A Dissertation entitled

"Effect of Cations on the Corrosion Behaviour of Galvanized Steel Sheet of Nepal in Wet-Dry Cyclic Condition"

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In Partial Fulfilment of Requirements for the
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By

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FOREWORD

The dissertation entitled **"Effect of Cations on the Corrosion Behaviour of Galvanized Steel Sheet of Nepal in Wet-Dry Cyclic Condition"** submitted by **Ms. Nilima Singh** for the M. Sc. Degree in Chemistry has been carried out under my supervision in the academic year 2010-2011. During the research period (April 2010 to December 2011), she had performed her work sincerely & satisfactorily. No part of this thesis has been submitted for any other degree.

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LETTER OF APPROVAL

The dissertation entitled

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Submitted by

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Abstract

In this study, effect of cations on the corrosion behaviour of galvanized steel sheet of Nepal has been investigated in simulated wet-dry cyclic conditions. Three cations namely ammonium, magnesium and sodium of sulfate were used as corrosive medium. The wet-dry cycle consisted of 18 hours wet period and 6 hours dry period in one cycle and conducted for 14 days. The corrosion performance has been evaluated using weight loss method, Tafel slopes and corrosion potential variation with exposure time. It was found that ammonium ion enhanced the corrosion rate by participating in the cathodic reaction. On the other hand, magnesium ion inhibited the corrosion by forming the oxide layer. The corrosion rate was found to be 0.10 $mm.y^{-1}$, 0.03 $mm.y^{-1}$ and 0.06 $mm.y^{-1}$, respectively, in ammonium, magnesium and sodium ions. After 14 days of corrosion in ammonium sulphate solution there was red rust due to corrosion of iron. The amount of red rust was less in sodium sulphate solution comparing to ammonium sulphate. The SEM image shows a highly porous rust layer in ammonium and sodium sulphate solutions compared to a thin and compact rust layer in the magnesium sulphate solution showing inhibition of corrosion by magnesium ion. The potentiodynamic polarization curves showed the inhibition of anodic reaction by magnesium ion probably due to formation of stable oxide layer.

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Table of Contents

Page No.

Letter of Approval i

Foreword ii

Table of Contents iii

Acknowledgements iv

Abstract v

1. Introduction 1

    1.1 Concept of corrosion 1

    1.2 Corrosive environment 2

    1.3 Atmospheric corrosion 2

    1.4 Atmospheric factors 4

    1.5 Atmospheric environment 6

    1.6 Theory of atmospheric corrosion 6

    1.7 Corrosion rate estimation 8

    1.8 Galvanized steel 9

    1.9 Stability diagram of zinc in water 10

    1.10 Literature survey 11

    1.11 Objectives 14

2. Experimental Methods 15

    2.1 Preparation of sample 15

    2.2 Set up of wet-dry cyclic chamber 15

    2.3 Corrosion test 15

    2.4 Measurement of corrosion potential 16

    2.5 Weight loss measurements 16

    2.6 Potentiodynamic polarization 17

    2.7 Surface characterization 17

3. Results and Discussion 18

    3.1 Weight loss with wet-dry cycle 18

    3.2 Corrosion rate from weight loss 19

3.3 Corrosion potential variation 20

3.4 Surface observation 21

3.5 Potentiodynamic polarization 24

Conclusion ` 29

References 31

CHAPTER I

1. Introduction

1.1 Concept of Corrosion

The word corrosion is derived from the latin word “corrosus” which means eaten away or consumed by degrees; an unpleasant word for an unpleasant process [1]. Corrosion is known commonly as rust, an undesirable phenomena which destroys the luster and beauty of objects and shortens their life. Corrosion can be defined as the destruction and unintentional attack of a material by reaction with its environment. As demanded by the thermodynamic principle, corrosion returns the metal to its combined state in chemical compounds that are similar to the mineral from which the metals were extracted. Up to the 1960s, the term corrosion was restricted only to metals and their alloys and it did not incorporate ceramics, polymers, composites and semiconductors in its regime. The term corrosion now encompasses all types of natural and man-made materials including biomaterials and nanomaterials, and it is not confined to metals and alloys alone. The scope of corrosion is consistent with the revolutionary changes in materials development witnessed in recent years. Considerable progress towards the modern understanding of corrosion was made by the contributions of Evans [1], Uhlig [2] and Fontana [3].

Corrosion is a potent force which destroys economy, depletes resources and causes costly and untimely failures of plants, equipment and components. The economic cost of corrosion is very high. It has been estimated that approximately 3-4 % of the Gross National Products (GNP) of an industrialized nation is spent on corrosion prevention, maintenance or replacement of products lost or contaminated as a result of corrosion reaction. Moreover, it is assumed that about 40 % of this GNP loss can be avoided by improving corrosion properties of engineering materials. For example, the US is losing more than 276 billion dollars [4]. The petroleum, chemical, petrochemical, construction, manufacturing, pulp and paper and transportation (railroad, automotive and aerospace) industries are the largest contributors to corrosion expenditure.

Although corrosion is inevitable, its cost could be reduced if proper corrosion management system is used. Therefore, knowledge of corrosion is important to minimize the loss. Understanding the fundamentals of corrosion is necessary not only for identifying corrosion mechanisms, but also for preventing corrosion by appropriate corrosion protection means and for predicting the corrosion behavior of metallic materials in service conditions. Understanding the mechanisms of corrosion is the key to the development of a knowledge-based design of corrosion resistant alloys and to the prediction of the long-term behavior of metallic materials in corrosive environments.

In Nepal, there is not so much basic research on the corrosion of materials used in infrastructures such as Roofing, GI pipe, and automobiles [5,6]. In addition, there is no data on the atmospheric environment and its effect on the corrosion of common used infrastructural materials. Therefore, the research on corrosion of infrastructural materials is required.

