

THE INHIBITIVE CHARACTERISTICS OF MIXED INHIBITOR COMBINATIONS UNDER HEAT AND MASS TRANSFER CONDITIONS

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Abstract The inhibitive characteristics of mixed inhibitor combinations on mild steel, under controlled conditions of heat and mass transfer have been investigated using a rotating cylinder electrode system. Potentiostatic polarization experiments were carried out in both the inhibited and uninhibited brackish water solutions, under isothermal and heat transfer conditions. The optimum concentrations of the used inhibitors were estimated under the isothermal and dynamic conditions.

Under isothermal conditions, the limiting current density values of oxygen reduction in the brackish water followed Eisenberg equation. The presence of heat transfer enhanced the oxygen transfer rate over and above the value under isothermal conditions. The corrosion and passivation potentials, and the passive current density values were a complex function of temperature, flow rate and heat transfer. The anodic current density values increased with the increase in temperature, flow rate and the presence of heat transfer. The mixed inhibitor combinations showed high protection efficiency under the studied heat and mass transfer conditions.

Key words: corrosion, inhibitors, steel, RCE.

INTRODUCTION

Corrosion is defined as the destruction or deterioration of a material because of the reaction with its environment. The importance of corrosion science is threefold, economic, improved safety, and conservation (Uhlig and Revie, 2000).

Iron and its alloys are of universal importance in the chemical process industries, cooling water systems (Moccari, 1999), power plant installations, and many other industrial applications. Water and/or seawater are two of the most important aqueous mediums that are in contact with metals of the iron group in the chemical industries. When iron is immersed in water or seawater exposed to atmosphere, corrosion occurs (Fontana and Greene, 1978).

A metal or alloy is passive if it substantially resists corrosion in an environment where thermodynamically there is a large free-energy decrease associated with its passage from the metallic state to appropriate corrosion products. Some metals can be made passive by exposure to passivating environments (e.g. iron in chromate or nitrite solutions) or by anodic polarization at sufficiently

high current densities (e.g. in H₂SO₄). For that the formation of passive films on ferrous alloys has received the attention of many workers (Evans, 1960).

In solutions containing aggressive anions such as chloride, pitting corrosion readily occurs on passivated metals polarized at potentials more noble than the critical pitting potential (Mercer and Lumbard, 1995).

An inhibitor is a substance that when added in small concentrations to an environment, decreases the corrosion rate. In a sense, an inhibitor can be considered as a retarding catalyst (Fontana and Greene, 1978). There are several classes of inhibitors, conveniently designated as: passivators, organic inhibitors and vapor phase inhibitors. Passivators are compounds that promote the passivity on the metal surface (Rozenfeld, 1981). In general, they are primarily used to inhibit the corrosion of metals and alloys that demonstrate active passive transitions, such as iron and its alloys. Passivators are reduced at cathodic areas, at a current density equivalent to a true current density at anodic areas, equaling or exceeding $i_{critical}$ for passivation (Gomma, 1995).

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Phosphates are non-oxidizing compounds that effectively passivate iron in the near-neutral range, though facilitating the adsorption of dissolved oxygen. Traditionally, chromate was used as a corrosion inhibitor in many water systems. Now, due to environmental concerns many alternatives are being studied, the best being, a molybdate based inhibitor combination (Shams El Din, et al., 1997). Nitrites (Ramasubramanian, et al., 2001) are inorganic oxidizing inhibitors that passivate the metal and shift the corrosion potential towards the noble direction.

The electrochemical behavior of a metal, under controlled conditions of heat and mass transfer, can be achieved using one of the rotating electrodes (disc or cylinder). Laminar or turbulent flow conditions can be achieved using rotating electrode, by controlling its rotational velocity (Bastidas et al., 1995).

EXPERIMENTAL WORK

Under controlled conditions of heat and mass transfer, a set of experiments using deionized water containing 1000 ppm chloride ions, pH = 7.5 (i.e.: brackish water), in the presence and absence of different inhibitors, were carried out using a rotating cylinder electrode (RCE) system. A set of experiments, under isothermal ($T=50\text{ }^{\circ}\text{C}$) and dynamic conditions (RPM= 600) were carried out in brackish water, containing different sodium nitrite concentrations (100, 200, 300, ..., 1000 PPM), in order to estimate the optimum concentration of this inhibitor.

