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Evaluation of corrosion resistance properties of N, N′-Dimethyl ethanolamine corrosion inhibitor in saturated $Ca(OH)_2$ solution with different concentrations of chloride ions by electrochemical experiments

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HIGHLIGHTS

- Mild steel rebar in saturated $Ca(OH)_2$ with NaCl and DMEA inhibitors are studied.
- DMEA significantly reduces corrosion of steel rebar in saturated $Ca(OH)_2$ with NaCl.
- EIS studies revealed the protective mechanism of DMEA inhibitor.
- Potentiodyamic explain pitting resistance of DMEA in saturated $Ca(OH)_2$ with NaCl.
- Formation of adsorbed passive film is explain by schematic diagram.

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ABSTRACT

Steel rebars attain passivity in concrete environment. Passive film can be destroyed by acidification through carbonation and chloride ions from NaCl in concrete. There are different techniques have been employed to mitigate the corrosion problem of steel rebars embedded in concrete. Among different methods inhibitors are very popular and frequently used. Commercially available N, N′-Dimethyl ethanol amine (DMEA) inhibitor is studied in different concentrations of NaCl in saturated $Ca(OH)_2$ solution. The performance of inhibitor was evaluated by potential time, electrochemical impedance spectroscopy and potentiodynamic techniques. DMEA inhibitor is showing 63–74% efficiency and effectively reduces the corrosion rate.

1. Introduction

Corrosion of concrete reinforcement steel is caused by breakdown of passive film which is being formed in concrete environment. The passivity of reinforcing steel is imparted by alkalinity of concrete and it is due to high pH of concrete pore solution. The protective oxide or passive film can be destroyed by diffusion of chloride ions from deicing salt or impurities of concrete aggregates and the decrease in pH of concrete by carbonation through atmospheric CO_2 [1]. These types of corrosion attack on steel reinforcement bars are due to poor workmanship and bad quality of concrete composition. The corrosion of rebars started due to increased threshold level of chloride ion [2]. European standard EN 206 has reported a reduction in corrosion of rebars by using high quality concrete (low water/cement ratio) and adequate concrete cover. To mitigate the corrosion of reinforcing steel; different methods had been used i.e. stainless steel, cathodic protection, fusion bonded epoxy coating, inhibitors and admixtures [3]. Among these methods; the corrosion inhibitors are the most popular, cost effective and convenient in use. The inhibitors reduce the initiation period of corrosion process or stop the propagation of already corroded structure [2,4–9]. There are different types of corrosion inhibitors being used frequently such as nitrite based inorganic [10–15], surface applied admixtures on concrete cover i.e. mono-fluoro-phosphate [16,17], organic inhibitors i.e. alkanol amine and amine. Alkanol amine and amine based corrosion

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inhibitors are working as migratory corrosion inhibitor [18–25] to mitigate the corrosion process of steel reinforcement bars.

Inorganic corrosion inhibitors are mainly nitrite based and being used since 1940s. The nitrite based corrosion inhibitors are having a negative impact on concrete as well as reinforcing steels. It decreases the strength of concrete and as a result that leads to the spalling of concrete. For proper protection of steel reinforcement in concrete; large dosage of it is required. These types of inhibitors are also not environmental friendly and when they are used in concrete structures that are immerged in water or sea environments, they cause harmful effect to living organism and phytoplankton. It is carcinogenic in nature and researcher are now avoiding using these types of inhibitor. There are many conflicting statements given by different researchers on performance of nitrite based corrosion inhibitors [26–32].

Due to negative effects of nitrite based corrosion inhibitors; since last two decades organic based inhibitors are very popular and it is frequently being used. The organic corrosion inhibitors are having chelating effect with iron metal and formed covalent bond with lone pair of electrons of hetero atoms of organic compounds. The hetero atoms work as nucleophile and iron metal as electrophile. Lone pair electrons of hetero atoms donate to vacant d-orbital of iron metal and formed very strong covalent bond [33,34].Therefore, it is adsorbed on metal surface and form very protective passive film.

Organic inhibitors especially amines and alkanolamine containing functional groups are frequently used as corrosion inhibitor due their high solubility in aqueous solution. There are no harmful effects observed for organic corrosion inhibitors on fresh and hardened concrete materials. Due to the functional groups in organic inhibitors; they adsorbed on metal surface with lone pair of electrons of nitrogen and oxygen atoms. Iron ions are working as Lewis acid and these ions accept electrons from donor group i.e. nitrogen and oxygen atoms. The bond between nitrogen/oxygen and iron metal form very strong covalent bond and it adsorbed significantly on surface of steel rebars [34]. Therefore, the amino group containing inhibitors are popularized and reducing the corrosion of steel reinforcement in contaminated concrete pore solution. These types of organic inhibitors are reducing or slowing down the corrosion process of steel rebars through adsorption of polar group of hetero atoms and form very thin layer of organic compounds [34].

