

CHAPTER – I

1. Introduction

1.1 Concept of Corrosion

Corrosion can be defined as the destruction of material by chemical reaction with environment. As demanded by the thermodynamic principle, corrosion returns the metal or alloy to its combined state in chemical compounds that are similar to the mineral from which the metals were extracted. The serious consequences of the corrosion process have become a problem of worldwide concern. In addition to our everyday encounters with this form of degradation, corrosion causes plant shutdowns, waste of valuable resources, loss or contamination of products, reduction in efficiency, costly maintenance, and expensive over design. The economic costs of corrosion are very high. It has been estimated that approximately 3-4% of an industrialized nation's income is spent on corrosion prevention, maintenance or replacement of products lost or contaminated as a result of corrosion reaction [1].

Virtually all metals suffer corrosion, so its effects permeate nearly every aspect of human endeavour and this fact alone makes the study of corrosion and its control more important. As a spontaneous process, corrosion cannot be perfectly prevented, however by application of present knowledge; one third of its cost could be controlled. Corrosion is an electrochemical phenomenon involving two reactions: an anodic (site of oxidation) that releases electrons and a cathodic (site of reduction) that consume electrons. The anodic reaction is:



Where,

'M' stands for a metal,

'x' stands for the number of electrons (e^{-}) that an atom of the metal will easily release.

According to the environment where corrosion is taking place, the possible cathodic reactions can be of the following types [2].

a) Oxygen reduction in acidic solution:



b) Oxygen reduction in neutral or basic solution



c) Hydrogen evolution in acidic solution



d) Hydrogen evolution from neutral water



e) Metal reduction



1.2 Forms of corrosion

The different forms of corrosion represents corrosion phenomenon categorized according to their appearance. Robert Boyle reported a very early study of corrosion in 1675, which mentioned about technical term of “Corrosiveness” and “Corrodibility”[2]. The 32-gun frigate, HMS alarm, is said to be a first subject of bimetallic corrosion or galvanic corrosion[2].. So far from the 20th century, the century of industrialization, together with new materials and their applications the corrosion scientists have to face more diversification of types of corrosion, for examples, uniform corrosion, galvanic corrosion, crevice corrosion, pitting corrosion, hydrogen damage, fatigue corrosion, intergranular corrosion and erosion [3].

The corrosion can be classified into two main forms i.e. uniform corrosion and localized corrosion.

1.2.1 Uniform corrosion

It is characterized by corrosion attack proceeding homogeneously over the entire surface area or a large fraction of the total area. The corrosion of metal takes place until failure. On the basis of tonnage wasted, this is the most important form of corrosion. However, as uniform corrosion is relatively easily measured and predicted, disastrous failures can be prevented. The breakdown of protective coating systems on the structures often leads to uniform corrosion. If uniform corrosion is permitted to continue, the surface may become rough, and surface corrosion can lead to more serious forms of corrosion. Atmospheric corrosion is probably the most prevalent example of uniform corrosion [4].

1.2.2 Localized corrosion

Localized corrosion can be defined as the corrosion occurring at one part of metal surface at a much higher rate than that over the remaining surface. Various form of localized corrosion is listed as follows [4]:

- Grain boundary and intergranular corrosion
- Environmental induced cracking
- Erosion corrosion
- Crevice corrosion

1.2.2.1 Grain boundary and intergranular corrosion

The microstructure of metals and alloys is made up of grains, separated by grain boundaries. Atoms at the grain boundaries are thermodynamically less stable than those at perfect lattice site and have great tendency to corrode. A common type of grain boundary corrosion is intergranular corrosion, which is defined as the attack along the grain boundaries or immediately adjacent to grain boundaries, while the bulk of the grains remain largely unaffected.

1.2.2.2 Environmental induced cracking (EIC)

Brittle fracture of a normally ductile alloy in the presence of an environment that causes minimal uniform corrosion is defined as the environmentally induced cracking. Three related but distinct types of failure are included in EIC: stress corrosion cracking (SCC), corrosion fatigue cracking (CFC) and hydrogen-induced cracking (HIC).

1.2.2.3 Erosion corrosion

Erosion corrosion is the cumulative damage induced by electrochemical corrosion reactions and mechanical effects from relative motion between the electrolyte and the corroding surface. The same stagnant or slow-flowing fluid will cause a low or modest corrosion rate, but rapid movement of the corrosive fluid physically erodes and removes the protective corrosion product film, exposes the reactive alloy beneath, and accelerates corrosion.

1.2.2.4 Crevice corrosion

Crevice corrosion is a localized form of corrosion usually associated with a stagnant solution on the micro environmental level. Such stagnant microenvironments tend to occur in shielded area such as those formed under gaskets, washers, insulation material, fastener heads, surface deposits, disbonded coating, threads, lap joints, and clamps. Because oxygen diffusion into the crevice is restricted, a differential aeration cell tends to be set up between crevice (microenvironment) and the external surface (bulk environment) [5].

1.2.3 Pitting corrosion

In all aspects the galvanic corrosion and hydrogen damage corrosion may be classed as localized corrosion. Galvanic corrosion occurs when dissimilar metallic materials come into contact in the presence of an electrolyte. Such damage can also occur between metal and alloys and other conducting materials such as carbon or graphite. An electrochemical corrosion cell is set up due to differences in the corrosion potentials of the dissimilar

materials. The material with the more noble corrosion potential then becomes the cathode of the corrosion cell, whereas the less noble material is consumed by anodic dissolution. The area ratio of the two dissimilar materials is extremely important. If the anode to cathode surface area ratio is small the galvanic current can be concentrated on a small anodic area. Galvanic corrosion is a particularly important form of corrosion for zinc applications, whether as a coating, an anode, or zinc-dust paint. The galvanic corrosion of zinc has been used to prevent the steel structures from corroding in natural environments [3].

1.3 Corrosion control

Corrosion is an inevitable process. Every year huge amount of metal is being lost due to corrosion. So its control has become the main topic for many corrosionists throughout the world. Complete control of corrosion is somewhat impossible task but it can be controlled to some extent by using different methods, some of which are as follow; [5]

1. Environmental method
2. Coating
3. Corrosion inhibitors

1.3.1 Environmental method

Studies have suggested that, although to the small extent, the corrosion can be controlled by choosing proper controlling the corrosive environment. The soil as well as the nearby area may contain aggressive ions like chloride, sulphide etc. which are responsible for corrosion. Selecting suitable site and building materials that fit to particular environment can be helpful to control such unnecessary failure. For this, advice of engineer and corrosion expert can be useful [4].

1.3.2 Coating

Corrosion protection of over-ground and underground structures by protective coatings is one of the most proven corrosion control methods. By applying coatings of high resistivity, such as epoxies, vinyls, chlorinated rubbers, etc. the flow of electric current to the metal surface is impeded. The higher the thickness of the coating, the higher would be the electrical resistance of the corrosion. A much higher resistance to the current flow would, therefore, be offered. Thus increasing the electrical resistance of metals by coating offers an excellent method of corrosion prevention. They are typically utilized in three different ways: barrier coating suppresses both oxygen and ionic transmission to the cathode reaction to an extent that corrosion may be precluded, Inhibitive/passivation coating decreases corrosion rates by chemically modifying the interfacial condition against the metal and cathodic coatings prevents galvanic corrosion by acting as cathode compared to the substrate which acts as an anode. Metallic coatings are included in this category. It is generally used to protect unalloyed or low alloyed steel. Metallic coatings can be divided in two groups, cathodic coatings, which are nobler than the substrate, and anodic or sacrificial coatings, which are less noble than the substrate, i.e. the coatings that have, respectively, a higher and a lower corrosion potential than the substrate in the environment in question. The cathodic coatings will most often act by the barrier effect only, but for some combinations of substrate and environment the substrate can also be anodically protected (on uncovered spots). The anodic coatings will in addition to the barrier effect provide cathodic protection of possible spots or parts of the surface where the coating is imperfect and the substrate is exposed to the corrosive environment. For such reason, anodic coatings sometimes are referred to as “sacrificial” coating. Galvanized coating is one of such examples [3].

1.3.2.1 Galvanized Steel

A galvanized steel is a steel surface coated by a thin layer of zinc in a galvanization process carried out at about 460 °C. Galvanization ensures that the steel does not get corroded by rust. This process is named after its inventor, an Italian called Luigi Galvani. Although galvanization can be done with electrodeposition processes, the most common

method currently used is hot-dip galvanization, in which steel parts are submerged in a bath of molten zinc which reacts with the steel and forms a coating. The object to be galvanized is immersed in a molten bath of zinc at 460°C[6]. A hot dipped galvanized coating consists mainly of two parts: an inner layer of zinc and steel in contact with the base metal, and an outer layer of unalloyed zinc as shown in Fig.1[6].

