

Scientific paper

Localized Dissolution Kinetics of Low Carbon Steel

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Received: 07-09-2007

Dedicated to the memory of professor Vojko Ozim

Abstract

Localized dissolution of low carbon steel in saturated calcium hydroxide with different amount of sodium chloride has been investigated, using a dc technique. Potentiokinetic polarization curves indicated that pitting potentials (E_{pit}) decrease linearly with the log of chloride concentration. The rate of pit nucleation ($1/t_i$), and the rate of pits growth increases with increasing concentration of Cl^- ions. Initiation of pitting attack could be ascribed to the adsorption of Cl^- ions on the oxide surface. Adsorption of Cl^- ions is physisorption and follow the Langmuir isotherm with $\Delta_{\text{ads}} G^0 = -21.1$ kJ/mol.

Keywords: Pitting corrosion; adsorption isotherm; low carbon steel; simulated interstitial solution.

1. Introduction

The concrete interstitial solution has a complex composition that includes a variety of compounds beside calcium hydroxide, and is characterized by a very high p-H, which prevents corrosion of reinforcing steel through the formation of a passive film. The performance of a material is controlled by the quality of the surface oxide, composed of an iron oxide (Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$) as found by some studies.^{1,2} Smialowska, et al., using ellipsometry, concluded that the passive films formed in $\text{Ca}(\text{OH})_2$ or sodium hydroxide (NaOH) solutions were closer to an iron oxyhydroxide (FeOOH) than to Fe_3O_4 or Fe_2O_3 .^{3–5} Pou, et al., found incorporation of water in the passive film and it is seen, that this water facilitated chloride ion attack.⁶ Serious corrosion such a localized corrosion may occur, if the film loses persistency at chloride attack. This is a failure problem of many metals and alloys.

Conventional experiments rank resistance to pitting corrosion by the pitting potential, an electrochemically measured parameter which describes the minimum electrode potential at which pitting can occur. The mechanism of pitting corrosion is a complex one, and the nucleation and propagation of pits occur in several steps.^{7–15} Pits grow by metal dissolution and this occurs only if the local

solution inside the propagating pit has become sufficiently concentrated in the aggressive ion to maintain the dissolution reaction. Although pitting is often defined by the pitting potential, it is known that pits nucleate, and may also propagate into metastable growth state, below the pitting potential. Nucleation and metastable propagation of pits are important steps.

Irrespective of the mechanism of nucleation and propagation of pits, it is evident that it must be preceded by an adsorption of aggressive ion at the passive film, which will be favored by a high anion concentration and by a higher interfacial potential difference between the oxide film on the metal and solution.^{16–18} The determination of the type of adsorption isotherm corresponding to the adsorption at the metal oxide – electrolyte phase boundary gives thus much valuable information to the adsorption process, in that it makes it possible to determine such quantities as the standard free energy of adsorption, the nature of the adsorption layers on the metal oxide – electrolyte phase boundary, the magnitude and character of interactions between molecules of the adsorbed substance, or that between these molecules and the surface atoms of metal.

The objective of the present work was to study the efficiency of Cl^- ions on corrosion of low carbon steel, commonly used as reinforcing steel, in simulated intersti-

tial solution (saturated $\text{Ca}(\text{OH})_2$ solution) in terms of the pitting potential, the rate of pit nucleation and the rate of pit growth. The adsorption behavior of Cl^- ions was examined to determine the appropriate adsorption isotherm and the standard free energy of adsorption ($\Delta_{\text{ads}} G^0$). Study was made using the dc polarization technique.

2. Experimental

Electrochemical measurements were carried out on a low carbon steel of 1 cm^2 circular area exposed to the solution. The chemical composition of steel is presented in Table 1.

Table 1. Composition of low carbon steel in mass percents

C	Si	Mn	Fe
0.17	0.16	0.35	bal.

The simulated concrete pore solution was a saturated calcium hydroxide ($\text{pH} \sim 12.5$) at room temperature with and without the addition of NaCl (concentration range 8.6–170.9 mM in Cl^-). It was prepared from distilled water and of analar grade reagents.

Potentiokinetic polarization plots were measured using the Tacussel model PJT 35-2 potentiostat with the interface IMT 1 and a personal computer. The measuring cell was a Green three electrode cell, with the steel working electrode, a saturated calomel electrode (SCE) as reference electrode, and Pt as counter electrode. Before each measurement, the sample was consecutively abraded with emery paper 400, 600, 800, 1000-grade and polished with 9- μm and 1- μm diamond paste. Finally the specimens were washed with distilled water, degreased with acetone and cathodically cleaned 10 minutes at $-1800 \text{ mV}_{\text{SCE}}$. Sample was then allowed to reach a stable open circuit potential, which was attained after about 20 minutes. Afterwards, cyclic polarization curves were obtained in saturated calcium hydroxide to confirm passivity of the specimen, then a determined amount of NaCl was added to the solution and another cycle was measured. The scanning rate applied in this study was 3 mV/s .