1.2 Corrosive Environment

Corrosion cannot be defined without a reference to environment. All environments are corrosive to some degree; it may only be slow or fast. Reaction of metals with dry air or oxygen is considered as a chemical corrosion. High temperature oxidation of metals and tarnishing of metals like copper, silver etc. fall in this category. Of late this is also considered to be an electrochemical process with the diffusion of oxygen (inwards) and metal ions (outwards) through the oxide layer, the electromotive force at metal-oxide interface being the driving force. Electrochemical corrosion occurs in the presence of electrolyte. The reaction is considered to take place at the metal-solution interface with the creation of local cathodic and anodic sides on the metal surface. According to the thickness of electrolyte layer present on the corroding surface corrosion has been classified as atmospheric and aqueous corrosions [7].

1.3 Atmospheric Corrosion

Atmospheric corrosion can be defined as the corrosion of materials exposed to air and its pollutants, rather than immersed in a liquid. It is a complex process whereby metals deteriorate and degrade in the dynamic atmosphere as a result of electrochemical and chemical process taking place on their surfaces. It proceeds under extremely thin, often invisible electrolyte film resulting from the deposition of atmospheric particles and adsorption and condensation of moisture on the surface of metal. A change in the thickness of the electrolyte layer due to daily wet-dry cycles affects a number of phenomenon taking place on the surface, for example, the mass transport of dissolved oxygen, accumulation of corrosion products, and the hydration of dissolved metal ions.

Tamashov [7] has put forward a model to better understand the atmospheric corrosion process according to the thickness of the electrolyte layer on the metal surface. According to this model atmospheric corrosion can be classified into different categories as shown in Fig.1.

1. Dry atmospheric corrosion, when electrolyte thickness is less than 10 nm.
2. Most atmospheric corrosion, when the electrolyte layer thickness is between 10 nm and 1 um.
3. Wet corrosion, when the electrolyte layer thickness is between 1 um and 1mm.
4. Complete immersion, when the electrolyte layer thickness is greater than 1mm.

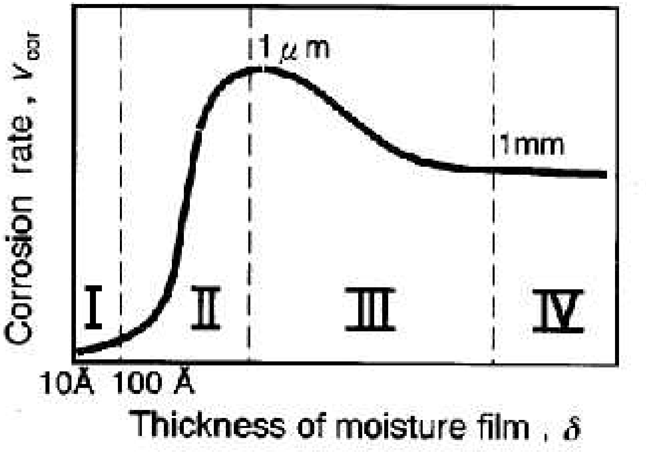

Figure 1. Dependence of the corrosion rate on the water layer thickness (schematic after Tomachov [7]

According to this model maximum corrosion rate is achieved in transition from moist (anodic control) to wet corrosion (cathodic control). The water layer present at this transition has been reported to be as thick as 1 μm. Therefore, atmospheric corrosion can be classified into dry, damp, and wet types according to the thickness of electrolyte layer on the surface of corroding material.

Atmospheric corrosion is reported to account for more failures in terms of cost and tonnage than any other factor. General uniform attack is the normal mode of atmospheric corrosion. Atmospheric corrosion is the most prevalent type of corrosion of zinc and galvanized steel owing to extensive outdoor applications.

1.4 Factors for atmospheric corrosion

Atmospheres in different geographical locations vary greatly with respect to solar radiation, temperature, moisture, wind, air constituents, and air pollutants. Atmospheric corrosion of a metal or alloy is affected by many factors [7-9], particularly those affecting surface wetness and precipitation of pollutants [10, 11].

The time period over which a surface remains wet is called time of wetness (TOW). The duration and form of wetness are important in determining the corrosion behavior of materials as it directly relates to the electrochemical corrosion processes. The TOW depends on the position and orientation of the sample. For the same time of wetness, rain could cause more corrosion of zinc than dew [11]. Temperature and relative humidity plays important role in controlling the water content of air. The amount of water in air increases with the increase of temperature and relative humidity. At a relative humidity of 100 %, water will condense in the form of dew which depends on the substrate temperature. Surface contaminants and corrosion products affect the relative humidity for condensation. It has been calculated that the relative humidity for condensation decreases from 98 % to 50 % as pore radii of porous corrosion products decreases from 360 to 15 Å [7].

The relative humidity at which a substance begins to absorb moisture from the atmosphere is called critical relative humidity (CRH). Below the CRH, a substance does not absorb atmospheric moisture. The primary value of the critical relative humidity denotes that humidity below which no corrosion of the metal in question takes place. However, it is important to know whether this refers to a clean metal surface or one covered with corrosion products. In the latter case a secondary critical humidity is usually found at which the rate of corrosion increases markedly [12].

The primary critical RH for uncorroded metal surfaces seems to be virtually the same for all metals, but the secondary values vary quite widely. The type of cations of a salt affect its CRH, for example, Sulfate of sodium, magnesium and ammonium has the CRC of 82 %, 87 % and 79 %, respectively [12]. Therefore, its corrosiveness should depend on the relative humidity.