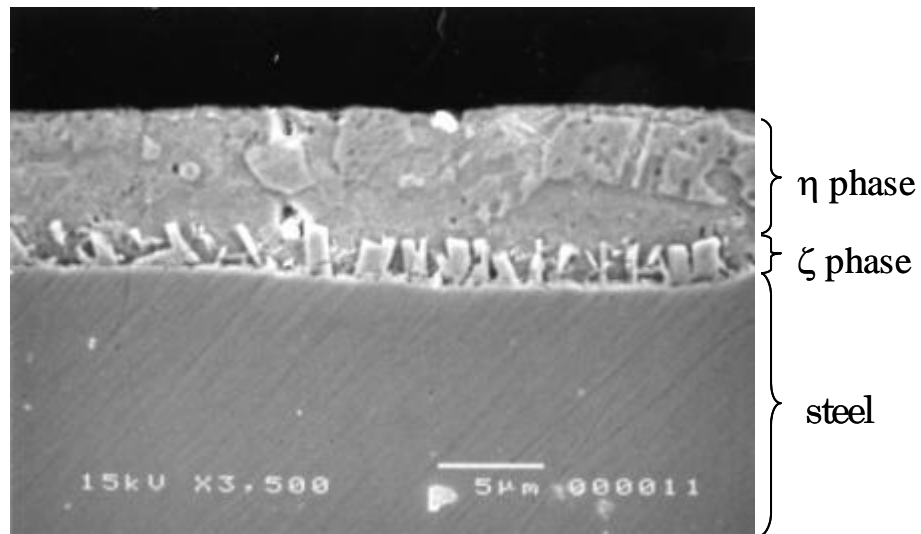


Figure 1. SEM photograph of cross section of a galvanized steel[6].

Various metals, such as aluminium, tin etc. to the zinc bath to modify the coating. Addition of aluminium produces an even coating and addition of tin improves adhesion while addition of silicon limits the formation of alloy layer.

Galvanized steel is available in a variety of forms, such as pipes, sheets and wire. It is used everywhere from automobiles body parts to several household appliances such as washing machines, air conditioning housings, hair dryers, etc. which are an integral part of our daily life. . All these materials are used in atmospheric environment where zinc reacts with corrosive environments and forms rust layer such as zinc oxide.

Corrosion of zinc in oxygenated solution comprises the anodic dissolution of zinc,[5].



And the cathodic reduction of molecular oxygen,



Because the solubility product K_{sp} of zinc hydroxide is markedly low, 3×10^{-17} Zinc hydroxide precipitates on the surface of zinc substrate and changes gradually to zinc oxide

Resulting in the formation of passive film to prevent zinc corrosion. In the presence of inorganic cations, a protective hydroxide layer is formed that acts as barrier to oxygen diffusion and therefore suppresses the cathodic process.



Since most of the inorganic cations are classified into hard acids according to the hard acid and soft base principle, they react with hydroxide ion, a hard base to form precipitates of stable salts or complexes without difficulty. The solubility product of hydroxide with cation of harder acid is lower than that of zinc hydroxide in general. Hence the cation of harder acid than Zn^{2+} can form a precipitate layer of its hydroxide on a corroding zinc surface, resulting in inhibition of zinc corrosion by covering the surface with the hydroxide layer?

The protectiveness of the zinc coating and rust layer formed depends on the factors such as type of corrosive environment, time of wetness, relative humidity, temperature, rain fall among others. To increase the life time of zinc coating of galvanized steel, various corrosion inhibitors and surface treatments have been used [5].

1.3.3 Corrosion Inhibitors

A corrosion inhibitor is a chemical compound which when added to corrosive environment (aqueous solution, oil fuels atmosphere) reduces the corrosion rate [7].

There are different types of inhibitors:

1. Cathodic corrosion inhibitors
2. Anodic corrosion inhibitors
3. Adsorption corrosion inhibitors
4. Volatile corrosion inhibitors (VCI)

1.3.3.1 Cathodic Corrosion Inhibitors

Cathodic inhibitors reduce the corrosion rate due to retarding cathodic reactions. A cathodic inhibitor causes formation of insoluble compounds precipitation on the cathodic sites in form of barrier film. The effective cathode area is one of the factors of galvanic corrosion, therefore its reduction results in decrease of corrosion rate.

Followings are some compounds which are being used as cathodic inhibitors:[8].

- Zinc salts (zinc hydroxide, zinc phosphate);
- Calcium salts (calcium carbonate, calcium phosphate);
- Magnesium salts;
- Polyphosphates etc.

1.3.3.2 Anodic Corrosion Inhibitors

Anodic inhibitors reduce the corrosion rate due to retarding anodic reactions. An anodic inhibitor shifts the equilibrium of the corrosion process to the passive zone causing formation of a then invisible passivation oxide film on the anodic sites, which increases the anode potential and depresses the oxidation process. Reduction of the effective anode

areas results in decrease of corrosion rate. An anodic inhibitor has a serious disadvantage: at low concentrations, they cause increase of corrosion rate and hence it is important to avoid decrease of the inhibitor content below the optimum level.

Followings are some compounds which are being used as anodic inhibitors:

- Chromate (CrO_4^{2-})
- Nitrate (NO_3^{2-})
- Molybdate (MoO_4^{2-})
- Orthophosphate (PO_4^{3-}) etc.

1.3.3.3 Adsorption Corrosion Inhibitors

Adsorption inhibitors reduce the corrosion rate due to polarization of the metal by extremely thin layer of their molecules adsorbed on the surface. Decrease of the effective surface area results in reduction of the corrosion rate. Adsorption inhibitors are substances (mainly organic) capable to form chemisorbed bonds with surface metal atoms [9].

Followings are some compounds which are being used as adsorption inhibitors:

- Amines (R-NH_2)
- Carboxyl (R-COOH)
- Thioureas (NH_2CSNH_2)
- Phosphonates ($\text{R-PO}_3\text{H}_2$)
- Benzoate ($\text{C}_6\text{H}_5\text{COO}^-$) etc.

1.3.3.4 Volatile Corrosion Inhibitors

Volatile corrosion inhibitors (VCI) reduce corrosion in closed spaces (package bags). VCI compound is emitted (vaporized) by the material enclosing the space. The vapours condense in the metal surface in form of microscopic crystals, which dissolve in the moisture film present on the surface. The ions of the dissolved VCI displace water

molecules from the metal surface and form monomolecular insoluble protection film reducing the corrosion rate. Volatile corrosion inhibitors may be added to various package materials: polymer film (e.g. low density polyethylene), paper, foam, powder, oils, etc.) [10].

Followings are some compounds which are being used as volatile corrosion inhibitors:

- Cyclohexylamine
- Dicyclohexylamine
- Guanine
- Amino alcohols
- Nitrites etc.

1.4 Cerium as Corrosion Inhibitor

Chromate conversion coatings have been widely used in industry for a long time to improve the corrosion resistance for aluminium alloys [11, 12, 13] and galvanized steels [14, 15]. Hexavalent chromium, however, has high toxicity and carcinogenesis. Therefore, alternative and more environmentally friendly surface treatments need to be developed. Rare earth metal ions, such as cerium, lanthanum, and yttrium, have been recognized as an effective corrosion inhibitor for some aluminium alloys in a chloride-containing solution. Hinton et al. [16] have reported that cerium-based oxide conversion coatings are a promising alternative to chromate conversion coatings in the middle of 1980s. Cerium conversion coatings are obtained by electrochemical reactions at the metal surface/solution interface by dipping metal substrates into an aqueous solution containing cerium salts, forming a protective layer on the metal surface. Many researchers have carried out the research on the cerium-based conversion treatments for aluminium alloys magnesium alloys (galvanized steels and stainless steel) [12, 17,18]. However, there is different view with regard to effectiveness of the Ce(III) and Ce(IV) ions as corrosion inhibitors.

1.5 Review of pertinent literature

Metal pre-treatments are essential to ensure long-term performance of painted steel. The pre-treatment must act as an adhesion promoter and also provide corrosion protection. For over 100 years chromium has been used as very effective and inexpensive corrosion inhibitors for many alloy systems including aluminium, zinc and steel in a wide range of aqueous environments. However, due to increase environmental concerns and [19] legislation limiting the use of Cr^{6+} based chemicals due its toxicity and carcinogenicity, there is worldwide research to develop effective alternative inhibitors. Since early 1990s efforts have been made on the use of rare-earth (RE) salts as adhesion promoters and corrosion inhibitors and they have been successfully applied to control aqueous corrosion of several metals and alloys such as aluminium, zinc and steel [12,17,18]. The most investigated REs are cerium, yttrium, lanthanum, praseodymium and samarium [20] that were successfully applied to zinc aluminium and steel. The pioneering studies in the field are those of Hinton and Wilson and Hinton [16,21]. Those works report the use of cerium chloride for corrosion inhibition on zinc and aluminium and propose a cathodic mechanism to explain the formation of the RE oxide film. According to that mechanism, the cathodic reactions (oxygen reduction and hydrogen evolution) generate an alkaline environment that leads to localised precipitation of cerium oxides and thus to the formation of the surface film.