Linear polarization curves (scan rate 10 mV min^{-1}) were also recorded and measurements of the polarization resistance were made. The ohmic drop (IR) correction was assumed to be negligible because of the close placement of the SCE bridge tube to the electrode and the sufficient conductivity of the solution.

3. Results and Discussion

Fig. 1 shows the cyclic polarization curves of steel specimens in saturated $\text{Ca}(\text{OH})_2$ solutions containing dif-

ferent amounts of chloride ions. It is shown that an extended passive region exists on the anodic polarization part for uncontaminated chloride solution. This region began immediately after the corrosion potential (E_{corr}) and continued to the breakdown potential at $660 \text{ mV}_{\text{SCE}}$ (curve 1 of Fig. 1) with almost constant current density i_{pass} . The return scan on the cyclic polarization scan retraces the path of the forward scan. In solutions with progressively increasing concentration of $\text{Cl}^-(\text{aq})$ ions from 8.6 mM to 171 mM, the steel was not resistant to the onset of localized corrosion, and this is manifested in anodic polarization curves with the significant degree of hysteresis, i.e. with the reverse scan remaining at high current values until the applied potential attains the repassivation potential (E_{rep}), and by the lowering pitting potential (E_{pit}) to less anodic values.

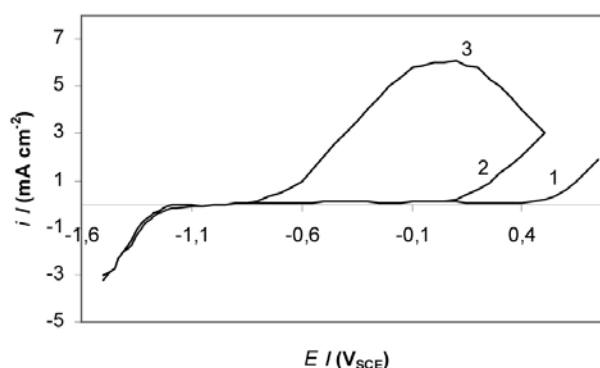


Figure 1. Cyclic potentiodynamic polarization curves of low carbon steel in saturated calcium hydroxide solution with various concentrations of chloride ions: (1) 0 mM, forward and reversed scan; (2) 17.1 mM, forward scan; (3) 17.1 mM, reversed scan.

Electrochemical data obtained from the respective polarization curves are summarized in Table 2. The pitting potential (E_{pit}) was determined at current rise to 1 mA cm^{-2} and the repassivation potential (E_{rep}) at current intersection of the reversed and forward scan. The polarization resistance (R_p) was calculated from the slope of the linear current-potential curves in the vicinity of the corrosion potential.

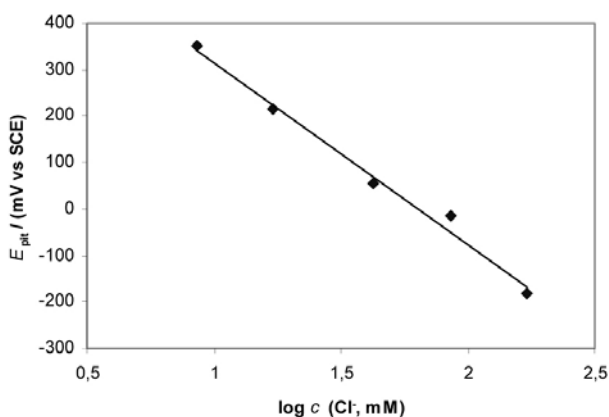
The increase in Cl^- ion concentration generally enhances the passivation current density (i_{pass} , Table 1), which is a criterion of anodic dissolution of the metal in passive state. These findings could be attributed to weakness and thinning of the passive film as a result of adsorption of Cl^- ions on the oxide surface. The adsorbed Cl^- ions tend to enhance the dissolution of the oxide film. After the incubation time (t_i), when a certain critical potential (E_{pit}) is reached, the passive current density begins to rise suddenly, indicating passivity breakdown and initiation of pitting attack.