Rain has an effect of not only wetting the surface of an exposed metal but also washing away pollutants and corrosion products. In some cases, the rain can be polluted (e.g., acid rain), which increases its corrosiveness. Moisture, in the form of rain or dew, on metal surface will evaporate under the drying effect of temperature, radiation, or wind, thus causing an exposed metal surface to continuing undergo cycles of wetting and drying. The drying solidified the corrosion products and pollutants on the surface of a metal. The duration of wetting and drying as well as the frequency of the cycles has a significant effect on the morphology and compactness of corrosion products [12].

Pollutants or other atmospheric contaminants increase atmospheric corrosion by enhancing the electrolytic properties and stability of water films that condense from the atmosphere. The major air pollutants are sulfur dioxide, hydrogen sulfide, oxides of nitrogen, aerosols, and metal ions. Near the seacoast, the air is laden with sea salts, particularly NaCl. In industrial area, appreciable amount of SO_2 and lesser amount of H_2S, NH_3, NO_2, and other suspended salts are encountered [7]. The type and concentration of pollutant may vary from location to location with the form of water precipitation.

Sulfur dioxide forms sulfuric acid when dissolved in the surface film and accelerates the corrosion rate.

$$SO_2 + O_2 + 2e^- \rightarrow SO_4^{2-}$$

The adsorption of SO_2 on the metal surface increases with increase relative humidity. It has been observed that surface adsorption on zinc is somewhat lower than that on iron, but higher than that on copper and aluminum [13]. In addition, the types of cations of sulfate have been found to affect the corrosion rate of such materials [14].

The magnitude of corrosion would depend upon the sensitivity of a particular metal or alloy to a specific environment. Therefore, predictability of atmospheric corrosion requires a complete understanding of the corrosion process and interdependence of the contributing parameters.

1.5 Atmospheric Environments

The atmospheric environments can be classified into four basic types or combinations of these Viz. rural, urban, industrial and marine (Table 1) [15].

Rural atmosphere is relatively least corrosive with principal corrodents, moisture, oxygen, and carbon dioxide. The urban atmosphere consists of area near urban centers where the major pollutants present are SO_x and NO_x coming mostly from vehicular exhaust and domestic fuel emission. The industrial atmosphere consists of area where there are many industrial activities and factories, processing and or power plants present. The major pollutants present are sulfur oxides, hydrogen sulfide, chlorides, phosphates, and nitrates. The marine atmosphere consists of area near the sea. The major pollutant is air born chloride. The environment in Kathmandu valley is a combination of urban and industrial type with major corrodents SO_x, NO_x and metal ions.

Table 1. Types of atmosphere according to corrosivity of the environment [15]

Types of atmosphere	Major pollutants
Rural	CO_2, Dust, Moisture
Urban	SO_x, NO_x
Industrial	SO_x, NO_x, H_2S, Cl^-, PO_4^{2-}
Marine	Cl^-

1.6 Theory of Atmospheric Corrosion

Atmospheric corrosion like aqueous corrosion occurs by electrochemical process. Therefore, presence of electrolyte layer is very crucial for it. In atmosphere, the chemical in the environment and humidity acts as an electrolyte which is generally present in very thin layers. Some parts of the metal surface act as anode and rest act as cathode. Oxidation of anodic part takes place and it results in corrosion at anode, while reduction takes place at cathode. The generalized anodic reaction that corresponds to the rate-determining step of atmospheric corrosion is shown below:

$$M \rightarrow M^{n+} + ne^{-}$$

As the corrosion proceeds, the corrosion product is formed on the surface of the metal between anode and cathode. The critical humidity level changes with the formation of rust and the presence of atmospheric pollutants. The overall rate of the anodic metal dissolution process depends on the type of corrosion products formed, the solubility of corrosion products in the surface electrolyte, and the formation of passive films.

It should be noted that corrosive contaminant concentrations can reach relatively high values in the thin electrolyte films, especially under conditions of alternate wetting and drying. Oxygen from the atmosphere is also readily supplied to the electrolyte under thin-film corrosion conditions. The nature of cathodic reaction depends on the pH of the solution and presence or absence of air. If it is assumed that the surface electrolyte is extremely thin layers and is neutral or even slightly acidic (above 4), then the reduction of oxygen takes places:

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$$

Two reaction steps may actually be involved, with hydrogen peroxide as an intermediate, in accordance with (Eqs) [15].

$$O_2 + 2H_2O + 2e^{-} \rightarrow H_2O_2 + 2OH^{-}$$

$$H_2O_2 + 2e^{-} \rightarrow 2OH^{-}$$

On the other hand, in acidic solution, the main cathodic reaction is the reduction of hydrogen (below pH4):

$$2H^{+} + 2e^{-} \rightarrow H_2$$

In the case of corrosion occurring under wet-dry cycle, the kinetic modeling rather than equilibrium assessments appears to be appropriate. A framework for treating atmospheric corrosion phenomena on a theoretical basis, based on six different regimes, has been presented by Graedel [16]. The regimes in this so called GILDES-type model are the gaseous region (G), the gas-to-liquid interface (I), the surface liquid (L), the deposition layer (D), the electrodic layer (E), and the corroding solid (S).

1.7 Corrosion Rate Estimation

Measurement of corrosion rate is essential in assessing the life time of a material in a particular environment. There are various ways to estimate the corrosion rate. Natural weathering tests done outdoors [17-21] is the simplest of all corrosion rate monitoring techniques as it provides corrosion rate in real environment over the extended period of service life. It involves exposing a specimen of material to the corrosive environment for a given period of time, and then removing the specimen for determining the weight lost by corrosion. Corrosion rate in mm.y^{-1} is then calculated using the relationship [3]:

$$\text{Corrosion rate } (\text{mm.y}^{-1}) = \frac{87600 \text{ x weight loss (g)}}{\text{Area } (\text{cm}^2) \text{ x time (hrs) x Density } (\text{g cm}^{-3})}$$

Natural weathering tests, although very necessary, require a long time to complete. Hence it has been complemented by accelerated corrosion test methods, like salt spray test and combined cyclic wet-dry corrosion test [22, 23]. Wet-dry cyclic test provides a more realistic simulation of the atmospheric environment [24]. The corrosion rate using accelerated test is also measured by gravimetric method using the weight loss of the sample over a specific time period.

