Anodic Polarization of Mild Steel in Saturated Ca(OH)$_2$ Contaminated with NaCl in Presence of NaNO$_2$

Aprael S. Yaro and Hany S. Hassan

Chemical Engineering Department - College of Engineering - University of Baghdad - Iraq

Abstract

The corrosion behavior of mild steel in saturated aerated and de-aerated Ca(OH)$_2$ solution was investigated using electrochemical measurements. The work was carried out with small coupons immersed in solutions containing different quantities of NaCl in presence of various NaNO$_2$ concentrations as corrosion inhibitors. It has been found that:(1) In presence of NaCl, the time required to reach O$_2$ evolution potential in de-aerated Ca(OH)$_2$ polarized at 10µA/cm^2 is function of inhibitor concentration and it becomes lass as NaNO$_2$ increases compared with zero presence indicating the effectiveness of NaNO$_2$ as anodic corrosion inhibitor. (2) In absence of NaCl, the time required to reach O$_2$ evolution potential in de-aerated solutions is less that in aerated solutions when inhibitor increases from 0 to 0.3 wt.%. (3) In presence of sufficient chloride in de-aerated Ca(OH)$_2$ solution, the passive film may broken down locally.

Keywords: anodic polarization, alkaline solution, galvanostatic technique, O$_2$ evolution potential.

Introduction

The electrochemical behavior of steel in stagnant alkaline solutions, especially saturated Ca(OH)$_2$, has been previously investigated [1-2]. It was found that the oxidation processes that takes place previously on steel are determined by the degree of surface oxidation of the sample and dissolved oxygen, but not by the type of cation present. In aerated solution, ferrosoferric oxide (Fe$_3$O$_4$) is the intermediate oxidation product on the steel surface while ferrous hydroxide (Fe(OH)$_2$) is the intermediate product in de-aerated solution [1], therefoe immersed steel in aerated or de-aerated solution of Ca(OH)$_2$ always becomes passivated. Such passivity is destroyed, however, when chlorides Cl$^-$ and other corroding materials are present as admixtures in the alkaline solution [3].

Corrosion inhibitor by NaNO$_2$ is a problem of both practical and theoretical significance. Corrosion of steel can be prevented in neutral and alkaline solutions by NaNO$_2$. It is of advantage over chromates in that it has no known effect on the skin. NaNO$_2$ is of theoretical interest in that it is an inhibiting material which does not form an insoluble with iron [4].

It is believed, that the present study of the corrosion behavior of steel in aerated and de-aerated saturated Ca(OH)$_2$ is similar in many respects to the aqueous phase of cement in reinforcement, so it will contribute to better understanding of the behavior of embedded reinforcement. Keeping in mind that the induced applied current, which causes polarization of the immersed mild steel in the anodic direction compared to its free corrosion potential in the study was about 10µA/cm^2 using galvanostatic pulse technique [5].

Experimental Work

The evaluation of an anodic corrosion inhibitor for mild steel immersed in stagnant alkaline solution was investigated using half-cell and galvanostatic polarization techniques.

Steel coupons of 3x1x0.1 cm^3 dimensions and chemical composition (C:0.014, Mn: 0.309, Si: 0.004, P: 0.005, S: 0.007, Cr: 0.021, Ni: 0.01, Mo: 0.009, Cu: 0.012, Al:0.004, Fe: the remainder) wt.% were used.

The coupons were first polished using emery paper of grades No. 220, 320, 400, and 600, degreased by benzene

and acetone, rinsed with distilled water and then pickled in 50% HCl acid. The clean steel was coated with epoxy in such away that only about 3 cm² area was always exposed to corrosive media.

De-aerated abd aerated Ca(OH)₂ at 30°C were used as a corrosive media (i.e. saturated Ca(OH)₂ was prepared by dissolving 1.53 g of Ca(OH)₂ crystals in 1 liter of pure distilled water). All potential values mentioned are with respect to saturated calomel electrode. For de-aerated test solution, high purity of 99.9% N₂ gas was bubbled into the test solution for about 1.5 hr.