Davenport and co-workers [22] also investigated cerium deposition on aluminium alloys and showed that cerium can be oxidised from Ce^{3+} to Ce^{4+} in solution by dissolved oxygen and in a final step it precipitates as insoluble CeO_2 on the cathodic sites which is more corrosion protective than oxide of Ce (III).

In spite of the efforts focussed on the use of cerium, other REs also show promising possibilities. Among these, yttrium and lanthanum [19] have been investigated and the results suggest that they lead to increased corrosion resistance when applied to aluminium and its alloys and to steel. Therefore, the possibility of pre-treatments based on these RE metals is also a field to be investigated [20].

The cerium-based conversion coatings on galvanized steel were investigated and the influence of SO_4^{2-} on the corrosion behaviour was evaluated by Kobayashi et al. [23]. The addition of SO_4^{2-} to the coating solution considerably improved the corrosion resistance of the conversion coatings. Atomic force microscope observation shows that deposits prepared from the solution with SO_4^{2-} have smaller crystalline size than those prepared without SO_4^{2-} . The results of X-ray photoelectron spectroscopy demonstrate that SO_4^{2-} ions are incorporated in the coating during the conversion process. This indicates that SO_4^{2-} acts as a grain refiner and/or growth inhibitor, thus enhancing the corrosion resistance of cerium conversion coating. It has been reported that both Ce (III) and Ce (IV) were detected in the coating layer. The formation of Ce (IV) has been explained by considering the oxygen reduction reaction which makes the local environment alkaline enough to promote the conversion of Ce (III) to Ce (IV). Some studies on the cerium-based conversion coatings on galvanized steels have shown the influence of anions, such as Cl^- , NO_3^- , and CH_3COO^- , in a coating solution on corrosion behaviour [23].

The work of Valverde [24] has demonstrated the improvement caused by the presence of small amounts of cerium or yttrium in the resistance of Cu-Zn-Al alloys to corrosion in sea-water at 80 °C.

Lu *et al.* [25] had reported on improvement of the corrosion resistant of hot-dipped galvanized steel sheets after treatment with $Ce(NO_3)_3 \cdot 6H_2O$. The results revealed that with increasing treatment time, the corrosion resistance of the film increases within 1 h due to the increased film thickness and decreases after 1 h because the cracking and flaking off gradually become dominant factor.

The mechanism of corrosion inhibition on zinc treated with cerium salts was also investigated by Aramaki [26], who reported the formation of a hydrated or hydroxylated Ce-rich layer that was constructed by adsorption on the hydroxylated zinc surface. This process leads to the formation of a Ce_2O_3 framework on the zinc surface, which suppresses the cathodic reactions. The inhibition efficiencies of Ce (III) and Ce (IV) ions were determined by polarisation measurement of zinc electrode. The efficiency

of Ce^{3+} was as high as 90% at concentration above 1×10^{-3} M, while Ce^{4+} ion showed negative efficiency, i.e. it enhanced the corrosion of zinc [26, 27, 28].

Tjong et al. [29] studied the effect of concentration of CeCl_3 and hydrogen peroxide on the corrosion of aluminum at 30°C . It was concluded that the entire surface was covered with a compact film only when immersed in a solution containing 10 g/L CeCl_3 and 100 mL/L H_2O_2 . XPS results indicated that cerium was incorporated as Ce^{4+} species in the hydrated oxide film. The formation of such hydrated conversion film on the composite resulted in low anodic current density and more noble pitting potential when exposed to 3.5% NaCl solution [21].

Hosseini et al.[30] Prepared a conversion coating consisting of 50 mM/L $\text{Ce}(\text{NO}_3)_3$ on an electro galvanized steel and tested in 0.5 M/L NaCl solutions for various immersion time. The corrosion performance was evaluated by Tafel polarization and electrochemical impedance technique and found that the newly developed cerium-based conversion coating was a promising candidate for replacing the conventional chromate treatments used at present for galvanized steel. The better corrosion performance was assigned due to hindering of the transport of oxygen to the substrate metal, thereby retarding the cathodic half-reaction [30].

1.6 Objectives of the work

The use of rare earth elements as corrosion inhibitors is very attractive because of their non-toxicity, as compared with the common chromate inhibitors. The most of the researches using rare earth conversion coating are based on aluminium alloy [11,12], zinc [16,26] and electroplated zinc [25] there are only limited works reported on hot dip galvanized coating. Among the various rare earth elements, cerium has been found to be more effective corrosion inhibitor than others. The corrosion inhibition offered by cerium salts depends on the anionic component of the salt and its valence state. Cerous perchlorate and Cerous acetate offer best corrosion inhibition while chloride salt ions are the most corrosive of anions. There is no data available on the effect of ammonium sulphate salt of cerium and there is conflicting view with regard to inhibition offered by Ce (III) and Ce (IV) ions. [14, 21, 22]

Therefore, this study aims to study the corrosion effect of Ce (III) and Ce (IV) ions on the corrosion of hot dip galvanized steel sheet in aerated 0.5 M Na_2SO_3 solution. The cerium salt used was ceric ammonium sulphate.

CHAPTER-II

2.EXPERIMENTAL

2.1 Preparation of Sample

Galvanized iron (GI) sample of size 2.25 cm² was cut from the sheet, it was cleaned by ultrasonicing in ethanol for 5 minutes and edges were covered by epoxy resin.

2.2 Test Solutions

All the measurements were performed in aerated solution of 0.5 M sodium sulphite. To check the effect of cerium ion concentration, various salt concentrations were used in aerated 0.5 M sodium sulphite solution.

2.3 Electrochemical Measurements

Open circuit potential of the GI samples was monitored in aerated 0.5 M Na₂SO₃ solution and 0.5 M Na₂SO₃ containing 1x10⁻³ M ceric ammonium sulphate salt for 30 minutes using a three electrode system. Corrosion inhibition effect of cerium salt was studied by measuring both the anodic and cathodic polarization curve of GI samples in aerated 0.5 M Na₂SO₃ solution with and without cerium salt in different concentrations. The polarization was carried out by sweeping the potential from the open circuit potential to either anodic or cathodic direction at the sweep rate of 50 mV min⁻¹ and the output current was measured as the function of potential. Polarization measurements were carried out in a single compartment three-electrode cell using a Hokuto Denko HA-151 galvanostat/potentiostat interfaced with an X-Y recorder. A Ag-AgCl reference electrode (SSE) with 0.5 M Na₂SO₄ in agar agar as salt bridge was used in combination with platinum plate as a counter electrode. The area of the working electrode was controlled by using an O-ring of 9 mm and 7mm internal diameter.

2.4 Pulse Deposition of Ce (III) from Ce (IV)

In order to check the effect of Cerous ion, Ce (III), a potential pulse method was used to deposit Ce (III) from Ce (IV) by reducing it at -1.3 V vs. SSE. The pulse width was 2 s. An anodic potential pulse of -0.8 V vs. SSE for 2 s was used for the purposes of both cleaning the Ce (III) ion formed and oxidising the zinc so that composite of cerium and zinc could be formed. A pulse plan of 100 cycles was applied. Thus obtained GI samples were tested for its polarization behaviour as discussed above. The surface morphology of the sample was studied by using a Hitachi SU8000 scanning electron microscope.

2.5 X-ray photoelectron spectroscopy

In this study, X-ray photoelectron spectroscopy (XPS) analysis of samples prepared in three different conditions viz. 500 μA , 1.2 V and CV (50/5 mV sec^{-1}) were made using a Thermo Scientific Sigma probe instrument in which the vacuum of analysis chamber was better than 2×10^{-8} Pa. The X-ray source was Al k_{α} (1486.6 eV) at 400 micrometer beam size with fixed pass energy of 50eV at 0.1eV resolution for survey scan. For C1s, 50 cycles and for N1s, 100 cycles of scanning were performed for detail scan. Before making measurements, the surface was sputtered by using Ar^+ at 1.0 KeV for 2 min. The data were fitted using Thermo Advantage software.

CHAPTER – III

3. Results and Discussion

3.1 Variation of open circuit potential

The evolution of open circuit potential (OCP) of GI samples immersed in aerated 0.5M Na_2SO_3 solution and 0.5M $\text{Na}_2\text{SO}_3 + 10^{-3}\text{M}$ Ce(IV) is shown in Fig.1. The OCP in 0.5 M Na_2SO_3 solution slowly shifted in negative direction followed by stabilization. This is due to breakdown of the air formed oxide film on the coating and subsequent dissolution of zinc layer [6]. On the other hand, the OCP of GI sample immersed in sulphite solution containing 10^{-3}M Ce (IV) gradually shifted to positive direction. The potential shift in the cathodic direction indicates the formation of oxide film of cerium on the coating surface, which needs to be further investigated. The potential was not yet stabilised after approximately 30 min and showed some fluctuations during the experiment time.

