



Corrosion film breakdown of galvanized steel in sulphate–chloride solutions



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HIGHLIGHTS

- The effect of de-icers on the corrosion of galvanized steel was studied.
- The lowest corrosion rate was reported in the $\text{MgCl}_2 + \text{Na}_2\text{SO}_4$ solutions.
- Samples immersed in $\text{NaCl} + \text{Na}_2\text{SO}_4$ solutions had the highest corrosion rate.
- Galvanized steel does not form a passive film under these conditions.
- Hsu and Mansfeld formula underestimated the film thickness values.

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ABSTRACT

This work presents the corrosion performance of galvanized steel in sulphate–chloride solutions. The surface area changes, film breakdown susceptibility, and protectiveness of the corrosion products were studied using Potentiodynamic Polarization, Cyclic Voltammetry, Cyclic Polarization, and Electrochemical Impedance Spectroscopy. Samples immersed in MgCl_2 solutions had the lowest corrosion rate, while samples immersed in the NaCl solutions showed the worst performance. The longer expected durability of samples immersed in MgCl_2 was attributed to the lower corrosion kinetics, and a greater surface coverage by the corrosion product. However, results show that the formed corrosion layer is non-protective under any of the studied conditions.

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1. Introduction

The galvanized steel industry is large, consuming approximately half of the total zinc produced in the world [1]. Galvanized steel's improved performance is provided by the combination of three distinct mechanisms: the barrier action of the zinc layer, the secondary barrier action of the zinc corrosion products, and the cathodic protection provided by the galvanic interaction with zinc even when steel is exposed [2–4]. The corrosion of galvanized steel is a very complex process that involves several electrochemical and physical mechanisms. Studies on the corrosion of galvanized steel revealed that its corrosion behaviour consisted of three different stages as shown in Fig. 1 [2,4]: in stage 1, the electrochemical behaviour of galvanized steel is mainly related to the

dissolution of the zinc oxide layer which was formed in the air. In stage 2, the surface of the zinc layer is covered with thick, white rust and the underlying steel begins to corrode. During this stage, the corrosion rate of the zinc coating rapidly decreases, accompanied by a shift in the corrosion potential to a more noble potential. In stage 3, the amount of red rust on the coating surface rapidly increases; the galvanized steel shows almost the same corrosion potential as that of carbon steel, even though the zinc coating is still covering a few parts of the steel reinforcement. The underlying steel corrosion progresses by dissolution of iron and, therefore, at this stage, the zinc coating no longer acts as a sacrificial anode.

Three different mechanisms for the formation of zinc corrosion products, relevant to stage 1 mentioned above, have been proposed. The first mechanism is direct oxidation in which zinc corrosion products can be formed directly on the surface of the zinc metal by the reaction of zinc with hydroxyl groups, or ZnO could be formed directly from $\text{Zn}(\text{OH})_2$ when the pH range is between

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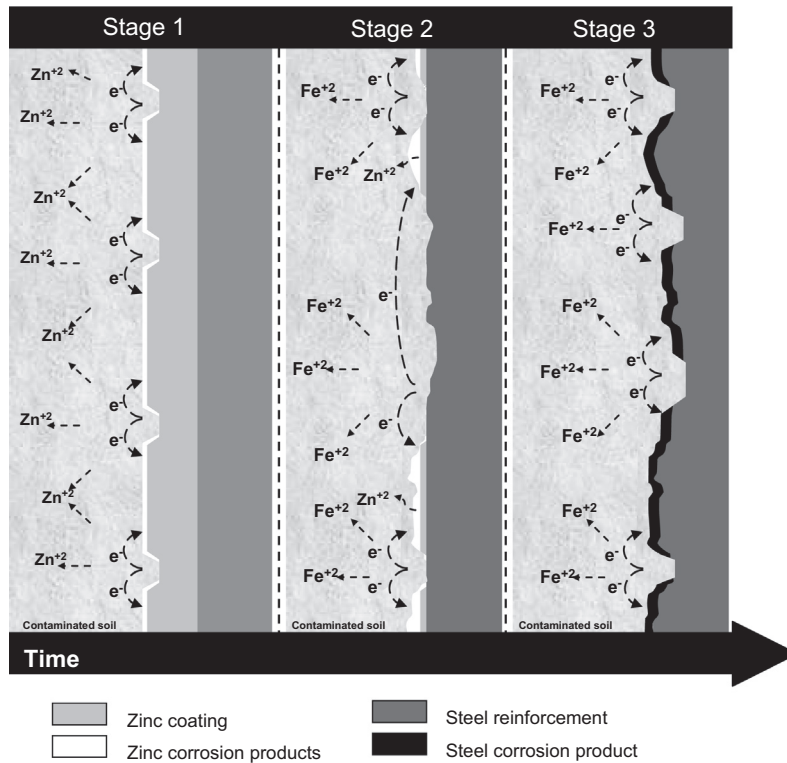


Fig. 1. Schematic presentation of the three stages of galvanized steel corrosion.