The conventional methods are very valuable in the study of atmospheric corrosion, however, they are limited in that they only permit average corrosion rates to be obtained and they provide no due to the instantaneous changes that occurs during cycling wetting and drying of the metal surface. From the average value of the corrosion rate, it is impossible to elucidate the corrosion mechanism. This problem can be resolved by applying electrochemical methods such as Tafel extrapolation method [25, 26], the polarization resistance method [25, 27], and various non-steady state methods, including the AC impedance method [25, 28-30].

In Tafel extrapolation method, the polarization curves for the anodic and cathodic reactions are obtained by applying potentials of few hundreds mV well away from the corrosion potential and recording the current. Plotting the logarithms of current (log *I) vs.* potential and extrapolating the currents in the two Tafel regions gives the corrosion potential (E_{corr}) and the corrosion current (i_{corr}).

On the other hand, in polarization resistance method or linear polarization method, the polarization resistance (R_p) of a corroding metal is estimated using Ohm's Law as the slope of a potential (E) *vs.* current density (log *i)* plot at the corrosion potential (E_{corr}). By measuring this slope, the rate of corrosion can be measured using the Stern-Geary relationship [30]:

$$I_{corr} = b_a b_c / R_p \, 2.3o3 \, (b_a + b_c)$$

Where, b_a and b_c are anodic and cathodic Tafel slopes, respectively obtained at around ±20 mV of the corrosion potential.

The advantage of these electrochemical methods is that they permit in-situ measurement of corrosion rate. Since corrosion reaction is electrochemical in nature, electrochemical measurement of corrosion rate in combination with the corrosion potential measurements provide valuable information on the corrosion mechanism [29].

1.8. Galvanized Steel

Galvanized steel is steel coated by zinc layer in order to protect it from corrosion by acting as a sacrificial anode. This process of coating by zing is called galvanization. French Chemist Paul Lacques Malouin in 1742 was the first to describe this process of coating iron by dipping it in molten zinc. However, the French Chemist Stanislas Sorel was the first to obtain a patent in this process in 1836. Hot-dip galvanization is a common process in which steel parts are submerged in a bath of molten zinc bath at about 450-480°C. The process of hot-dip galvanizing results in a metallurgical bond between zinc and steel with a series of distinct iron-zinc alloys layer formation at the steel and zinc boundary and outer layer of almost pure zinc [17].

Galvanized steels have found wide applications in various industries such as telecommunication industry, power transmission lines, thermal power plant, automotive industry, roofing, siding and fencing. The uses of galvanized steels in a variety of applications are increasing day by day due to the scarcity of lumber. The sacrificial zinc coating protects the iron and steel by three protective abilities:

- Original barrier action of coating layer.
- Secondary barrier action of corrosion product layer.
- Galvanic section of coating layer as sacrificial anode

The engineering quality of the coating depends on the physical and chemical nature of the Zn-Fe intermetallic layers formed. The thickness and composition of the alloy layers further depends on whether they are produced in a batch or in a continuous process [17].

1.9. Stability Diagram of Zinc in Water

Zinc is divalent in its all compounds. Compounds of Zn(I) do not exist naturally. Figure 2 shows the Pourbaix diagram of zinc in water [32]. The lines labeled with the letters a and b represent, respectively, the equilibrium conditions of the reduction of water to gaseous hydrogen and of the oxidation of water to gaseous oxygen, when the partial pressure of hydrogen and oxygen is 1 atm at 25°C. As it is evident from Fig. 2, the stable region of zinc is below line a, and hence it is thermodynamically unstable in water and aqueous solutions and tends to dissolve with the evolution of hydrogen gas over the whole pH range.

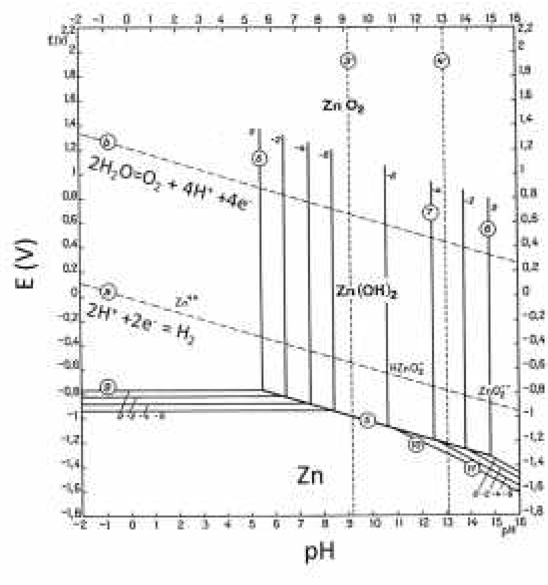

Figure 2. Potential-pH equilibrium diagram for the zinc-water system at 25°C [32]

In solutions of pH between approximately 8.5 and 11, zinc can be covered with a hydroxide film, which has the effect of inhibiting zinc dissolution. The stability of oxide and hydroxides of zinc in aqueous solution depends on pH. As shown in Fig. 3 zinc hydroxides are amphoteric. They dissolve in acid solutions to give zincic ions Zn^{2+} and in alkaline solutions to give bizincate or zincate ions $HZnO_2^-$ [32]. The solubility varies slightly with the type of hydroxides and oxides. At room temperature, ε-$Zn(OH)_2$ is the most stable compound whereas amorphous $Zn(OH)_2$ is the most unstable [33].