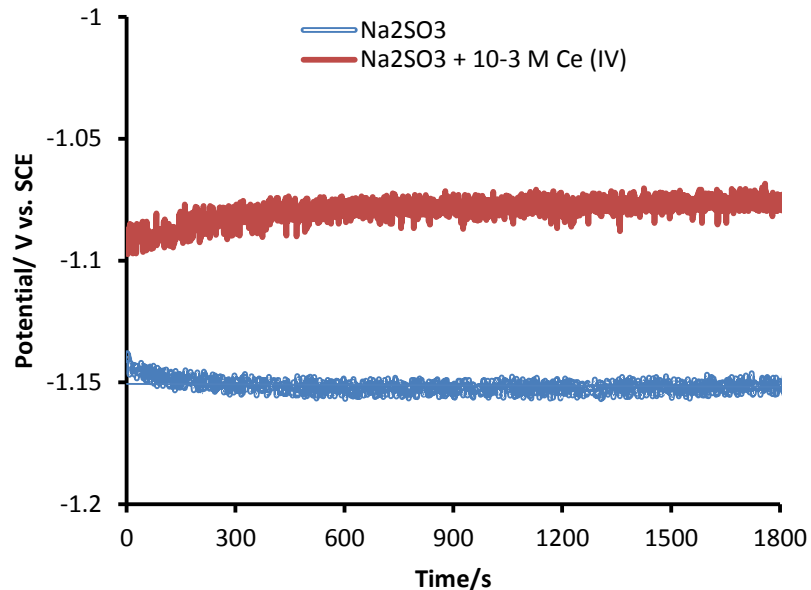


Fig. 2: Variation of OCP with time

3.2 Potentiodynamic Polarisation

Polarisation curves of galvanised iron sample were measured in 0.5 M Na₂SO₃ solution containing different concentrations of Ce (IV) salt. Anodic and cathodic polarisations were measured just after immersion of the sample in the solution and after 1 hour of immersion. A potential sweep rate of 50 mV/min was applied in the cathodic and anodic direction starting from OCP. Figure 3 shows the potentiodynamic polarization curves of the galvanised iron sample obtained just after immersion in 0.5 M Na₂SO₃ solution with and without Ce (IV) salt. In 0.5 M Na₂SO₃ solution, an OCP of -1.05 V was observed with cathodic curve showing a limiting value due to oxygen reduction reaction.

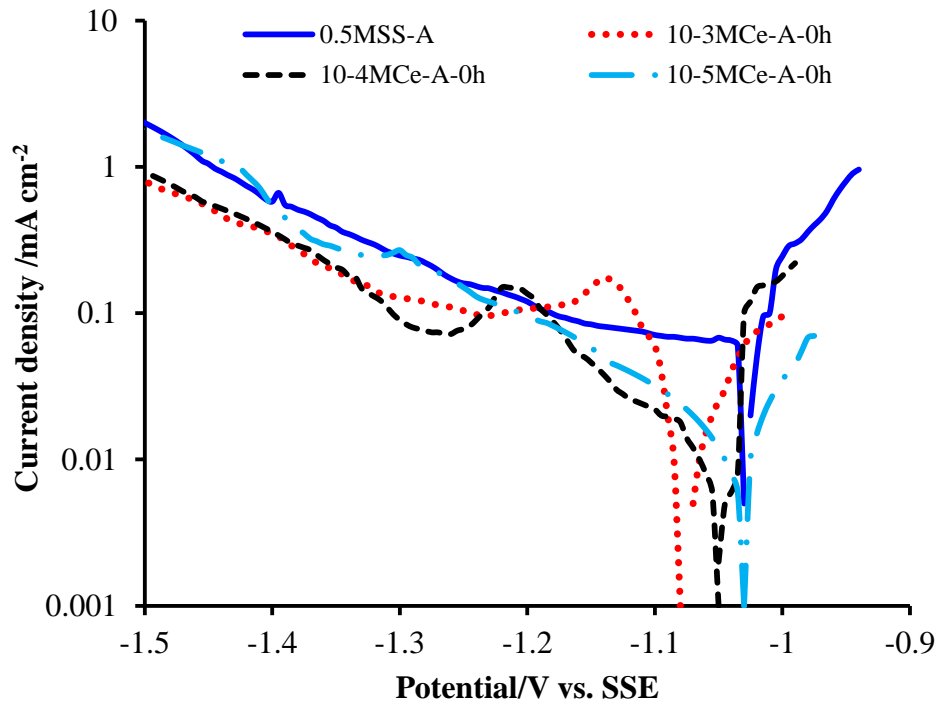


Fig.3: Anodic and cathodic polarisation of galvanised iron sample in different concentration

With the addition of some Ce (IV) salt, the OCP slightly shifted to negative direction and the cathodic branch of the polarization curves changed from limiting type to activation polarization type, while the anodic polarization curves did not show any significant change. The cathodic Tafel slopes changed from about 450 mV/decade to about

80mV/decade, 140 mV/decade, and 200 mV/decade, respectively in 1×10^{-3} M Ce (IV), 1×10^{-4} M Ce (IV), and 1×10^{-5} M Ce (IV) solutions. This change of slopes indicates the change of cathodic reaction from diffusion limited oxygen reduction to activation control hydrogen ion reduction. It is expected that due to strong oxidizing character of Ce (IV) salt, Ce (IV) will undergo cathodic reduction instead of reduction of oxygen and hydrogen ion. In this case, the limiting current should show an increase in its value. From the shift of OCP in negative direction in polarization curves, it seems that just after immersion the reaction is controlled by the dissolution of air formed zinc oxide on the coating and probably the reduction of Ce (IV) on oxide covered zinc surface is not easily. The effect of concentration of Ce(IV) salt is obvious only at high concentrations. At 1×10^{-5} M Ce (IV), the cathodic polarization curve is almost similar to that in 0.5 M Na_2SO_3 solution. A small shoulder in the cathodic polarization curve may be due to reduction of ZnO. The nature of anodic polarization curves was almost same irrespective of the concentration of Ce (IV) proving further that in the initial stage the dissolution of air formed ZnO was the main reaction. To clarify this point, polarization curves were measured after immersion of the samples in solution for 1 h. Figure 4 shows the polarization curves GI sample after immersion in 0.5 M Na_2SO_3 with and without containing 1×10^{-3} M Ce(IV) ion. There are obvious shift of OCP to noble direction in Ce(IV) ion containing solution. The shift of potential to negative direction in sulphite solution shows the dissolution of air formed oxide. On the other hand, the shift of OCP to noble direction by about 150 mV shows the deposition of oxides and hydroxide of cerium. The presence of 1×10^{-3} M Ce(IV) ion in sulphite solution has enhanced the cathodic limiting current by more than 20 times while the slope did not changes that much. This indicates that the enhancement of cathodic current is due to taking part of Ce(IV) ion in the cathodic reaction to convert to Ce (III). This is due to strong oxidising nature of Ce (IV) ion.



It is expected that as soon as sample is immersed in a sulphite solution containing Ce (IV) salt, a protective layer of $\text{Ce}(\text{OH})_4$ and/or CeO_2 should precipitate readily on the zinc surface owing to very low K_{sp} value 2×10^{-48} of $\text{Ce}(\text{OH})_4$ as compared to 3×10^{-17} for $\text{Zn}(\text{OH})_2$ and 1.6×10^{-20} for $\text{Ce}(\text{OH})_3$. Therefore, Ce (IV) ion enhanced the corrosion of

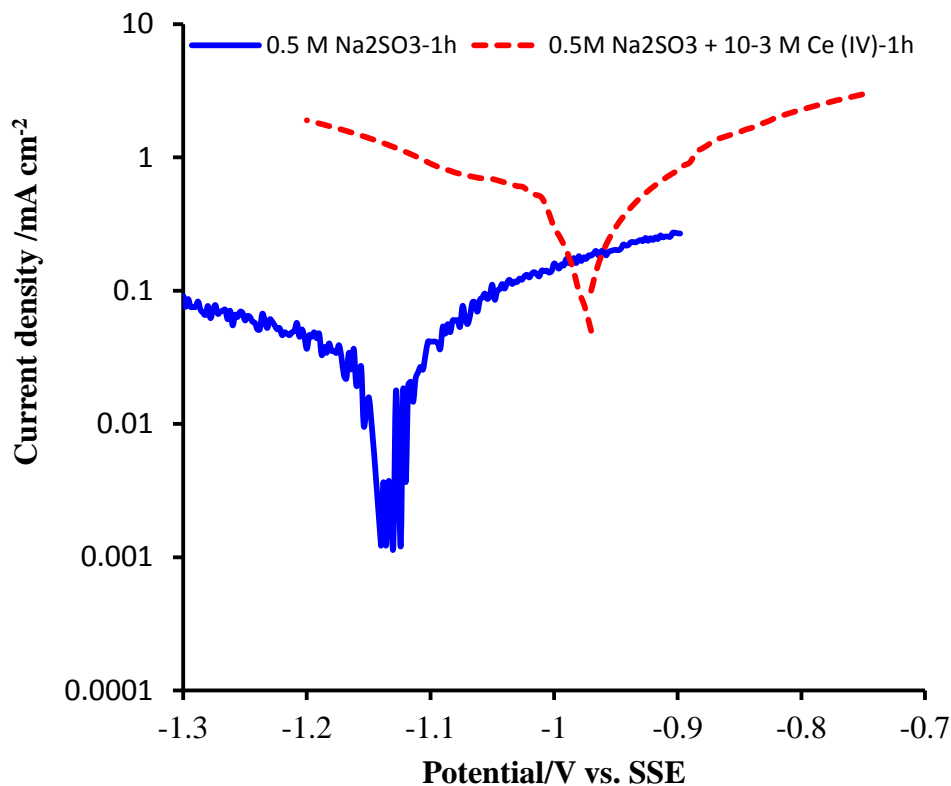


Fig. 4; Anodic and cathodic polarisation curves of galvanised iron samples immersed in sulphite solution with and without Ce (IV) salt for 1h.