Polarization measurements

Galvanostatic technique was used to make these measurements. The circuit diagram and procedure is shown in detail somewhere [6]. The potential of the steel electrode was recorded relative to that of the saturated calomel electrode at current density of 10 μA/cm² as a function of time. The experiments were carried out at 30°C.

Results and Discussion

Typical corrosion potential measurements as referenced to saturated calomel electrode (S.C.E.), for low carbon steel totally in aqueous solutions of saturated Ca(OH)₂, in absence and presence of both sodium nitrite (NaNO₂) and sodium chloride (NaCl) at different concentrations are tabulated in Table 1, with pH value for each experiment between parentheses. The variation of electrode potential with time is shown in Fig. 1-5.

Table 1 Open circuit potential of immersed low carbon steel in saturated Ca(OH)₂ (mv vs. SCE, pH values in parentheses for each potential reading)

NaNO₂ level	NaCl level				
	0%	0.1%	0.3%	1%	3%
0%	-219 (12.5)	-343 (12.5)	-388 (12.5)	-419 (12.5)	-545 (12.5)
0.1%	-210 (12.4)	-208 (12.5)	-251 (12.5)	-285 (12.5)	-405 (12.5)
0.3%	-205 (12.4)	-190 (12.4)	-204 (12.4)	-235 (12.5)	-315 (12.5)
1%	-210 (12.3)	-230 (12.3)	-194 (12.3)	-218 (12.3)	-253 (12.4)
3%	-235 (12.2)	-200 (12.3)	-206 (12.2)	-212 (12.2)	-243 (12.2)

The figures associated with corrosion potentials in Table 1 show that:

1. In presence of NaCl, increasing the inhibitor concentration (NaNO₂) from 0% to 0.3 wt. % shifts the E_corr to more positive direction indicating the effectiveness of NaNO₂ to polarize the metal anodically and shifting the E_corr to open circuit potential of the cathode. While increasing the concentration of NaNO₂ to 3 wt. % through 1% leads to shift the E_corr to negative direction.

2. Generally, the variation of steel potential with time in alkaline solution containing 0.1, 0.3, 1 , and 3 wt.% NaCl shifts to more positive direction at all inhibitor concentration levels, compared with 0% NaNO₂.

It can be concluded that under the particular directions of interest here, the low carbon steel at high pH, a film of oxides probably of few nano meters (nm) thickness covers the surface and responsible for the passive nature of the metal at the *low levels of NaCl concentrations content with* increasing NaNO₂ from 0.1 to 3 wt.%. this situation becomes more pronounced at high levels of NaCl wt. %.

Resenberg and Gaidis [7] in their study on the mechanism of nitrite inhibition of Cl⁻ attack on reinforcing steel in alkaline aqueous environment concluded that nitrite ion rapidly oxidizes Fe⁺² ion to Fe⁺³ ion, blocking future passage of Fe⁺² ion from the metal into the electrolyte.
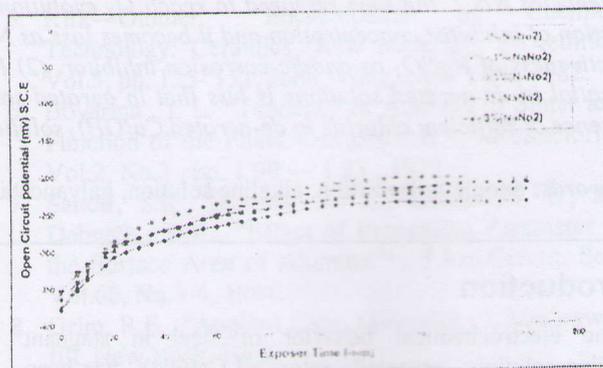

Fig. 1 Variation of corrosion potential with time for immersed steel in saturated solution of Ca(OH)₂ with different content of NaNO₂ in absence of NaCl