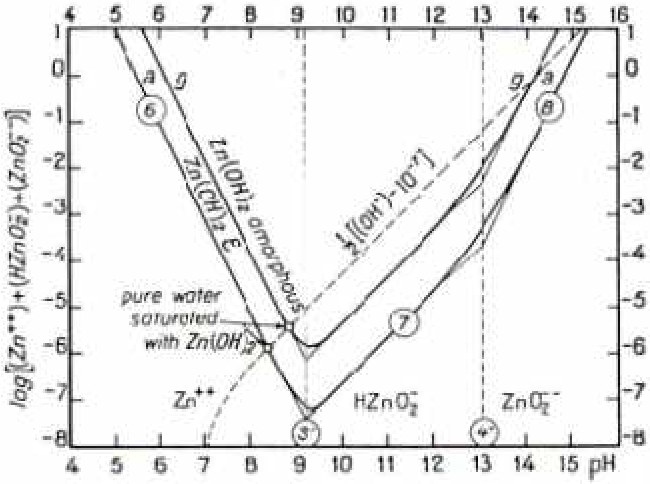

Figure 3. Influence of pH on the solubility of the zinc hydroxides in water at 25°C [33]

1.10 Literature Survey

The corrosion behaviour of galvanized steel in a wide variety of environments has been thoroughly investigated by Mardar and Goodwin [34, 35]. In areas where SO_2 is present in any appreciable quantity galvanized surface will be attacked. Particulate species in the atmospheres can accelerate corrosion of galvanized steel by increasing the conductivity of the surface layer after dissolution of soluble ions from the particulate. Lobing [36] has been reported on the effect of particles of $(NH_4)_2SO_4$ air-water-vapor mixtures on the corrosion of galvanized steel. Helwig [37] has studied the premature darkening of the zinc surface in atmospheric environments. Long exposure test of galvanized steel has shown to develop a film of basic zinc carbonate, $2ZnCO_3.3Zn(OH)_2$, [22, 38-40]. This film tends to inhibit further Zn corrosion; however, there are environmental conditions in which film removal processes compete with film formation.

Spence et al. [24] developed a model for predicting the corrosion of galvanized steel structures based on two competing mechanisms: the formation and dissolution of the basic zinc carbonate film that forms on zinc surfaces. According to Anderson [41] the atmospheric corrosion of zinc is dependent on the frequency of rain and dew, the acidity of condensates on the surface, and the rapidity of drying.

Gradeal [42] has done a detail study on the physical and chemical information on zinc/galvanized steel corrosion and information like layer formation, evolution, morphology, and chemical makeup in atmospheric environment are available. It is generally agreed that upon initial exposure zinc rapidly forms a thin film of zinc hydroxide, which under continued exposure transformed into various atmospheric products. Cramer et al. [25] have shown that the rates of zinc corrosion do not decrease with time, but rather appear to be responsive to changes in the local concentrations of corrodents. Legault and Pearson [43] have found that the surface facing upward tends to corrode much more rapidly than surface that face groundward. The corrosion rate on the skyward samples is linear with time, while the groundward corrosion is parabolic in form.

The influence of salt deposits on the atmospheric corrosion of zinc was studied in the laboratory by Lindstroem [44]. Four chloride-containing salts, NaCl, NH4Cl, $ZnCl_2$, and $MgCl_2$, and four sulfate-containing salts, Na_2SO_4 , $(NH_4)_2SO_4$, $ZnSO_4$, and $MgSO_4$, were investigated. The corrosion of zinc was directly correlated with the amount of sodium ion and did not depend on the presence of sulfate and chloride ions. The difference between sodium, and magnesium and zinc salts was explained by inhibition of cathodic reaction in the presence of Zn^{2+} and Mg^{2+}. These cations form less soluble salts and tend to precipitate in a form of hydroxide, oxide, or hydroxy salts in the cathodic areas, which are consequently blocked and unable to act as cathodes. It was also found that the corrosion rate of zinc in the atmosphere was related to the amount of sodium present on the surface, rather than to the amount of chloride or sulphate.

Prosek et al. [14] in a recent study has reported on the effect of sodium, calcium, and magnesium chlorides deposites on zinc surface under atmospheric conditions. The cations were found to strongly affect the corrosion rate of zinc. The corrosivity of cations of chloride salts for zinc increased in order of $Mg^{2+} < Ca^{2+} < Na^{+}$. It was confirmed that the sodium ion favors the formation of hydrozincite while magnesium and calcium ion favor the formation of simonkolleite by lowering the pH due to hydrolysis of these metal ions.

1.11 Objectives

The corrosion of galvanized steel is a serious problem due to its tonnage of usage. In Nepal there is a limited research in corrosion field. For atmospheric corrosion, type and amount of salts deposited on the surface of the materials in combination with the relative humidity play very important roles. Above CRH, the surface absorption of water vapor by the salt results in corrosion. It is well recognized that the anions present in the electrolyte influence the mechanism of atmospheric corrosion directly, *i.e.*, by taking part in the anodic reaction [15]. However, the influence of cations on the atmospheric corrosion has been disregarded and the corrosion rate of metals is usually associated only with the amount of chloride and sulphate on the surface. The effect of cations on the solubility of the salt, the ability to attract water vapour to form a solution, hydrolysis and pH of the surface solution, and the ability to form insoluble corrosion products on the metal surface are generally considered as less important.

Therefore, this study is aimed to study the effect of cations namely ammonium, magnesium and sodium on the corrosion behavior of galvanized steel sheet of Nepal under simulated wet-dry cyclic corrosion environment. All these cations were sued as sulfate salts. The corrosion performance was evaluated on the basis of weight loss measurement, corrosion potential changes, changes in Tafel slopes and surface appearance with time.