galvanized steel by accelerating the cathodic process markedly, as shown in Fig.3. There is conflicting report in this regard as some reports suggest the inhibition of corrosion by Ce (IV) [14] while some others report on the acceleration of corrosion like we found in this study [26,27,28].

Comparing the K_{sp} values of hydroxides of Ce (IV), Zn^{2+} , and Ce (III), it is plausible to expect inhibition of corrosion after the reduction of Ce (IV) to Ce (III) due to its low K_{sp} value compared to hydroxide of Zn. But, the result shows otherwise. It has been reported that after rapid reduction of Ce (IV) to Ce (III), a thick and cracked oxide layer was developed on the surface and sometimes pitting also appeared on such surface, therefore leading to acceleration of corrosion rather than inhibition as expected from K_{sp} values. Therefore, our next aim was to produce a composite of cerium and zinc by using a pulse method to reduce Ce (IV) to Ce (III) in cathodic pulse while simultaneously oxidizing zinc using anodic pulse [25, 30].

3.3 Pulse deposition of Ce (III) and its polarization behaviour

The main purpose of pulse deposition is to make a composite of cerium and zinc oxide/hydroxides on the surface of galvanized iron and check its polarization behaviour. A pulse plan comprising of cathodic pulse of -1.3 V vs. SSE and anodic pulse of -0.8 V vs. SSE was used. The pulse width was 2 s each and in total 100 pulses was applied. Figure 4 shows the pulse plan and corresponding current. The redox potential of Ce (IV)/Ce (III) has been reported to vary greatly depending on the type of anions and pH of the solution [21]. However, from the enhancement of the cathodic current and taking part of Ce (IV) in reduction at OCP, a cathodic pulse of -1.3 V was thought to be good enough to reduce Ce (IV) to Ce (III). Figure 4 shows that during anodic pulse, the current was large and it decayed very fast while during cathodic pulse the current only slightly increased to more negative value. During anodic pulse, oxidation of Ce (III) cannot take place; however it helps in cleaning the surface and dissolving zinc. Therefore, a composite of Ce (III) and Zn (II) is expected to be formed [26].

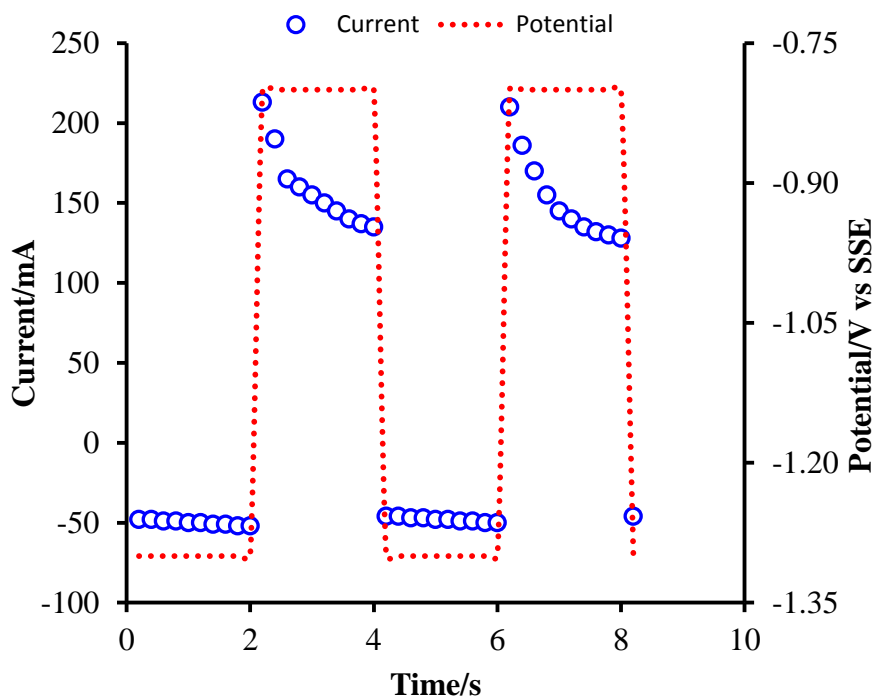
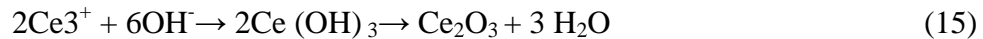


Figure 5: Pulse polarisation of galvanised iron sample

Figure 6 shows the anodic and cathodic polarization of galvanized iron sample after 100 cycles of pulse in Ce (IV) containing sulphite solution. The polarization curves of pulse polarized samples were recorded in sulphite solution with and without 1×10^{-3} M Ce (IV) salt and compared with the one obtained after one hour immersion in 0.5 M Na₂SO₃ solution (Fig.4). The polarization curves of sample in sulphite solution measured after 100 cycles of pulses showed a decrease of both the cathodic and anodic currents by about 50 times. Therefore, the pulse polarization has resulted in the formation of highly protective oxide/hydroxides of cerium and zinc. The cathodic Tafel slope changed from about 450 mV/decade in sulphite solution containing Ce (IV) ion to about 100 mV/decade after pulse polarization. Aramaki et al. [26,27,28] had reported almost similar change of Tafel slopes and proposed that deposition of oxides/hydroxides of cerium inhibits the oxygen reduction reaction and instead reduction of hydrogen is the main cathodic reaction. After pulse polarization of the GI sample, it is assumed that the surface film mainly composed of Ce(OH)₃ and Ce₂O₃ was formed with the incorporation of OH⁻ ions produced in cathodic oxygen reduction reaction,



Hinton et al. [16] have concluded that the inhibition of corrosion of zinc in chloride medium containing CeCl₃ was due to the formation of hydrated cerium-rich oxide film which markedly reduced the rate of cathodic process. The protective film contained a fair amount of Ce (IV) which was assumed to be formed by the oxidation of Ce (III) with the H₂O₂ afforded by the two electron transfer reduction of oxygen.

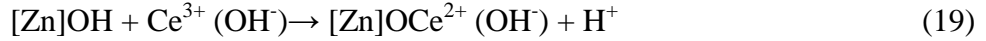
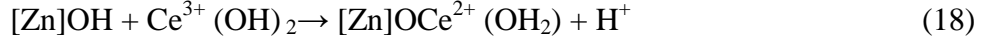


The formation of protective films containing Ce⁴⁺ has been demonstrated on aluminium and its alloys [11, 12]

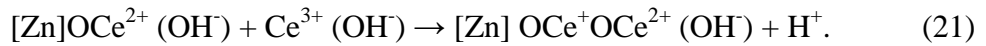
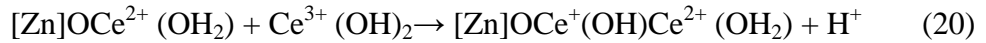
However, this mechanism does not explain the change of Tafel slope from about 400 mV/decade to 100 mV/decade in the pulse polarized samples. Such value of Tafel slopes resembles with the value that is obtained for hydrogen evolution reaction in an acid solution [25, 26],



From the analysis of surface of zinc by XPS, Aramaki [26] has proposed the formation mechanism of the protective film. At the initial stage, a layer of $\text{Zn}(\text{OH})_2$ is formed which reacts with hydrated or hydroxylated Ce^{3+} ,



These hydrated and hydroxylated Ce^{3+} ions react repeatedly,



Therefore, a framework of Ce^{3+} oxide layer containing H^+ is formed [25]. Ce^{3+} in the oxide layer combines with OH^- or H_2O to form the oxide and hydroxide layer. Protons incorporated in the layer are consumed in the cathodic reaction as discussed above or in the reduction of zinc oxide [14, 18 and 20] as



The cerium-rich oxide and hydroxide layer grows rapidly on the zinc surface by the direct reactions of hydroxide surface with hydrated and hydroxylated Ce^{3+} and the cathodic H^+ consuming reactions, of which Tafel slopes may be near to 120 mV/decade.

