INHIBITION OF PITTING CORROSION OF C-STEEL IN NaCl SOLUTION BY SOME INORGANIC COMPOUNDS

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ABSTRACT

Pitting corrosion potentials of a carbon steel electrode in different concentrations of sodium chloride solutions were measured using potentiodynamic technique. It was found that the increase in chloride ion concentration leads to a decrease in the pitting potential according to S-shaped curve. This curve was explained on the basis of formation of passivable, limiting active and continuously propagated pits depending on the concentration of chloride ion. Addition of the sodium salts of vanadate, molybdate and tungstate caused a shift of the pitting potential toward the noble direction accounting for increased resistance to pitting attack. The inhibitive properties of these anions were explained on the bases of their strong adsorption on the metal surface as well as formation of insoluble salts by combination with the dissolved metal ions. These insoluble salts resist the penetration power of chloride ion and consequently decrease the rate of pitting corrosion.

Keywords: Carbon steel, pitting corrosion, inorganic inhibitors.

1. INTRODUCTION

Pitting is one of the most dangerous and common types of degradation observed that attacks the metals and alloys. Some aqueous solutions containing halide ions can cause a destruction of the metal through initiation of pitting corrosion. The halide ions initiate the pitting corrosion only in the presence of a passive film on the metal surface. Various metals such as iron, aluminum, cadmium, zinc and copper as well as their alloys are susceptible to pitting corrosion [1-5]. It is well known that all the mentioned metals and their alloys form passive films on their surfaces in contact with aqueous solutions. The pitting potential characterizes the susceptibility of metal or alloy to pitting corrosion. Chromate, phosphate, tungstate and molybdate ions were used previously to inhibit the pitting corrosion of steel and zinc [7,8]. Uhlig and Gilman [9] used nitrate ions to inhibit pitting corrosion of stainless steel in ferric chloride solutions.

In the present work, trials were made to inhibit the pitting corrosion of C-steel electrode in 3.5% NaCl solution using the sodium salts of molybdate, vanadate and tungstate.
Experimental

Steel of type 5p x-L with composition of (0.26% C, 1.35% Mn, 0.04% P, 0.03% Ti, 0.02% V and 0.005% Nb) was used in the present study. It was made in form of a rod embedded so as to make the bottom area exposed to the solution is 1.0 cm². Pretreatment of the electrode included polishing with the finest grade emery paper, degreasing with acetone, rinsing with bidistilled water and drying between two filter papers. Complete wetting of the surface was taken as an indication of its cleanliness.

The solutions were prepared using chemicals of analytical reagent AR quality and bidistilled water. No attempts were made to deaerate them. The electrolytic cell was all Pyrex glass and described elsewhere [10].

Potentiodynamic anodic polarization of the electrode was performed at a potential scan rate of 1.0 mV using Wenking potentiocouc type POS 73. The current density-potential curves were recorded on x-y recorder type PL3. All experiments were carried out at 25 ± 1°C.

Results and discussion

i-Effect of Chloride ion concentration:

Fig.1 shows the potentiodynamic anodic polarization curves of carbon steel electrode in a varying percentages of chloride ions at a scanning rate of 1.0 mV. The slow scan rate permits more time for pitting initiation to occur at a less positive potential [11].

![Fig.1: Potentiodynamic anodic polarization curves of carbon steel in different percentages of NaCl.](image-url)
The presence of chloride ions leads to a sudden and marked increase of current at certain definite potential denoting the destruction of the passive film and initiation of visible pits. The higher the concentration of chloride ions the higher the shift of the pitting potential in an active direction.

The dependence of the pitting potential $E_{\text{pit}}$ of C-steel electrode on the percentage concentration of chloride ions is given in Fig. 2. Most studies of the pitting corrosion of metals and alloys reveal straight line relationship between $E_{\text{pit}}$ and concentration of chloride ions [12,13]. However, in present investigation a curve of segmoidal nature was obtained (Fig. 2). The following conclusion could be drawn from the curve of Fig. 2.

Fig. 2: The relationship between pitting potential and the percentage concentration of NaCl for carbon steel electrode.

At low concentration of chloride ions the pitting potential shifts slightly in the negative direction because the chloride ions are not sufficient to destroy completely the passive film on the metal surface. On the other hand, most of the pits formed under this circumstance undergo repassivation. As the chloride ions concentration was increased the penetration of the passive film and initiation of pitting corrosion
are established at more active potential. The formed pits are continuously propagate and can not undergo repassivation.

**ii-Inhibition of pitting corrosion:**
The effect of addition of increasing concentrations of sodium salts of vanadate, molybdate and tungstate as inhibitors of pitting corrosion of C-steel electrode was examined. Fig. 3-5 show effect of addition of tungstate, molybdate and vanadate, respectively, on the potentiodynamic anodic polarization curves of C-steel electrode in 3.5% NaCl solution. It was found that the pitting potential of the C-steel electrode to the noble (positive) direction with increasing of tungstate, molybdate and vanadate concentrations. This indicates an increase in the resistance to pitting corrosion.

![Fig. 3: Potentiodynamic anodic polarization curves of carbon steel in a solution of 3.5% NaCl containing different concentrations of sodium tungstate.](image-url)
Fig. 4: Potentiodynamic anodic polarization curves of carbon steel in a solution of 3.5% NaCl containing different concentrations of sodium molybdate.

Fig. 5: Potentiodynamic anodic polarization curves of carbon steel in a solution of 3.5% NaCl containing different concentrations of sodium vanadate.
Fig. 6 represents the relationship between $E_{\text{pit}}$ and the logarithm of inhibitor concentration ($\log C_{\text{inh}}$). Linear relationships were obtained for all used inhibitors giving an increase in the positive shift of the pitting potential as the inhibitor concentration was increased. The variation of pitting potential with inhibitor concentration obeys the following equation:

$$E_{\text{pit}} = a + b \log C_{\text{inh}}$$

where $a$ and $b$ are constants which depend on the type of additive.

Fig. 6: The relationship between pitting potential and the logarithmic of the molar concentration of additivies.

The inhibition action of these could be explained by their strong adsorption on the electrode surface. Formation of insoluble salts by their reaction with the dissolved metal ions which resist the penetration of chloride ions and consequently decrease the pitting is also expected [14].

It was found also from Fig. (2) that inhibition afforded by the used compounds at concentration of 0.01 M follows the following sequence:

$$\text{MoO}_4^{2-} > \text{VO}_5^{2-} > \text{WO}_4^{2-}$$

It is clear from the above sequence that $\text{MoO}_4^{2-}$ is the best of all the pitting corrosion inhibitors used in the present investigation. A similar result was obtained also by Kodama and Ambrose [15] who attributed it to the formation of the insoluble compound ($\text{FeMoO}_4$). The inhibition effect of molybdate anion can be explained also by the formation of polymolybdate anion. This polyanion may precipitate as a salt on the metal surface owing to its low solubility product [16]. Thus, the environment favorable to pit initiation stimulates the formation of polymolybdate, which enhance pitting resistance.
The inhibitive action of tungstate and vanadate anions could be explained by adsorption of them on the metal surface which posses a film of $\text{Fe}_2\text{O}_3$. The increased protective nature of the passive film may be a result of film strengthening through increased incorporation of adsorbed anion in $\text{Fe}_2\text{O}_3$ film.

REFERENCES