\

CHAPTER II

2. Experimental

2.1 Preparation of Sample

Commercial galvanized steel sheets of Nepal were used in this study. The coating thickness was not known. Samples of dimension 2cm x 2cm x 0.1cm were cut from the sheet of commercial sample and degreased with acetone and then distilled water before using them for corrosion test. The back side of each sample was first painted with nail polish and then covered with insulating tape so that only surface facing upward was corroded. To estimate the corrosion rate by weight loss method, several samples were exposed and taken out after a fixed time interval of 1 day (1d), 3 days (3d), 7 days (7d) and 14 days (14d). These samples were further used for potentiodynamic polarization and surface observation.

2.2 Set Up of Wet Dry Cyclic Chamber

Corrosion test was performed in a simulated wet-dry cyclic test in laboratory. A wet-dry cyclic chamber was prepared by taking two plastic boxes of similar dimensions. In one box, small holes were uniformly made at the basement along the lines parallel to each other. Box with the holes at the bottom was inserted inside another box keeping the gap of 5 cm between the bottoms of these two boxes and they were fixed with the glue. The joining of these two boxes was made air tight with plastic tape. Distilled water was filled up to 4 cm height in the lower chamber of the two boxes. When the upper box was tightly closed, relative humidity could reach up to 90%. This simulates the night time condition where due to the dew formation or condensation relative humidity reaches up to 90 % or even higher. Day like condition was maintained for the dryness of the sample by removing the lid of the upper box for a fixed interval of time of 6 hours every day. Therefore, one wet-dry cycle constituted 18 hours wet and 6 hours dry period in a day. The corrosion test was performed for 14 days comprising 14 wet-dry cycles.

2.3 Corrosion Test

In this study, corrosion test was performed in three different salts solutions. The salt solutions of $(NH_4)_2SO_4$, $MgSO_4$ and Na_2SO_4 were prepared by dissolving appropriate amount respective salts in double distilled water to prepare 0.5 M solution each. 50 μl/cm^2 of each test solution was placed on the sample surface and it was dried by placing outdoor. After the salt solution was dried up, about 25 μl of distilled water was put on the sample surface and the salt was homogenously distributed on the sample surface. After this the sample was placed inside the wet-dry test chamber and it was covered for 18 hours. This comprises the wet period. The sample was dried for 6 hours by taking out the lid from the upper plastic box and this sequence was repeated for 14 days.

2.4 Measurement of Corrosion Potential

The corrosion potential was measured in all the three solutions. For the measurement of corrosion potential, sample was connected with a copper lead wire and the exposed part of the sample was covered by epoxy resin. Corrosion potential was measured for one hour each day. For this, samples were taken out and immersed in respective solution as in-situ measurements of the corrosion potential was not possible due to presence of very thin layer of electrolyte on the sample surface. This gives representative corrosion potential of the samples in the three test solutions.

2.5 Weight Loss Measurements

For the weight loss measurement, several samples were taken out of the wet-dry cyclic test chamber and washed with distilled water before it was stored. The corrosion product of the sample was removed by immersing the sample into the saturated ammonium acetate solution and ultrasonicating it for 10 min until the sample was cleaned followed by light scrub [15[17].These samples were washed with distilled water, dried and weight was noted until a constant weight was obtained. Then the weight loss was calculated from the difference of initial weight and weight of the sample after removal of corrosion product. The corrosion rate in mm.y^{-1} was determined by using the relation given in page 8.

The effect of cations on the corrosion rate was analyzed by making a plot of corrosion rate againstexposure time in all cases.

2.6 Potentiodynamic Polarization

The electrochemical behavior of the samples was studied by doing potentiodynamic polarizations in both anodic and cathodic directions. A Hokuto Denko potentiostat/galvanostat (HA 150) in combination with an AD/DA convertor (Contec, 8 channel, 16 bit) controlled by a personal computer was used. A Platinum wire was used as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. The polarization was measured from -1.6 V to anodic direction at the scan rate of 1mV/s and the data was collected at the interval of 2mV. The samples taken out from the corrosion test after 1d, 3d, 7d, and 14d together with as received sample were used for the polarizations measurements. From the polarization curves, anodic and cathodic Tafel slopes, the corrosion potentials, and corrosion currents were determined to evaluate the effect of cations on the corrosion behavior of the galvanized steel used in this study.

2.7 Surface Observation

Surface observation of corroding sample provides very useful information with regard to corrosivity of the solution. In this study, digital photographs of samples corroding in different test solutions were taken every day. Microscopic examination of the surface was carried out by using SEM (Hitachi US8000). For this, only samples after 14d exposure in wet-dry cyclic test were used.

CHAPTER III

3. Results and Discussion

3.1 Weight Loss with Wet-Dry Cycle

Figure 4 shows the plot of weight loss against time of the galvanized steel sample corroded in wet-dry cyclic conditions in $(NH_4)_2SO_4$, $MgSO_4$ and Na_2SO_4. The weight loss is the average value of two replicate samples of $4cm^2$ area. The sample corroded in $MgSO_4$ solution shows the least weight loss and the one corroded in $(NH_4)_2SO_4$ the highest weight loss. In all the cases, the weight loss did not change that much after 7th wet-dry cycles. The weight loss after 1st wet-dry cycle was highest in the case of $(NH_4)_2SO_4$ salt ca. 4 µg cm^{-2}, almost 4-5 times higher than in other two solutions. At the end of 14th wet-dry cycles the weight loss was 2.9 µg cm^{-2}, 0.5 µg cm^{-2} and 1.8 µg cm^{-2}, respectively in $(NH_4)_2SO_4$, $MgSO_4$ and Na_2SO_4 solutions. It is obvious from the weight loss data that the cations affect the corrosion of galvanized steel. The reasons for the difference in the weight loss will be discussed later in potentiodynamic polarization section.