Under isothermal ($T=50\text{ }^{\circ}\text{C}$) and dynamic (RPM= 600) conditions, a set of experiments were carried out in order to get the optimum concentrations of sodium molybdate and sodium hexametaphosphate inhibitors. In these experiments, deionized water containing 1000-PPM chloride ions, 600-PPM nitrite ions, with different molybdate and hexametaphosphate concentrations were used.

Electrochemical measurements, under different temperatures, flow rates, and inhibitor concentrations were carried out, for both the isothermal and heat transfer conditions, in order to study the corrosion inhibition of mild steel in industrial cooling water systems.

Electrochemical polarization techniques were used to determine the polarization curves of mild steel under controlled conditions of heat and mass transfer. The heat flux from the working electrode to the solution was controlled to be 3.45 kW/m^2 . Several polarization experiments under isothermal and heat transfer conditions were carried out in deionized water containing 1000 PPM NaCl solutions at 200, 400, 600 and 800 RPM and at different bulk temperatures 303, 313 and 323 K.

Under isothermal conditions, the mild steel electrode was cathodically polarized from -900 mV to the breakdown potential by increasing the potential in steps

of 20 mV/min . In the case of heat transfer conditions, the mild steel electrode was cathodically protected at a potential of -1000 mV until a steady state heat flux was attained. Then the same procedure as in the isothermal conditions was repeated.

RESULTS AND DISCUSSION

I. Uninhibited Solutions (Brackish Water):

The limiting current density (LCD) values of oxygen reduction were taken in the cathodic polarization region at slope of $\Delta E/\Delta I \rightarrow \infty$. Under the isothermal conditions the LCD values were temperature and flow dependent as can be seen in Figure (1). At a constant rotational speed, the limiting current density increases as the bulk temperature increases. This can be attributed to the increase in the diffusion coefficient and the decrease in the kinematic viscosity (ν) as the temperature is increased. At a constant bulk temperature, increasing rotational speed, increases the LCD values as shown in Figure (1). This can be attributed to the increase in the mass transfer coefficient of oxygen, K . Also increasing the rotational speed, decreases the thickness of the

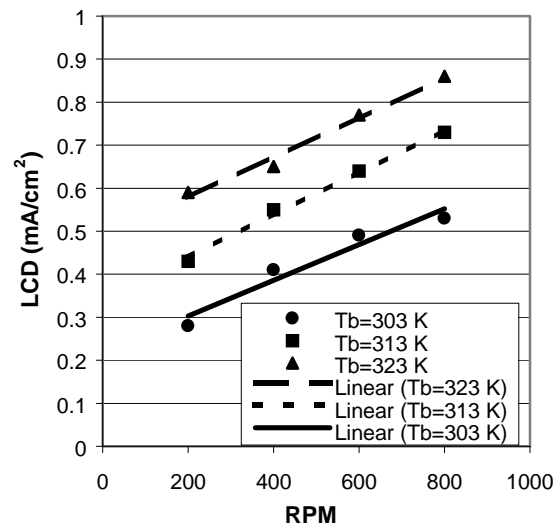


Fig.1 Experimental values of LCD of oxygen reduction on mild steel in uninhibited brackish water solution, under isothermal conditions.

diffusion boundary layer which resists the oxygen transfer to the RCE.

The charge transfer of the oxygen reduction is a four-electron process up to 323 K bulk or effective temperature. Above 323 K, the contribution of the two-electron process increases. The corrosion potential values (E_{corr}) were precisely measured using a digital multimeter and also from the corresponding potentiostatic polarization curves as shown in Table (1). E_{corr} is found

to be highly affected by the temperature as well as the rotational speed.