Fig. 2 Variation of corrosion potential with time for immersed steel in saturated solution of Ca(OH)₂ containing different concentrations of NaNO₂ in presence of 0.1 wt.% NaCl
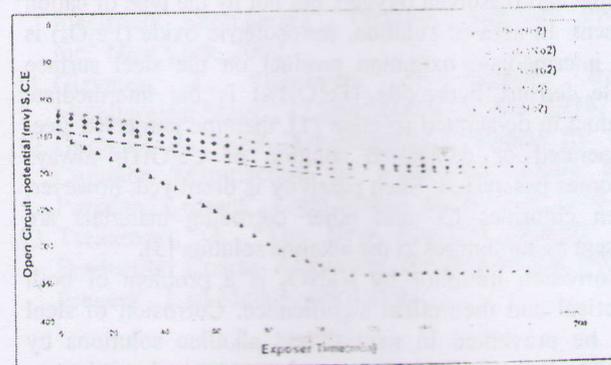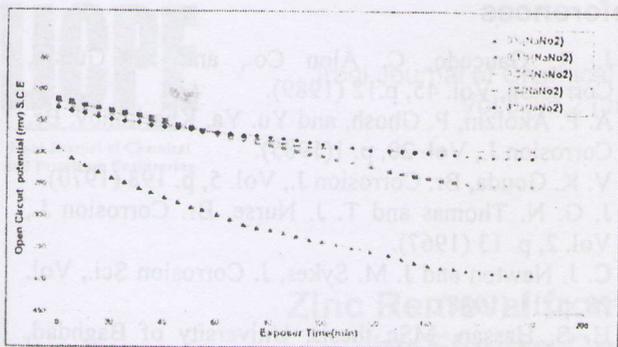
Fig. 3 Variation of corrosion potential with time for immersed steel in saturated solution of Ca(OH)$_2$ containing different concentrations of NaNO$_2$ in presence of 0.3 wt.% NaCl

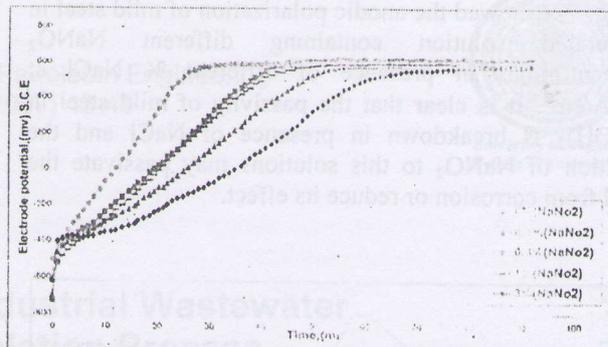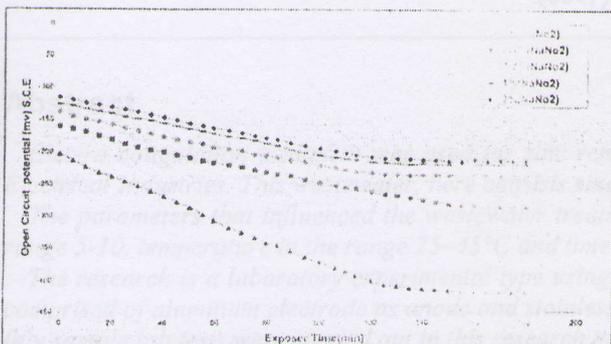Fig. 6 Anodic polarization of steel in de-aerated saturated calcium hydroxide solution at 10μA/cm^2 with different concentrations of inhibitor (NaNO$_2$) in absence of NaCl

Fig. 4 Variation of corrosion potential with time for immersed steel in saturated solution of Ca(OH)$_2$ containing different concentrations of NaNO$_2$ in presence of 1 wt.% NaCl

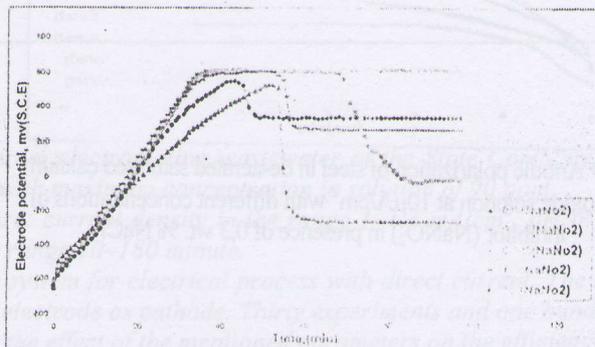Fig. 7 Anodic polarization of steel in de-aerated saturated calcium hydroxide solution at 10μA/cm^2 with different concentrations of inhibitor (NaNO$_2$) in presence of 0.05wt. % NaCl