Figure 6. Shows that when pulse polarized sample was immersed in sulphite solution containing 10^{-3} M Ce (IV) salt, the polarization curves did not show an enhancement of corrosion unlike in Fig.3. The corrosion potential was slightly shifted to noble direction. This shows that immersion of pulse polarized sample in Ce (IV) solution leads to deposition of mainly cerium containing oxide/hydroxide film. However, the interesting result was that the both cathodic and anodic currents were highly suppressed, almost 100 times lower current compared to samples without pulse polarization. Thus, the pulse polarization of GI samples seems to be a very effective method to produce a highly

inhibitive film on galvanized steel surface. However, characterization of such film is necessary for better understanding on the mechanism.

In order to understand the shift of OCP of pulse polarized sample immersed in sulphite solution containing Ce (IV) ion, a cross cut was introduced on such sample and polarization curves were measured and is depicted in Fig.7. The OCP slightly shifted to negative values and almost similar value to that observed for samples in sulphite solution was obtained. This was accompanied by decrease of anodic Tafel slopes showing the acceleration of zinc dissolution. However, cathodic Tafel slope did not change. The current remains almost similar to that before cross cut was introduced. All these findings indicate that the pulse polarization has indeed produced a protective film on GI sample.

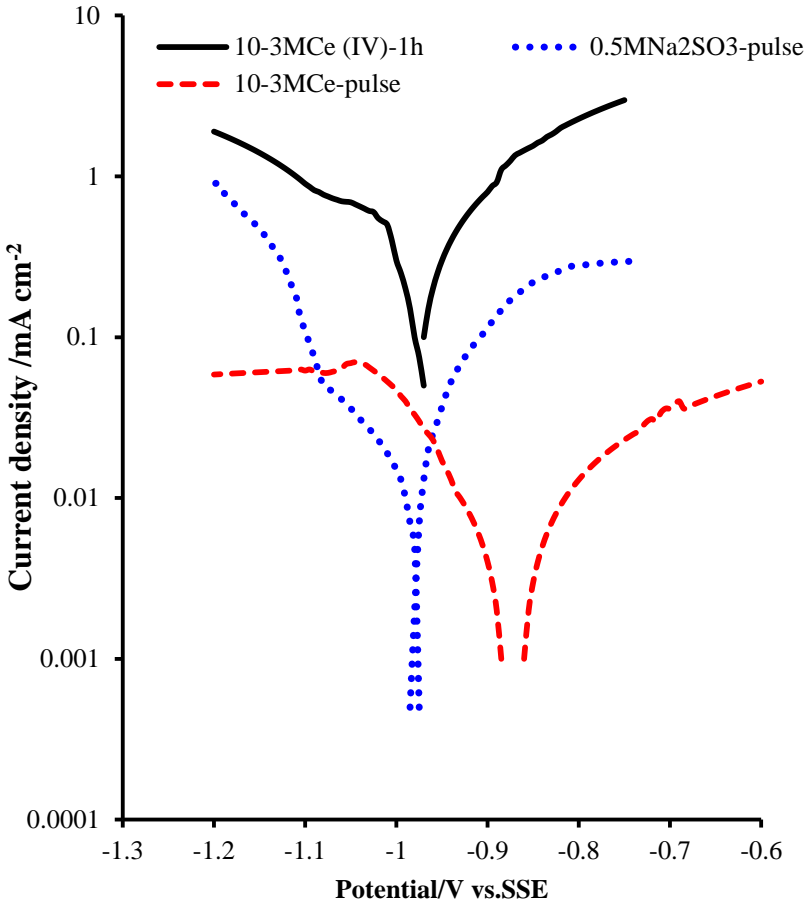


Fig 6; anodic and cathodic polarisation sample in different concentration.

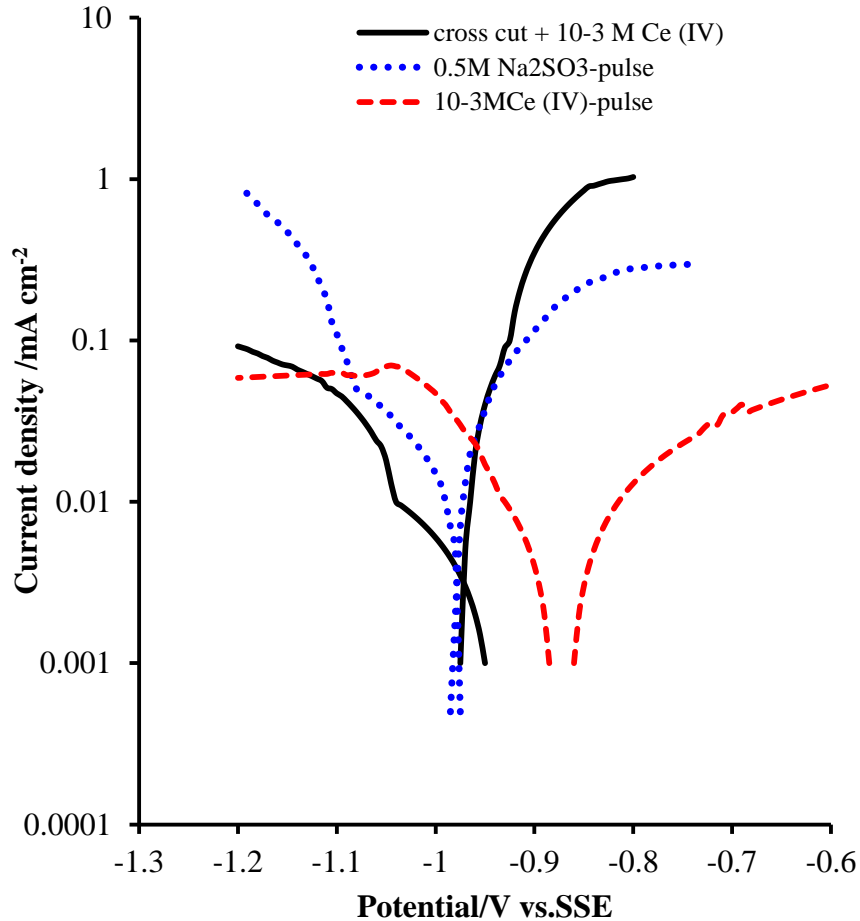


Figure7: Polarisation curve of sample after making cross on it.

3.4 Characterization of the Surface

Figure 8a-b shows the SEM images of the surface of the GI samples immersed for one hour in sulphite solution containing 1×10^{-3} M Ce (IV) salt. The area immersed in the test solution has developed white precipitate having cracks (Fig.8b) and some dark spots which may be due to pitting appeared on the surface. In order to confirm the composition of the precipitates, the sample surface was analysed by XPS. Figure 9a shows the survey spectrum which shows the peaks for Zn2p, Zn3s, Zn3d, Ce3d, Ce4d, Ce4p, O1s, Na1s, C1s and S2s.[26].

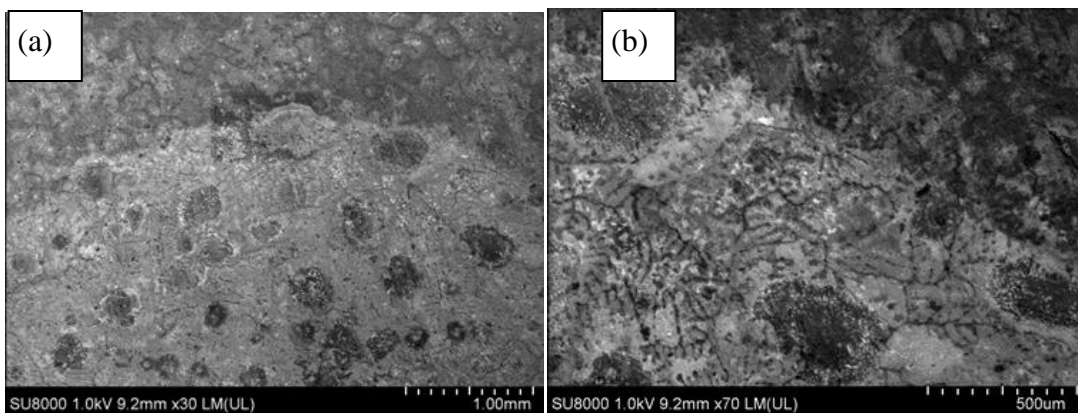


Fig8: The SEM images of the surface of the GI samples immersed for one hour in sulphite solution containing 1×10^{-3} M Ce (IV) salt. Figure 8b is the magnification of Fig.8a.