Amino alcohol based inhibitors are more effectively worked when the corrosion is relatively low or before the initiation of corrosion on steel reinforcement [35,36]. There are controversial statements given by different researchers about performance of amine and alkanol amine based corrosion inhibitors. Wombacher et al. suggested that this type of inhibitors are generally worked as mixed inhibitor which adsorbed on metal surface by forming thin film and block the active sites on metal surface [23] while Martin and Miksic reported that DMEA work as cathodic inhibitor by blocking active sites where oxygen pick up electrons and reduced into OH^- and adsorbed on anodic sites of working electrode [37]. The amino alcohol inhibitors are more effectively worked than nitrite based inhibitor i.e. Lithium nitrite in saturated $Ca(OH)_2$ with different concentrations of chloride ions as well as in accelerated test [38].

There are little afford had been done on corrosion studies of ethanolamine based corrosion inhibitors with different concentrations of chloride ions in saturated $Ca(OH)_2$ solution by electrochemical studies [38,39]. The saturated $Ca(OH)_2$ solution simulates the concrete environment and it is found in other literatures also [40–42]. These studies are based on effectiveness of low content of N, N′-Dimethyl ethanol amine (DMEA) corrosion inhibitors in saturated $Ca(OH)_2$ solution with different low concentrations of sodium chloride (NaCl) content by electrochemical studies.

2. Materials and methods

2.1. Materials

Commercially available DMEA corrosion inhibitor was used in this study and their physical properties are shown in Table 1. This inhibitor was mixed in saturated $Ca(OH)_2$ solution and it was made in double distilled water by proper mixing. The pH of saturated $Ca(OH)_2$ solution was 12.60 at room temperature (25 °C ± 1 °C). Different concentrations of NaCl were mixed in saturated $Ca(OH)_2$ solution with different content of inhibitor. The chemical structure of DMEA is shown in Fig. 1 and it contains tertiary amine with one hydroxyl group.

The mild steel rebars with 16 mm diameter were cut and mounted in acid/alkali resistance thermosetting resin. The mounted samples were polished with emery paper started from 180 to 1200 μ. Thereafter, cloth polished of steel rebar was carried out and degrease with acetone prior to start the electrochemical experiments. The chemistry of studied steel rebars are shown in Table 2.

2.2. Electrochemical studies

Prior to start the experiments, steel rebars were exposed in solution and the potential was stabilized with potentiostat. These electrochemical studies were performed by three electrode systems where steel rebar work as working electrode (WE), platinum wire as a counter electrode (CE) and silver-silver chloride as a reference electrode (RE). The area of working electrode was 0.78 cm^2 and it was fixed for every samples.

The electrochemical impedance spectroscopy (EIS) studies were carried out by changing the frequency of 10 mV sinusoidal voltage from 100 kHz to 0.1 Hz. Hz. DC polarization studies were performed at 1 mV/s scan rate from −0.3 V to +0.3 V Vs open circuit potential. The potentiostat was VersaSTAT (Princeton Applied Research, Oak Ridge, TN, USA) and data analysis were carried out by Metrohm Autolab Nova 1.10 software by fitting the experimental data in constant phase element (CPE) model.

3. Results and discussion

3.1. Corrosion potential time studies

The corrosion potential time studies were performed on steel rebars in saturated $Ca(OH)_2$ solution with different concentrations of NaCl and DMEA inhibitor. The corrosion potential time plots are shown in Fig. 2. Corrosion potential plots give very vital information regarding surface of steel rebars [43]. The steel rebars exposed in saturated $Ca(OH)_2$ with different concentrations of NaCl are showing active potential. The corrosion potential are increased actively as concentrations of NaCl increases and it may be due to more reaction on steel rebar/solution interface. This observation indicates that the surface is more susceptible to deterioration in NaCl saturated with $Ca(OH)_2$ solution and it enhances the localized and pitting corrosion of steel rebars [44]. The corrosion potential behavior of steel rebars in all studied concentrations of NaCl with 0.45 g/L and 1.81 g/L DMEA inhibitor in saturated $Ca(OH)_2$ solution are showing almost same trend and it is nobler than without inhibitors.

Table 1
Physical properties of DMEA.

Parameter	Value
Specific gravity	1.07
pH	11.9
Viscosity (cps)	11.0
Solid content (wt.%)	80.0

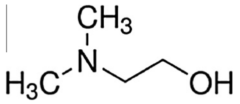

Fig. 1. Chemical structure of DMEA.