] It has been suggested that, in the presence of solid particles, the laminar sublayer is destroyed by the impact of particles and a local turbulence is set up, which leads to an increase in the rate of mass transfer.[2]

Table 7 Values of Limiting Current Density Obtained by Polarization Technique

Media	Velocity, m/sec	Limiting current density (i_L), mA/cm^2
Arabian Gulf water in deaerated condition*	0	0.06
Arabian Gulf water + 2% by volume silica sand in deaerated condition*	0	0.08
Arabian Gulf water	2.48	30.0
in deaerated condition	2.10	27.5
without suspended	1.70	20.0
solids	1.40	10.0
Arabian Gulf water	2.48	50.0
+ 2% by volume	2.10	40.0
silica sand in	1.70	25.0
deaerated condition	1.40	17.5

*Test media are the same, but the first two values are in the static condition (zero velocity) and the remaining values are for dynamic conditions.

1.10 *Variation of Open Circuit Potential with Time*

The open circuit potential of the aluminum alloy varies with time and stabilizes only after sufficiently long periods. The variation of open circuit potential is caused by a change in the mechanism of corrosion of aluminum from anodic to cathodic and by changes in the film thickness brought about by the competitive process of film formation and film dissolution, which continues until an equilibrium thickness is reached. Such variations can be used to predict the effect of suspended solids or other variables such as oxygen, temperature, inhibitor concentration, etc. The variation of open circuit potential with time is shown in Fig. 10 and 11. A shift of potential in the active direction (more negative) suggests propagation of pits and a shift in the less active direction of potential suggest film formation.[14] As shown by Fig. 10 and 11, the magnitude of shift of potential in the active (more negative) direction is higher in the presence

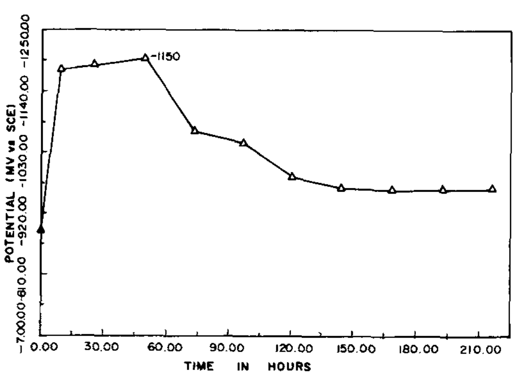

Fig. 10 Open circuit potential vs time behavior of aluminum alloy in nonaerated Arabian Gulf water in dynamic condition (velocity 2.48 m/sec).

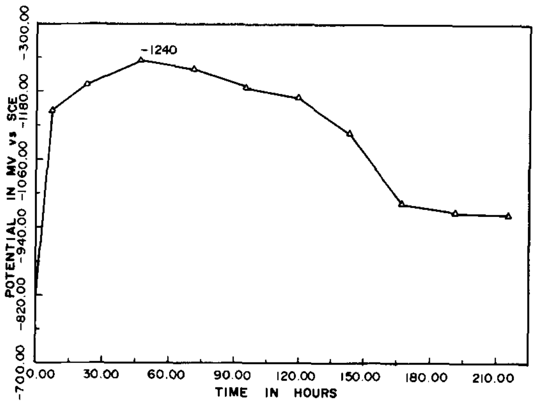

Fig. 11 Open circuit potential vs. time behavior of aluminum alloy in nonaerated Arabian Gulf water in dynamic conditions (velocity 2.4 m/sec) containing 2% by volume silica sand as suspended particles.

of suspended particles (–820 to –1240 mV_{SCE}) than in their absence (–889 to –1150 mV_{SCE}). The shift of potential in the active direction on the addition of suspended solids therefore suggests that the rate of pit propagation is increased by suspended particles. It is observed that, at a higher velocity (2.48 m/sec), the open circuit potential of the modified alloy in seawater containing suspended particles reaches a maximum in the active direction and remains in the active potential range for a longer period of time compared to the potential observed in seawater without suspended particles. The above observation explains the higher intensity of pitting observed in the alloy on exposure to seawater containing suspended solids. The variation of open circuit potential with time therefore predicts a decreased resistance of the alloy to pitting in seawater containing suspended particles.[15]

2 Conclusion

The rate of corrosion of modified Al-2.5Mg alloy in Arabian Gulf water increases appreciably with addition of 2% silica sand. The effect of suspended solids becomes more pronounced at higher velocities. The rate of corrosion of tubular specimens is observed to be higher than the flat plate specimens, which shows the effect of flow geometry on the rate of corrosion. The magnitude of corrosion depends on the flow regime, amount of suspended particles, and flow velocity. The increase in the rate of corrosion by the above factors appears to be caused by the breakdown of the passive film on the alloy surface.

The rate of mass transfer is increased appreciably by suspended solid particles, as suggested by a higher Sherwood number. The pitting potential of the modified aluminum alloy shifts to more active values of potential in the presence of suspended particles. The open circuit potential of the modified alloy also remains in the active pitting range for a longer period of time in seawater containing suspended solids. Both these observations suggest an increase in the intensity of pitting by suspended particles.

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