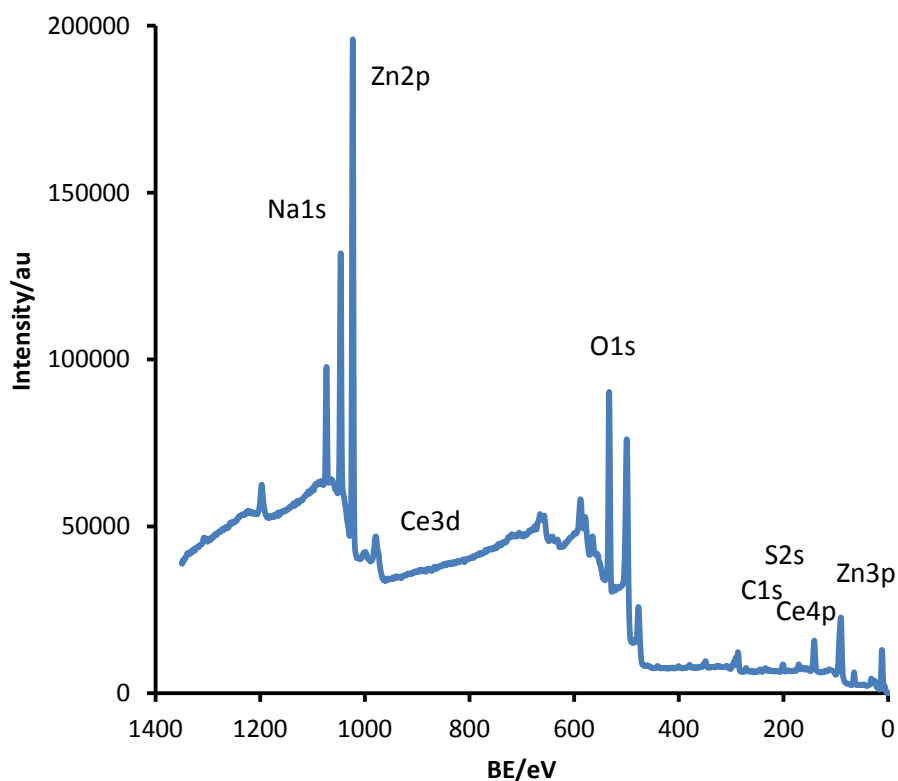


Figure 9(a): XPS survey spectra of GI sample after 1 h immersion followed by cathodic polarization in 0.5 M Na_2SO_3 + 1×10^{-3} M Ce (IV) salt solution

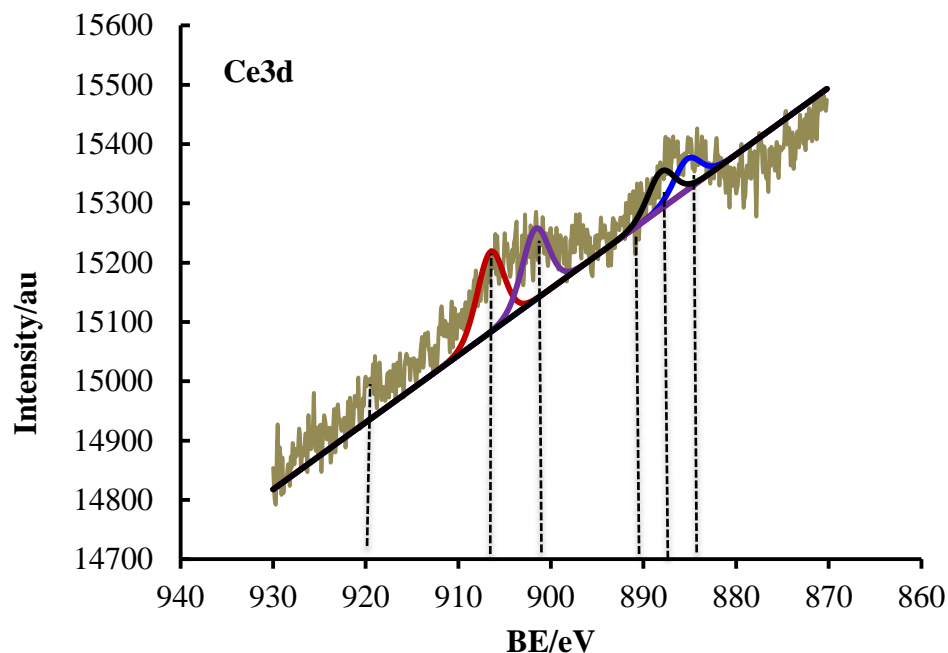


Figure 9(b): XPS spectra of Ce3d for GI sample after 1 h immersion followed by cathodic polarization in 0.5 M Na₂SO₃+ 1x10⁻³ M Ce (IV) salt solutions

Figure 9b shows the detail analysis of Ce3d spectrum in the range between 860 and 940 eV. It consists of complex structures with three distinct regions, (i) from 860 to 890 eV is associated with Ce 3d_{5/2}, (ii) from 890 to 910 eV being a mixture of Ce 3d_{5/2} and Ce 3d_{3/2} peaks and (iii) a peak at 917.5 eV due only to Ce⁴⁺. [8, 13]. The peaks in the first and second regions are due to both Ce³⁺ and Ce⁴⁺ and therefore difficult to understand the individual contribution of specific valence state of Ce. Therefore, peak at 917.5 eV which is solely due to Ce⁴⁺ is often used to describe the type of oxide/hydroxide formed on the surface of zinc after immersion in sulphite solution containing Ce (IV) salt. The presence of very small peak at 917.5 eV indicates that the surface mainly contains oxides/hydroxides of Ce³⁺. Therefore; XPS results support the cathodic polarization curve in Fig.3 where GI samples showed enhanced cathodic current due to reduction of Ce (IV) to Ce (III). The presence of Ce⁴⁺ has been reported in the oxide/hydroxides of Ce³⁺ due to the reason discussed above [14, 20,21,22].

Figure 10a shows the survey spectrum of GI samples after pulsed polarized for 100 cycles and then cathodically polarized in sulphite solution containing 1×10^{-3} M Ce(IV) salt. This spectrum shows the peaks for Zn2p, Zn3s, Zn3d, Ce3d, Ce4d, Ce3p, O1s, Na1s, C1s and S2s.

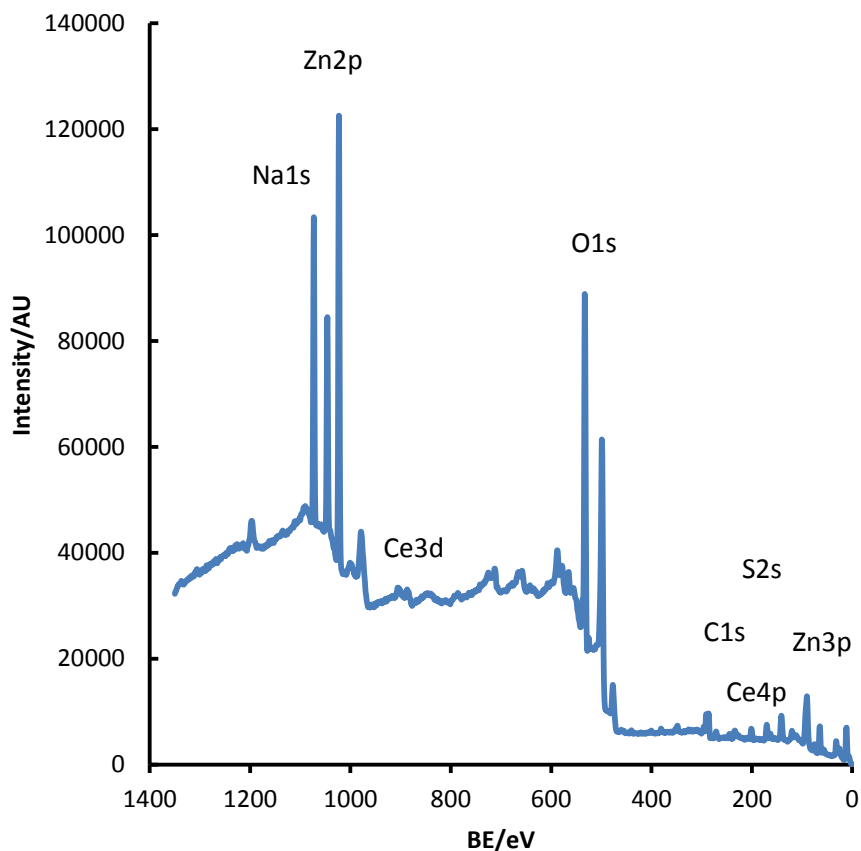


Figure10(a):XPS survey spectra of GI sample after 100 cycles of pulse followed by cathodic polarization in 0.5 M Na₂SO₃ + 1×10^{-3} M Ce (IV) salt solution