Under the heat transfer conditions, the LCD values, shown in Figure (2), were found to be higher than the corresponding values under the isothermal conditions. In addition to the increase in the LCD and diffusion coefficient values, the presence of heat transfer lead to form thermal eddies adjacent to the metal surface that enhances the transfer of oxygen towards the metal surface (Parshin, et al., 1982). Also in the vicinity of the metal surface the kinematic viscosity of the solution under heat transfer conditions is lower than that under isothermal conditions for the same bulk temperature T_b , leading to a higher local mass transfer, viz. higher LCD.

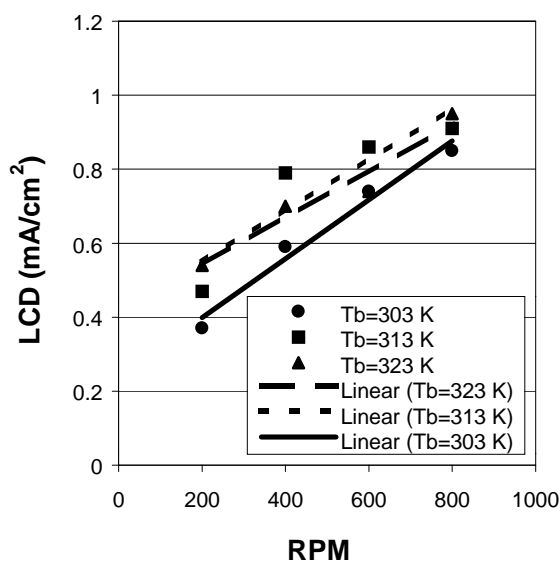


Fig. 2: Experimental values of LCD of oxygen reduction on mild steel in uninhibited brackish water solution, under heat transfer conditions.

It was found that the variation of charge transfer of oxygen reduction depends on the electrode, electrolyte composition (Alwash, et al., 1987), potential range (Delahay, 1950), pH (Patrich and Wanger, 1950) and temperature (Jaralla, 1984). It is worth mentioning that, under the heat transfer conditions, the heat and mass transfer coefficients that are calculated using Colburn analogy were found to be proportional to the rotational speed raised to power 0.7. This relation resembles to that of Sparrow and Gregg (Sparrow and Gregg, 1959) for the RCE.

It was found that the corrosion potential values under heat transfer conditions shown in Table (2) were more negative (less noble) than the corresponding values under the isothermal conditions. This can be attributed to the higher stimulation in the anodic kinetics due to the higher interfacial temperatures.

For the anodic region, it was observed from the potentiostatic polarization curves and data that, there is an active region in which the potential within a short potential range, varies linearly (with a constant slope) with the current density, indicating activation polarization controlled region. Beyond the constant slope region, the polarization curves rise sharply. The lower the flow rate and the temperature, the greater is the rise in the curvature of the polarization curves in the anodic region. The above fact confirms the presence of the concentration polarization at high anodic over potentials due to the presence of filming effect on the mild steel surface which shows flow and temperature dependence. All suggested mechanisms of iron dissolution and the findings of Foroulis (Foroulis, 1979) are in agreement with the above findings.

At an over potential (η) equal to 120 mV, the anodic current density values i_a were obtained graphically from the corresponding potentiostatic polarization curves, for both the isothermal and heat transfer conditions and were tabulated in Tables (3) and (4). It was observed that both the temperature and flow rates have a pronounced effect on i_a .

II. Inhibited Solutions:

To estimate the optimum concentration of Sodium Nitrite, different concentrations of the inhibitor were added to the brackish water solution. From the polarization curves it was found that the minimum concentration at which the passive state was achieved is 600 PPM. The passivation potential E_p , and the passive current density values i_p in brackish water, inhibited with 600 PPM NaNO_2 were estimated using potentiostatic polarization curves for both the isothermal and heat transfer conditions as shown in Tables (5)-(8).

It was observed that the temperature is highly influential on the passivation potential values as well as the flow rate. In an extensive experimental study of the active, passive and transpassive oxide films on iron in aqueous environments, Flory et al as quoted by Mercer (Mercer, 1990) concluded that $\gamma\text{-Fe}_2\text{O}_3$ is present in all passive films regardless of the pH of the solution. Sodium Nitrite inhibitor causes a large shift in the potential of steel toward the positive, bringing the metal into the passive state. The effect of nitrite ions on the passivation can be explained by the adsorption of these ions, which reduces the free energy of the system and impedes the passage of ion-atoms of metal from the lattice into the solution (Rozenfield, 1981).