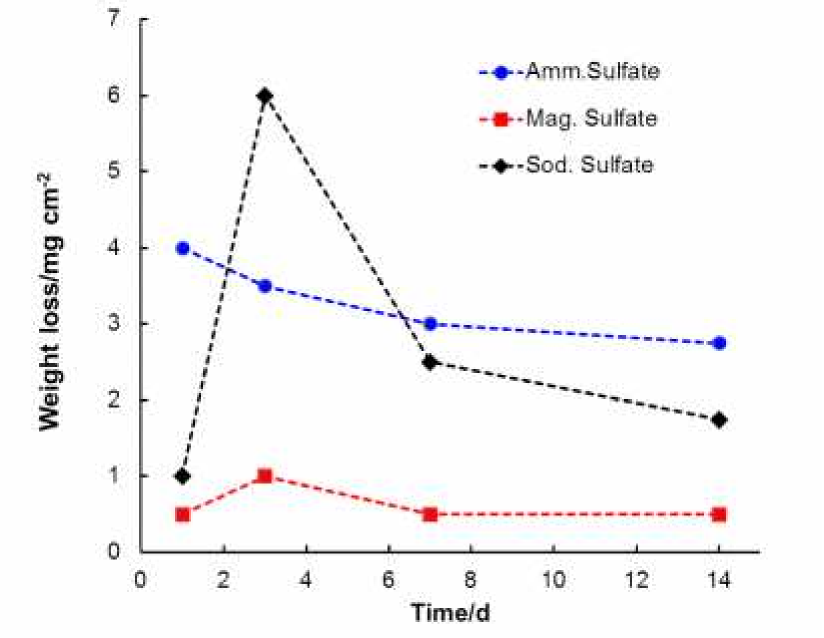

Figure 4. Change of weight loss vs. exposure time of galvanized steel corroded in wet-dry cyclic test consisting of deposited sulfate salts of ammonium, magnesium and sodium as a function of exposure time.

3.2 Corrosion Rate from Weight Loss

The weight loss data in Fig.4 was used to estimate the corrosion rates in mm.y^{-1} of galvanized steel samples corroded in three different salt solutions and is shown in Fig. 5. The corrosion rate after 1st cycle exposure was about 2.0 mm.y^{-1}, 0.25 mm.y^{-1}, and 0.40 mm.y^{-1}, respectively in $(NH_4)_2SO_4$, $MgSO_4$ and Na_2SO_4 solutions. The corrosion rate in the case of ammonium ion was almost eight times higher compared to magnesium ion and about five times higher compared to sodium ion. With the progress of wet-dry cycle, the corrosion rate decreased except in the case of sodium ion where decreased was observed after 3rd cycle. At the end of 14th cycle, the corrosion rate was observed to be 0.1 mm.y^{-1}, 0.03 mm.y^{-1} and 0.06 mm.y^{-1}, respectively in $(NH_4)_2SO_4$, $MgSO_4$ and Na_2SO_4 solutions. From this data it can be concluded that the corrosivity of the three ions decreased in the order $NH_4^+ > Na^+ > Mg^{2+}$.

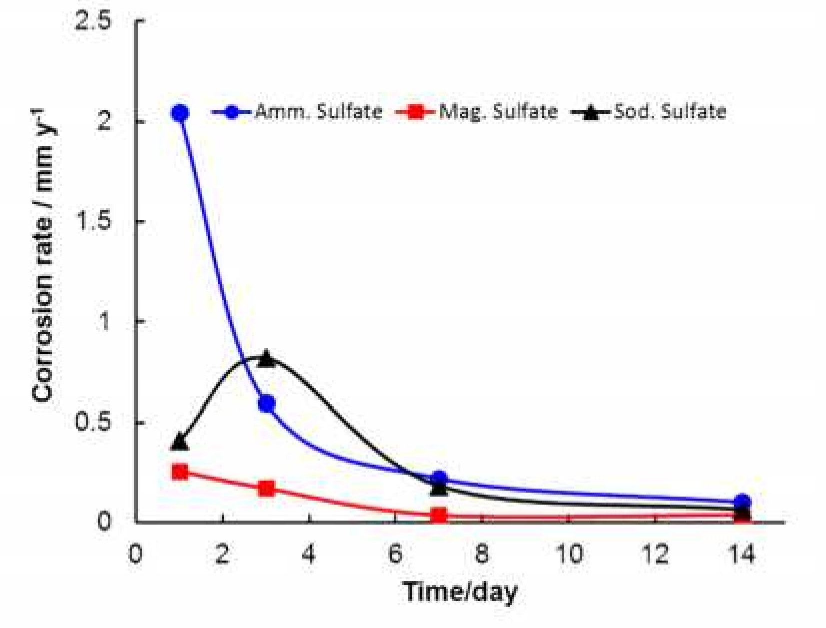

Figure 5. Corrosion rate in mm.y^{-1} of galvanized steel exposed in wet-dry cyclic test consisting of deposited sulfate salts of ammonium, magnesium and sodium.

Low initial corrosion rate of galvanized steel has been attributed to presence of air formed oxide. As the air formed oxide get dissolved therefore opening up the inner pure zinc layer the corrosion rate increases until the deposition of corrosion products acts as the barrier layer for the corrosive ions. Sanyal et al. [45] observed that sulfate of ammonium ion was less corrosive compared to sulfate of sodium at RH 80% and 40^0C. In contrast, Paterson et al. [46] concluded that sodium ion is more corrosive than ammonium ion due to low CRH value for salt of ammonium ion. Later, Lobing et al. [36] and Fedrizzi et al. [47] reported a high corrosion rate in ammonium sulfate solution and explained that ammonium ion take part in cathodic reaction and it helps the formation of less protective oxide film of zinc. In the present study, Tafel slopes will be analyzed to explain the difference in the corrosion rate due to cations of sulfate.