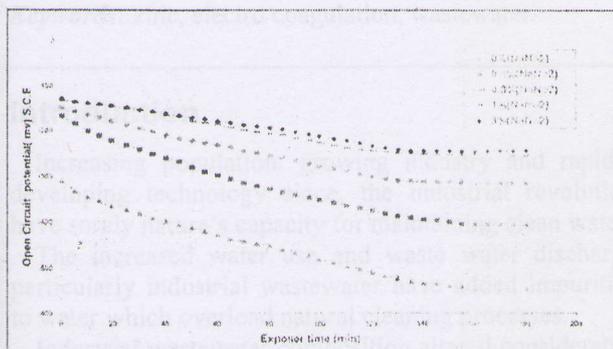

Fig. 5 Variation of corrosion potential with time for immersed steel in saturated solution of Ca(OH)$_2$ containing different concentrations of NaNO$_2$ in presence of 3 wt.% NaCl
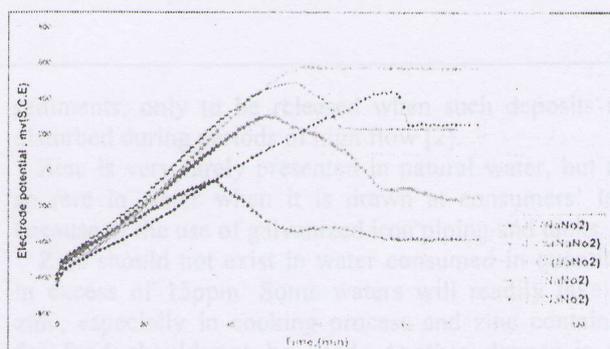

Fig. 8 Anodic polarization of steel in de-aerated saturated calcium hydroxide solution at 10μA/cm^2 with different concentrations of inhibitor (NaNO$_2$) in presence of 0.1wt. % NaCl

Fig. 6 shows that change in electrode potential as a function of time for mild steel anode in de-aerated saturated Ca(OH)$_2$ polarized anodically at 10 μA/cm^2. It can be seen that:

1. In absence of NaCl, all curves display a wave at Ca. 500 mV before that potential continues to rise to the O$_2$ evolution value, which is limited by the range of 0.55-0.65 V vs. SCE.

2. The time required for O$_2$ evolution is function of inhibitor concentration [8]. If the time is small the degree of inhibition is considered reasonably high, whereas if it is large, the degree of inhibition is comparatively low.

3. The time required to O$_2$ evolution becomes less in presence of 0.1, 0.3, and 1% NaNO$_2$ compared with zero presence of NaNO$_2$ indicating the powerful of this inhibitor on anodic behavior of the steel.

Fig. 7-9 showed the anodic polarization of mild steel in de-aerated solution containing different $NaNO_2$ concentrations in presence of different % NaCl at $10\mu A/cm^2$. It is clear that the passivity of mild steel in $Ca(OH)_2$ is breakdown in presence of NaCl and the addition of $NaNO_2$ to this solutions may passivate the steel from corrosion or reduce its effect.
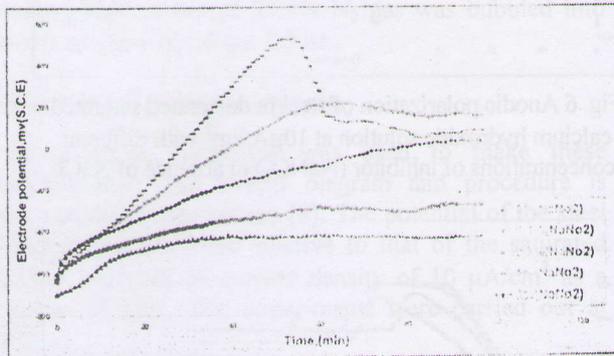

Fig. 9 Anodic polarization of steel in de-aerated saturated calcium hydroxide solution at $10\mu A/cm^2$ with different concentrations of inhibitor ($NaNO_2$) in presence of 0.3 wt. % NaCl

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