Under the heat transfer conditions, the passivation potential values at 800 and 400 RPM, (Table (4)), were more noble than the corresponding values under the isothermal conditions, and this can be attributed (in addition to the previous investigation) to the increase in the interfacial temperature, which increases the solubility of the formed stable film (Fe_2O_3 and $\gamma\text{-Fe}_2\text{O}_3$) and as a

result more noble potential values are required for passivation.

Tables (5) & (6) indicate that the effect of temperature on the passive current density values is very significant. At a constant rotational speed, the passive current density values increase with the increase in bulk temperature. This can be attributed to the increase in the solubility of the protective films formed with the increase in the temperature. Also the increase in temperature increases the electrical conductivity of the passive film, which increases the current density needed for passivation.

Under the heat transfer conditions the passive current density values were lower than the corresponding values under the isothermal conditions. This can be attributed to the fact that, the formed films on the metal surface under the heat transfer conditions, were more compact and thicker than those formed under the isothermal conditions.

For the mixed inhibitor containing solutions (brackish water containing 600 PPM sodium nitrite, 200 PPM sodium molybdate and 200 PPM sodium hexametaphosphate) both the passivation potential (E_p) and the current density values (i_p) were estimated using the polarization curves for both the isothermal and the heat transfer conditions, Tables (9)-(12).

The passivation potential values were shifted to more negative values in the presence of molybdate, than the corresponding values for nitrite only containing solutions, see Tables (8.1, 8.2, 8.7 and 8.8). It was observed that increasing the temperature at a constant rotational speed shifts the passivation potential values to more noble values. This can be attributed to the fact that, increasing the temperature increases the solubility of the protective films, and as a result more noble potentials are required (Lizlovs, 1976).

Sodium Hexametaphosphate (SHMP) inhibitor shifted the potential to more negative values, and it was proved to be the prime decelerator of the cathodic reaction (Rozenfield, 1981). SHMP also has the property that creates soluble complexes with the ions of metals, as a result of which, the iron ions are retained in the solution. It can be concluded that the mixed inhibitor combination formed adsorbed films on the cathodic sites of the metal surface, which shifted the potential to the cathodic region.

Tables (7) and (8) show that i_p values in the mixed inhibitor containing solutions are temperature and flow dependent, and the i_p values under the heat transfer conditions are, in general, higher than those of under the isothermal conditions. This can be attributed to the high increase in the solubility of the passive film due to the high interfacial temperature under the heat transfer conditions (Jaralla, 1984). Flynn (Flynn, 1972) obtained a thicker passive film under heat transfer conditions for the

Fe-H₂O system. He attributed this behavior to a higher solid-state diffusion under heat transfer conditions.

CONCLUSIONS

I. Uninhibited Solutions:

Increasing the temperature and/or flow increased the limiting current density values (i_p) of oxygen reduction rate and the values were in agreement with Eisenberg equation.

The charge transfer (z) of the oxygen reduction was a four-electron process up to a temperature of 323 K, above which, the contribution of the two-electron process appeared.

The corrosion potential values were shifted to more active values by increasing the temperature (bulk or effective), while increasing the flow rate shifted the corrosion potential to more noble values.

The anodic current density values under the heat transfer conditions were higher than the corresponding values under the isothermal conditions.

The anodic dissolution showed activation control, and the effect of temperature was more predominant than the flow rate on it.

Both the temperature and flow rate affected significantly the precursor film formed on the anode.

II. Inhibited Solutions:

The optimum concentrations of the mixed inhibitor combination were found to be 600-PPM sodium nitrite, 200-PPM sodium molybdate and 200-PPM sodium hexametaphosphate.

The sodium nitrite inhibitor, shifted the potential of mild steel towards the noble region, and brought the mild steel into the passive state, by shifting the passivation potential towards the negative.