The E_{pit} is depicted as a function of Cl^- ion concentration in Figure 2. It is observed that the values of E_{pit}

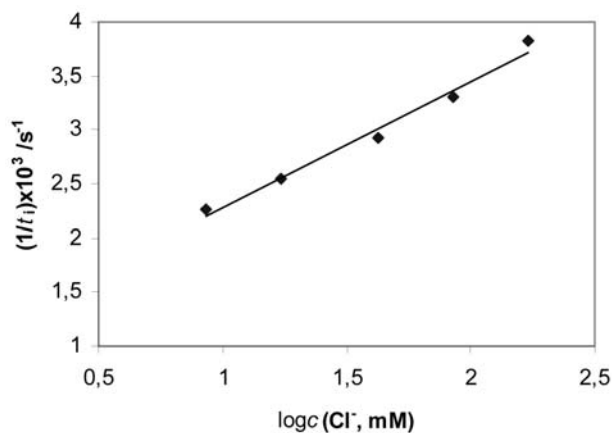
Table 2. Electrochemical parameters of low carbon steel obtained from polarization curves in chlorides containing saturated $\text{Ca}(\text{OH})_2$ solution

$\text{Cl}^- /$ (mM)	E_{corr} (mV _{SCE})	E_{pit} (mV _{SCE})	E_{rep} (mV _{SCE})	i_{pass} ($\mu\text{A cm}^{-2}$)	t_i (s)	Q (A s cm^{-2})	R_p ($\Omega\text{ cm}^2$)
0.0	-970	660		58		0.0	486
8.6	-1069	350	-756	63	440	0.9	284
17.1	-1120	214	-833	71	394	1.2	153
42.7	-1150	56	-893	83	342	1.6	133
85.5	-1190	-15	-857	147	303	2.0	79
170.9	-1200	-182	-800	174	262	2.2	48

decreases linearly with $\log [\text{Cl}^-]$ and the empirical relationship is found to be $E_{\text{pit}}/(\text{mV vs SCE}) = 708 - 392 \log ([\text{Cl}^-]/\text{mM})$.

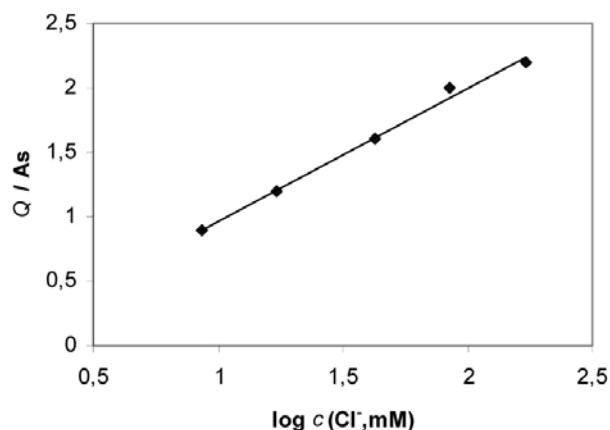
**Figure 2.** The influence of chloride ion on the pitting potential for low carbon steel in saturated $\text{Ca}(\text{OH})_2$.

An incubation time (t_i) is necessary before pit growth to occur and is caused by the time required for local removal of the passive film via the sequence of Cl^- adsorption, penetration and formation of readily soluble complexes. It is found that the t_i decreases, and hence the

**Figure 3.** Dependence of the pits nucleation rate on chloride concentration for low carbon steel in saturated $\text{Ca}(\text{OH})_2$ solution.

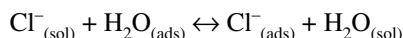
rate of pit growth increases, with increasing concentration of Cl^- ions. These observations were confirmed by plotting the rate of pit nucleation, i.e. the number of events per unit time defined as $(1/t_i)$, vs. concentration of Cl^- ions. As it is seen in Figure 3, the rate of pit nucleation also follows a linear relationship with $\log [\text{Cl}^-]$.

Once a pit is nucleated, pitting growth is believed to proceed in the active dissolution mode.^{18–19} It is presumed that at reversed polarization region no new pit is formed. The current density flowing through the pits during the pitting process indicates the rate of anodic dissolution of metal within the pits, and thus the reversed cyclic polarization curves were integrated between E_{rep} and E_{pit} to determine the charge density Q , related to the pit growth rate. This charge was found to be a linear function of the logarithm of the chloride concentration, as it is shown in Figure 4. Apparently, there is no enhanced dissolution below the critical chloride concentration which is about 1.7 mM in saturated $\text{Ca}(\text{OH})_2$ solution, congruent with the experimental findings.

**Figure 4.** Dependence of the pits growth rate (shown as charge density, Q) on chloride concentration for low carbon steel in saturated $\text{Ca}(\text{OH})_2$ solution.

Irrespective of the mechanism of nucleation and propagation of pits, it is evident that it must be preceded by an adsorption of aggressive ion at the passive film. The proposed mechanism of an aggressive ion adsorption is a

substitutional adsorption process²⁰ between the aggressive ion in the aqueous solution ($\text{Cl}^-_{(\text{sol})}$) and water molecules adsorbed on the passive film ($\text{H}_2\text{O}_{(\text{ads})}$):



The values of surface coverage (θ), corresponding to different concentrations of chloride, were used to determine which isotherm best describes the adsorption process. The correlation coefficient was used to choose the isotherm that best fit the experimental data.