Figure 10b shows the detail analysis of Ce3d spectrum in the range between 860 and 940 eV. It consists of complex but fine structures with three distinct regions, (1) from 860 to 890 eV is associated with Ce 3d_{5/2}, (ii) from 890 to 910 eV being a mixture of Ce 3d_{5/2} and ce 3d_{3/2} peaks and (iii) a peak at 917.5 eV due only to Ce⁴⁺ as discussed above [14,18]. According to the literature, the Ce3d spectrum of Ce⁴⁺ exhibits characteristic 3d_{5/2} peak at 882.0eV, 3d_{3/2} peak at 899.9 eV and satellite peak at 917eV[21] and

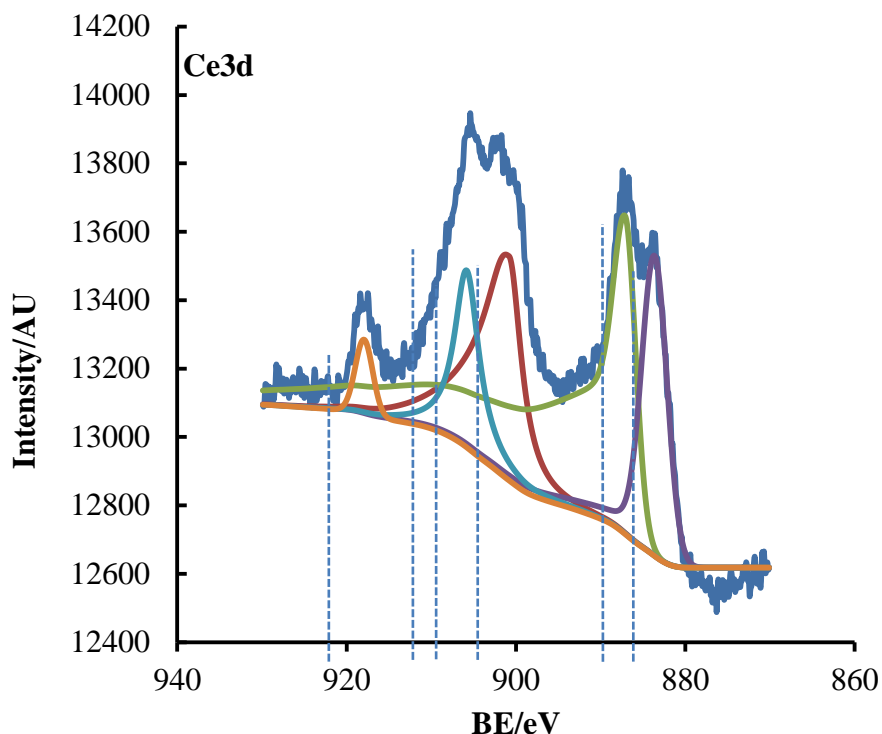


Figure10(b): XPS spectra of Ce3d for the GI sample after 1 h immersion followed by cathodic polarization in 0.5 M Na₂SO₃ + 1x10⁻³ M Ce (IV) salt solution

characteristic peaks for Ce³⁺ appeared at 880.6eV, 885.9eV, 898.9 eV and 904.2 eV [22].All together Ce⁴⁺ shows 7 peaks and Ce³⁺ 4 peaks and interpretation of spectra is complicated. Satellite peak could arise from electronic transitions such as shake-down or shake-up or from electron interactions such as multiplet splitting or hybridization [14] during photoemission process. Shake-up like occurs when an outer shell electron is excited to an unoccupied orbital during photoemission. This leads to an energy loss as a result of electron excitation. Multiplet splitting is resulted from an interaction between spin of excited electrons with valence unpaired electrons. Hybridization is associated with an interaction between cerium and its neighbouring atoms. The peaks in the first and second regions therefore result from both Ce³⁺ and Ce⁴⁺ and therefore difficult to understand the individual contribution of specific valence state of Ce. For this reason, peak at 917.5 eV which is solely due to Ce⁴⁺ is often used to describe the type of oxide/hydroxide formed on the surface of zinc after immersion in sulphite solution containing Ce (IV) salt. From Fig. 9b, the Ce3d spectrum shows a distinct satellite peak at

917.5 eV, demonstrating that the film consists of good amount of Ce^{4+} compared to the sample which was not pulse polarized, Fig.8b. It is considered that the H_2O_2 produced during reduction of oxygen promotes the oxidation of Ce^{3+} into Ce^{4+} species during the film deposition [14,20,22].

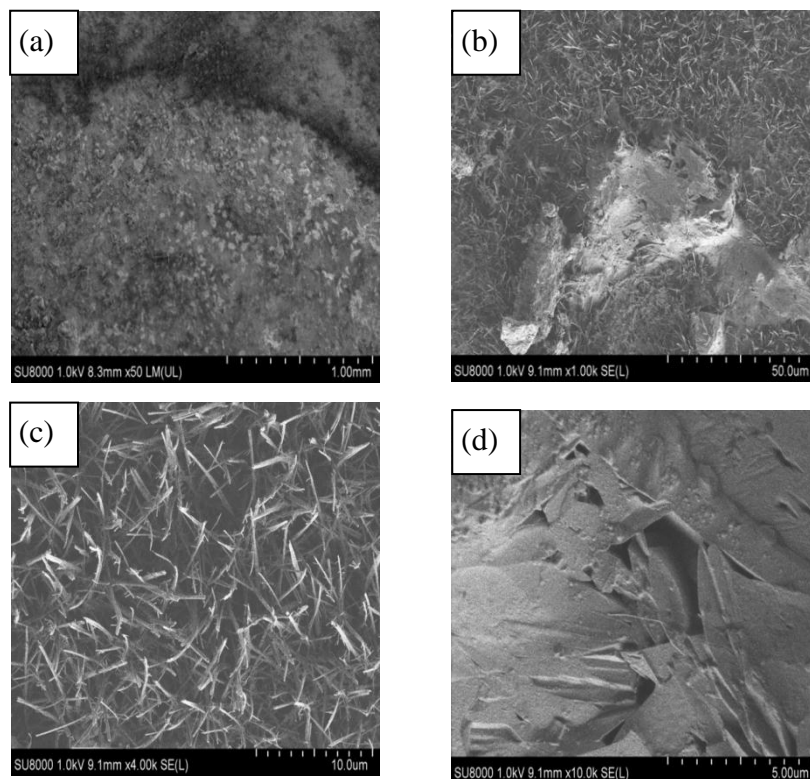


Fig11a-d: SEM images of GI sample after pulse polarized in sulphite solution containing 1×10^3 M Ce (IV) salt and cathodically polarized in same solution from OCP till -1.3 V vs. SSE. Figures 11b-d are the magnified images of Fig.11.

The formation of cerium hydroxide or hydrated ceriumoxide can be verified from the O1s spectrum of conversion film, not shown here. A broad spectrum for O1s was observed centered at 533.0 eV with a full width at half maximum (FWHM) of about 4 eV. This spectrum was deconvoluted at least into two peaks located at 531.0 and 534.0 eV, which correspond to oxide and hydroxide of cerium, respectively.

Figure 11a-d shows the SEM image of the sample pulsed polarized for 100 cycles and then cathodically polarized in sulphite solution containing Ce (IV) salt. Fig.11b shows the

appearance of two distinct regions on the surface of the sample. One having needle like structure showing the growth of a layer and another white region which has developed as a thin film. Fig.11d shows that such white layer as a thin and compact layer. Such thin and compact layer without cracks is thought to be the reason for inhibiting the corrosion of such samples. Therefore, it can be sum up that the pulse polarization of GI samples inCe(IV) salt solution has resulted in the formation of a composite of cerium and zinc layer that inhibits both cathodic and anodic reaction by the formation of a compact protective layer composed of Ce^{3+} , Ce^{4+} and Zn^{2+} [14].

Conclusions

In this study, effect of cerium ions on the corrosion behaviour of hot dip galvanized steel was studied in aerated sodiumsulphite solution using potentiodynamic polarization method. Simple immersion of GI sample in Ce (IV) containing sulphite solution shifted the OCP to noble values due to deposition of oxides/hydroxides of cerium. However, the presence of Ce(IV) ion had enhanced the corrosion of galvanized steel by about 20 times compared to so sulphite solution without Ce (IV) ion. This enhancement of corrosion by Ce(IV) ion was attributed to the taking part of Ce (IV) in cathodic reaction instead of oxygen reduction reaction. A composite of Ce (III) and Zn (II) was prepared by using cathodic and anodic pulse of -1.3 V and -0.8 V and tested for its corrosion behaviour. It was found that the pulse polarized GI samples showed an inhibition of corrosion by approximately 50-100 times. The XPS analysis of the surface showed the presence of both Ce (IV) and Ce (III) compared to mainly Ce (III) in the case of sample without pulse polarization. The inhibition of corrosion was due to formation of highly protective film composed of Ce (IV), Ce (III) and Zn (II)

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