The addition of molybdate inhibitor to the nitrite containing solutions shifted the passivation potential towards the active region, due to the insoluble and highly protective Fe³⁺ molybdate complex formed on mild steel surface.

The hexametaphosphate inhibitor shifted the corrosion potential of mild steel to more negative values, and it was the prime decelerator of the cathodic reaction.

The passivation potential and the passive current density values were a complex function of the temperature, flow rate, heat transfer and all the parameters affecting the strength and the stability of the protective films formed on the mild steel surface.

The used mixed inhibitor combination, showed highly protective properties on mild steel under the simulated industrial conditions (cooling water systems, power plants and many other chemical and petrochemical process industries).

Table(1): The corrosion potential values of mild steel in brackish water under isothermal conditions, E_{corr} , mV (SCE)

RPM	Bulk Temperature (K)		
	303	313	323
200	-400	-465	-495
400	-400	-440	-480
600	-390	-420	-455
800	-375	-390	-400

Table (2): The corrosion potential values of mild steel in brackish water under heat transfer conditions, E_{corr} , mV (SCE).

RPM	Bulk Temperature (K)		
	303	313	323
200	-453	-460	-472
400	-420	-440	-455
600	-417	-428	-430
800	-395	-415	-420

Table (3): The anodic current density values at 120 mV over potential for brackish water under isothermal conditions, i_a (mA/cm²).

RPM	Bulk Temperature (K)		
	303	313	323
200	0.24	0.29	0.35
400	0.26	0.33	0.39
600	0.26	0.37	0.43
800	0.30	0.37	0.46

Table (4): The anodic current density values at 120 mV over potential for brackish water under heat transfer conditions, i_a (mA/cm²).

RPM	Bulk Temperature (K)		
	303	313	323
200	0.30	0.35	0.47
400	0.32	0.40	0.52
600	0.35	0.43	0.59
800	0.40	0.50	0.63

Table(5): The passivation potential values in inhibited solution (600 PPM NaNa₂) under isothermal conditions, mV (SCE).

RPM	Bulk Temperature (K)		
	303	313	323
200	-208	-300	-290
400	-320	-280	-245
600	-237	-285	-200
800	-284	-298	-337

Table (6): The passivation potential values in inhibited solution (600-PPM NaNa₂) under heat transfer conditions, mV (SCE).

RPM	Bulk Temperature (K)		
	303	313	323
200	-320	-305	-280
400	-260	-180	-165
600	-220	-335	-215
800	-240	-260	-220

Table (7): The passive current density values ($i_p \times 10^4$) in inhibited solution (600 PPM NaNa₂) under isothermal conditions, mA/cm².

RPM	Bulk Temperature (K)		
	303	313	323
200	12	31	50
400	40	62	58
600	50	63	32
800	33	47	60

Table (8): The passive current density values ($i_p \times 10^4$) in inhibited solution (600-PPM NaNa₂) under heat transfer conditions, mA/cm².

RPM	Bulk Temperature (K)		
	303	313	323
200	24	57	40
400	12	12	6
600	24	19	26
800	50	34	12

Table (9): The passivation potential values in the

mixed inhibitor solutions under isothermal conditions mV (SCE).

RPM	Bulk Temperature (K)		
	303	313	323
200	-280	-275	-260
400	-360	-280	-265
600	-340	-255	-270
800	-380	-285	-240

Table (10): The passivation potential values in the mixed inhibitor solution under heat transfer conditions, mV (SCE).

RPM	Bulk Temperature (K)		
	303	313	323
200	-320	-300	-300
400	-320	-300	-200
600	-255	-255	-255
800	-240	-320	-300

Table(11): The passive current density values ($i_p \times 10^4$) in the mixed inhibitor solutions, under isothermal conditions, mA/cm².

RPM	Bulk Temperature (K)		
	303	313	323
200	90	43	20
400	90	40	45
600	80	23	40
800	90	38	27

Table (12) The passive current density values ($i_p \times 10^4$) in the mixed inhibitor solutions, under heat transfer conditions, mA/cm².

RPM	Bulk Temperature (K)		
	303	313	323
200	120	84	220
400	110	130	23
600	46	44	60
800	39	100	290

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