The value of the degree of coverage of the surface of low carbon steel with chloride ions was obtained from the polarization resistance (R_p), given in Table 2. Smaller R_p values, obtained by increasing concentration Cl^- ions, were associated with an elevated porosity of the oxide films, formed on steel electrodes in this environment. Surface coverage by adsorbed Cl^- ions was calculated by comparing polarization resistance in the absence of Cl^- ions, R_p with that in the presence of Cl^- ions, $R_{p,\text{Cl}}$ using the simple relation, $\theta = (R_p - R_{p,\text{Cl}})/R_p$.

The results obtained for Cl^- ion adsorption on the surface of passive steel, can be interpreted using a Langmuir type isotherm and are presented in Figure 5. The isotherm is: $\frac{c}{\theta} = \frac{1}{K} + c$, where θ is the surface degree coverage, c is the equilibrium chloride ion concentration and K is the constant of the adsorption process, which is correlated to $\Delta_{\text{ads}}G^0$ by: $K = \frac{1}{55.5} e^{-(\Delta_{\text{ads}}G^0/RT)}$. The obtained value of $\Delta_{\text{ads}}G^0 = -21.1 \text{ kJ/mol} \pm 5\%$, indicating the spontaneity of the adsorption reaction of Cl^- on steel surface. It is well known that values of $-\Delta_{\text{ads}}G^0$ of the order of 20 kJ/mol or lower indicate a physisorption, thus in the Cl^- ion adsorption process physisorption prevailed.

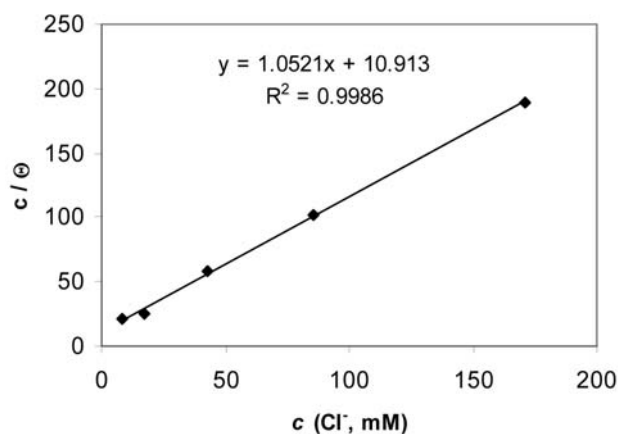


Figure 5. Langmuir adsorption isotherm of Cl^- ions on the surface of low carbon steel in saturated $\text{Ca}(\text{OH})_2$ solution.

4. Conclusion

The cyclic polarization curves and linear polarization studies of the pitting corrosion of low carbon steel in natural aerated saturated $\text{Ca}(\text{OH})_2$ solution in the presence of Cl^- showed that:

- In pure $\text{Ca}(\text{OH})_2$ solution passivity of steel can be observed.
- Addition of the Cl^- ions to the solution, above critical concentration, induces pitting corrosion at specific pitting potentials.
- An incubation time (t_i) is necessary for the pit nucleation and before the pit growth to occur.
- The charge density (Q) can be taken as a measure of the rate of pits growth.
- The rate of pit nucleation ($1/t_i$), and the rate of pits growth increases with increasing concentration of Cl^- ions. Pitting potential (E_{pit}) decreases with increasing concentration of Cl^- ions.
- Initiation of pitting attack could be ascribed to the adsorption of Cl^- ions on the oxide surface. Adsorption of Cl^- ions followed Langmuir isotherm with $\Delta_{\text{ads}}G^0 = -21.1 \text{ kJ/mol} \pm 5\%$.

5. References

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Povzetek

S pomočjo dc tehnike smo raziskovali lokalizirano raztapljanje malo- ogljičnega jekla v nasičeni raztopini kalcijevega hidroksida ob dodanih različnih množinah natrijevega klorida. Poteciokinetične polarizacijske krivulje so pokazale, da se kritični porušitveni potencial (E_{pit}) linearno zmanjšuje z logaritmom koncentracije kloridnih ionov. Hitrost nastajanja luknjic ($1/t_i$) in hitrost rasti luknjic se povečuje s povečanjem koncentracije Cl^- ionov. Iniciacijo točkaste poškodbe lahko pripišemo adsorpciji Cl^- ionov na oksidno površino. Adsorpcija Cl^- je fizisorpcija in sledi Langmuirjevi adsorpcijski izotermi z $\Delta_{ads}G^0 = -21.1$ kJ/mol.