Corrosion inhibition of carbon steel by dipotassium hydrogen phosphate in alkaline solutions with low chloride contamination

A. Mohagheghi, R. Arefinia *

Chemical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

HIGHLIGHTS

- There was a critical [DKP]/[Cl⁻] ratio to passivate the carbon steel surface.
- The impact of phosphate on the stability of the passive film depends on the [Cl⁻]/[OH⁻] ratio.
- In a mildly alkaline solution, phosphate inhibits pitting and uniform corrosions.
- In a highly alkaline solution, phosphate is efficient to uniform corrosion.
- Phosphate acts as an anodic inhibitor through forming a duplex layer passive film.

ABSTRACT

This work deals with the corrosion inhibition of carbon steel by dipotassium hydrogen phosphate (DKP) in both mildly and highly alkaline solutions (pH 8 and 12) contaminated with low levels of chloride (1–5 mmol L^{-1}). To this end, the electrochemical methods of potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) together with different surface analysis methods including scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and Raman spectroscopy were employed. In mildly alkaline solution, the [DKP]/[Cl⁻] ratio should be greater than the critical value (3.7) to form a stable passive film on the metal surface; additionally, the best inhibition against uniform corrosion was achieved at [DKP]/[Cl⁻] = 5.5, while the passive film resistance to pitting resistance continuously improved as the [DKP]/[Cl⁻] ratio increased. The effect of chloride concentration on the characteristic of passive film was described by a logarithmic relationship. In highly alkaline solution, addition of 11 mmol L^{-1} DKP has a significant effect on uniform corrosion. The surface analysis methods demonstrated the formation of a duplex layer on the metal surface composed of an inner layer of iron oxides and an outer layer of iron phosphate complexes mainly as $FeHPO_4$ and $Fe_3(PO_4)_2$.

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1. Introduction

Inhibitors are promising chemical compounds that are used to suppress the corrosion of metals in aqueous solutions [1]. Phosphate compounds as inorganic inhibitor [2–5] and antiscalant material [6] are particularly popular due to their low cost and low toxicity. Different phosphate compounds such as disodium hydrogen phosphate (Na_2HPO_4) [1,3], disodium mono fluoride phosphate (Na_2PO_3F) [7,8], zinc phosphate [9], and lithium zinc phosphate [10] have been used to control the corrosion process especially against localized corrosion induced by aggressive anions like chloride.

The inhibition mechanism of phosphate has been well investigated and documented [11,12]; however, it is somehow controversial [13,14]. Some researchers have found that phosphate is an anodic inhibitor which functions through the formation of a passive film on the metal surface [3,15], while cathodic or mixed inhibition mechanism has been also reported [5,16]. In the case of anodic protection for steel in an alkaline solution, the passive film is mainly made of two parts [15]: the inner layer of iron oxides mainly involving magnetite (Fe_3O_4) or/and maghemite (Fe_2O_3) [17] as well as the outer layer of iron phosphate such as $FeHPO_4$, $Fe_3(PO_4)_2$ and $FePO_4$. The presence of phosphate compounds within the structure of the outer layer has been confirmed before using different surface analysis methods such as XPS and AES analysis [15], Raman spectra [5], ellipsometric [11], and x-ray [18]. Nishimura et al. [19] have studied the breakdown mechanism of passive film on the iron surface in the phosphate and borate

solutions containing high chloride content at pH 8.42 and 11.5. They reported that the ion selectivity of the passive film has an important effect on the nucleation and growth of pits.

Phosphate compounds can be efficiently employed to control the pitting corrosion of steel reinforcement in concretes which is supported by the finding of so many studies in the literature [20–22]. The primary focus of these studies is on the competitive adsorption between phosphate and chloride ions on the steel surface in various simulated concrete pore solutions [14,23,24]. Yohai et al. [5,13,25,26] have extensively investigated the inhibition mechanism of phosphate by varying $[PO_4^{3-}]/[Cl^-]$ ratio and $[Cl^-]/[OH^-]$ ratio in simulated pore solutions of concretes. They have pointed out the significant effect of phosphate and its dosage relative to that chloride on the pitting corrosion resistance.

In this field, the primary concern of most studies has been on the evaluation of the phosphate inhibition in synthetic solutions with a high-chloride concentration and commonly at high pH values around 12. However, chloride contamination is controlled by the diffusion of chloride ions within concrete pores and, consequently, high chloride contamination probably occurs after a long time exposure. Before this, it is reasonable to state that the corrosion within the pore solution develops at low chloride contamination. Recently, Nahali et al. [27] have studied the influence of phosphate ions on the diffusion coefficient of chloride ions in mortar and they have found a low chloride concentration within the cells simulating concrete pores even after 100 days of immersion at pH = 12. Nevertheless, a few studies have investigated the effect of varying phosphate and chloride concentration on the phosphate inhibition at low chloride contamination and at different pH values. These factors may cause significant effects on both uniform and pitting corrosion of steel.