7 and 9 [5]. Thomas et al. [6] observed that in the pH range from 7 to 10, relevant to field applications, acidity arising from anodic processes and metal hydrolysis undermine the passive layer formation favouring the formation of a more porous corrosion product, such as $\text{Zn}(\text{OH})_2$. The second mechanism consists of a dissolution-precipitation process [7], in which a porous type of zinc oxide (Type I zinc oxide) precipitates onto the electrode due to the saturation of $\text{Zn}(\text{OH})_4^{2-}$ ions near the metal surface. And finally, a third mechanism consists of the formation of a passive oxide when adsorbed species like $\text{ZnOH}(\text{ads})$ reject protons at a critical potential.

Additionally, it has been observed that, depending on the exposure conditions, $\text{ZnO}/\text{Zn}(\text{OH})_2$ can further react to form more complex corrosion products. The two most commonly reported have been simonkolleite $\text{Zn}_5(\text{OH})_8\text{Cl}_2$ and hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ [8], and some authors have reported others such as hydroxysulphate $\text{Zn}_4\text{SO}_4(\text{OH})_6$ [9]. Regardless of the formation mechanism, it is believed that the formation of the type I film is a prerequisite for the type II film [7].

In stage 2, the zinc cover partially dissolves and the underlying steel is exposed to the soil and, therefore, in addition to zinc, steel is also involved in the corrosion reaction. During this short second stage, Zn^{2+} dissolved from ZnO and $\text{Zn}(\text{OH})_2$ products suppress the crystallization and particle growth of $\beta\text{-FeOOH}$, thus providing an inhibitory effect [10,11]. It has been proved that during this stage, zinc corrosion products successfully protect the exposed metallic surface providing a protection against the corrosion [12], and zinc undergoes a higher corrosion rate in the vicinity of exposed steel. While the anodic process still occurs mainly on the zinc surface, the oxygen reduction process takes place on the steel surface [13].

The availability of oxygen will also have an effect on the end product of the corrosion process of bare steel. The formation of red rust is expected when oxygen and moisture are readily available [14]. The main iron corrosion products presented that formed during this stage are ferrous hydroxide $\text{Fe}(\text{OH})_2$ and iron(III) hydroxide $\text{Fe}(\text{OH})_3$. Previous research supports that the formation

of Akaganéite, a poor crystalline form of iron(III) hydroxide, is favoured during the corrosion of galvanized steel [10,15]. Usually steel corrosion products, such as $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$, will tend to further oxidize to produce secondary corrosion products or even tertiary corrosion products.

In general, there is a good understanding of the corrosion process of galvanized steel under control conditions. Previous work suggests that in alkaline pH and under certain exposure conditions zinc should form a protective film [6,16–18]; while others caution that at high pH values ($\text{pH} > 12.5$) zinc dissolution and hydrogen evolution takes place [19]. However, the early failure of some galvanized, steel-reinforced structures in porous media, such as bridges [20], Mechanically Stabilized Earth (MSE) walls [21,22], and water pipes [23,24], to mention just a few, have raised concerns of the existing understanding of the factors that lead to early corrosion.

A major concern for long-term performance of steel-reinforced structures is the presence of chemicals that accelerate corrosion by destroying the protective corrosion product. These corrosive agents can either be native to the environment or added later by human activities. A good example of these is de-icing salts applied to the highways [25]. The main salts used are sodium chloride (NaCl), magnesium chloride (MgCl_2), and calcium chloride (CaCl_2) [26–29], less common is acetates industry [25]. The individual effect of these corrosive agents on the corrosion performance of galvanized steel has been well documented [3,27,29–31]. It has also been reported in the past that sulphur compounds have a great effect on corrosion since sulphur compounds lower the local pH on the surface of the metal [32], depleting the zinc protection faster or preventing the metal from forming a protective layer and thus increasing zinc solubility in the presence of sulphate ions and accelerating corrosion [33]. On the other hand, sulphates have been reported to be beneficial in some cases because their presence prevent the solution pH to rise to pH values higher than 13.3 [34]; which would cause the active dissolution of zinc. Earlier

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