In this study, the inhibitive effect of dipotassium hydrogen phosphate (DKP, K_2HPO_4) on both uniform and pitting corrosion of carbon steel was investigated in mildly alkaline solutions (pH of about 8.8) with low levels of chloride contamination by varying phosphate and chloride concentrations. In addition, the effect of phosphate at a certain concentration on the uniform and pitting corrosion of carbon steel was studied in a highly alkaline solution (pH 12). The selected conditions correspond to the cooling waters and the early stage of corrosion in the concrete pores. Electrochemical methods including potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) together with surface analysis techniques of the scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and Raman spectroscopy were employed to study the phosphate inhibition mechanism at the selected conditions of this work.

2. Experimental

2.1. Materials and electrolyte

Dipotassium hydrogen phosphate (DKP), as the inhibitor, was prepared from Merck Co. as an analytical grade. The chemical composition of carbon steel A106 as the working electrode is presented in Table 1. The specimens were mounted with epoxy when the remaining surface area was 1.0 cm^2 as a square shape. In prior electrochemical tests, the surface of specimens was abraded by 300, 600, 1200, and 2000 grades of emery paper, degreased and rinsed with acetone and distilled water, respectively, and then immediately dried to prevent any corrosion occurrence.

Table 2
Variation of solution pH with DKP concentration.

DKP concentration (mmol L^{-1})	Blank	7	11	17	23
pH	7.78	8.73	8.80	8.82	8.89

The inhibition mechanism of phosphate ions was studied in a 2 mmol L^{-1} chloride solution at different concentrations (0, 7, 11, 17 and 23 mmol L^{-1}) of phosphate and at room temperature (25 ± 2 °C). In addition, the effect of chloride concentration including 0, 1, 2, 3 and 5 mmol L^{-1} on the corrosion of carbon steel was quantitatively evaluated in an 11 mmol L^{-1} phosphate solution at room temperature. The increase in phosphate concentration has a negligible effect on the solution pH because of the buffer nature of DKP, as demonstrated in Table 2.

2.2. Electrochemical measurements

All the electrochemical measurements were performed using an Autolab potentiostat/galvanostat (PGSTAT 302N) in a glass cell with three electrodes: a saturated calomel electrode (SCE) as reference, a graphite rod of large area as counter electrode and a mounted carbon steel as working electrode. In addition, all electrochemical measurements were repeated at least three times until a good reproducibility was observed.

The potentiodynamic polarization test was performed from −400 mV below OCP to reach the pitting or oxygen evolution potential at the scan rate of 0.5 mV/s. Since the corrosion state may be as active, active-passive and completely passive, in each case, the value of corrosion current density (i_{corr}) was determined using known methods. For the active state, i_{corr} was obtained by the application of Tafel extrapolation at potentials about 100 mV far from the E_{corr} where a linear behavior (Tafel region) is observed, while, for the passive state, corrosion current density has in fact the same meaning as passive current density (i_{pass}). Therefore, for the systems with an active-passive transition state, both corrosion current and passive current (i_{corr}/i_{pass}) were determined. For all the systems, determination of cathodic Tafel slope (β_c) may be still useful in analyzing the reduction behavior of electrolyte components. It should also be noted that the value of anodic Tafel slope (β_a) is meaningful only for the active or active/passive states of corrosion and not for the completely passive. Moreover, the value of passive potential (E_{pass}) was considered equal to the corrosion potential (E_{corr}) for completely passive systems, while for active/passive systems, E_{pass} was determined from the beginning of the passive region in polarization curves where the current density was approximately constant by sweeping the potential.

The electrochemical impedance spectroscopy (EIS) was conducted at an amplitude perturbation of 10 mV versus OCP over the frequency range of 10 kHz–10 mHz. The EIS analysis was made through fitting the recorded spectra to the suitable equivalent circuits in Zview software.

2.3. Weight loss measurements

The inhibition effect of DKP on the corrosion of carbon steel in the long term was evaluated by measurement of weight loss during 45 days of immersion at room temperature in aerated conditions according to ASTM D 2688. The working specimens had a

Table 1
Chemical composition of carbon steel A106.

Elements	Fe	C	Mn	P	S	Si	Cr	Cu	Mo	Ni	V
Composition (wt. %)	balance	0.35	1.06	0.04	0.04	0.10	0.40	0.40	0.15	0.40	0.08