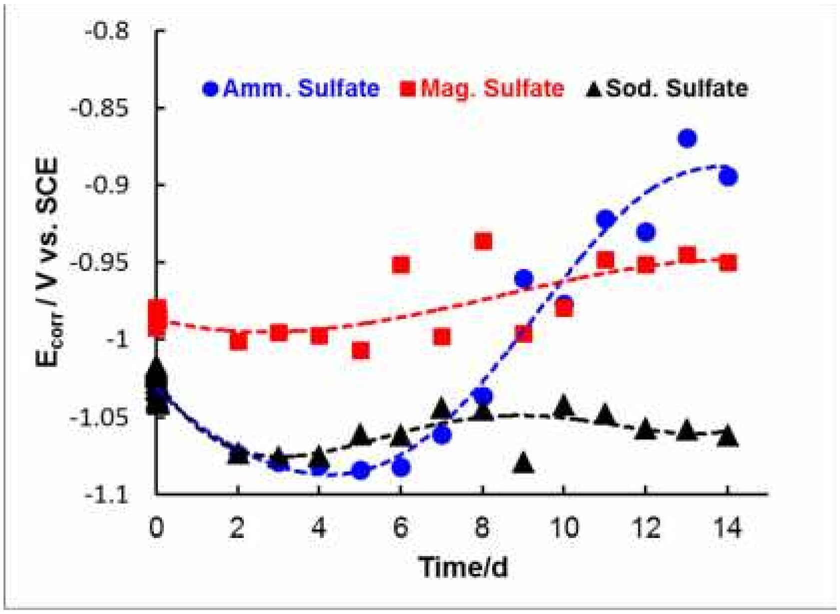

Figure 6. The Variation of corrosion potential of galvanized steel with time in sulfate salts of ammonium, magnesium and sodium.

3.3 Corrosion Potential Variation

Variation of corrosion potential with exposure time provides important electrochemical information regarding the surface state of corroding surface. Figure 6 shows the plot of E_{corr} of galvanized steel sample in sulfate solution of three different cations. The corrosion potential in the case of magnesium sulfate solution was about -980 mV vs. SCE just after immersion. The change of E_{corr} with time was not significant and it almost stayed at the same value throughout the corrosion test. This indicates that the corrosion was minimum and magnesium ion suppressed the corrosion of zinc. On the other hand, the Ecorr shifted to negative values till 3^{rd} cycles in both the ammonium and sodium sulfate.

The corrosion potential shifting to negative values in early stage of corrosion is attributed to corrosion of air formed oxide surface. As the air formed oxide corrodes and inner pure zinc layer started to get corroded the corrosion potential shifted to negative value. However, this is accompanied by the deposition of rust layer on the surface and therefore the corrosion potential gradually shifted to noble directions due to barrier effect of rust layer that polarizes the anodic reaction.

In the case of ammonium salt, the shift of Ecorr to noble value after 7th cycle was drastic and at the end of 14th cycles the corrosion potential about -870 mV which was nobler by about 150 to 200 mV compared to magnesium and sodium salt solutions. The observation of change of Ecorr with time indicates that the magnesium ion was least corrosive among the three cations.

3.4. Surface Observation

Figure 7a-c shows the digital photographs of samples taken at different exposure time in wet-dry cyclic test. The white precipitate shows the deposition of salt and the corrosion products. The samples corroded in magnesium sulfate solution did not show significant deposition of the corrosion products. In addition, no red rust was observed the end of 14th wet-dry cycle. This shows that there was little corrosion in this medium. On the other hand, severe corrosion was observed to occur in ammonium and sodium sulfate solutions. The amount of red rust was more in the case of ammonium salt. Therefore, nobler Ecorr in the case of ammonium salt can be explained. This appearance of red rust indicates that the corrosion of underlying steel or intermetallic Zn-Fe alloy layer takes place. It has been reported by Yadav et al. [48] that the corrosion rate of intermetallic layer is lower than both the zinc and iron. Therefore, it appears that the red rust was probably due to corrosion of intermetallic layer.

Figure 8a-c shows the SEM image of samples after 14 days exposure in respective solutions. The magnification of images is different due to technical problem. A highly porous corrosion product is seen in the sample corroded in ammonium and sodium sulfate solutions. In contrast, very compact and thin corrosion products layer could be observed in magnesium sulfate solution. This confirmed the weight loss, corrosion rate and Ecorr data obtained for magnesium sulfate solutions. The SEM image shows that corrosion products formed in ammonium sulfate solution was less solidified compared to the one in sodium sulfate solution. This indicates the formation of less protective rust layer in former case. It has been reported that ammonium ion inhibit the formation of stable oxide due to lowering of pH at anodic site and increasing of pH at cathodic site due to release of ammonia [36].

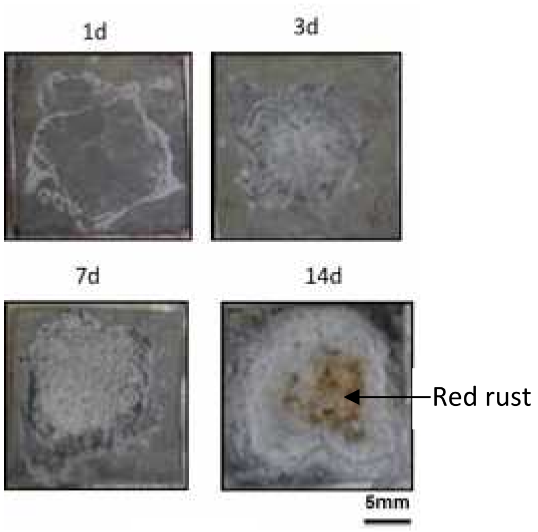

Fig.7a

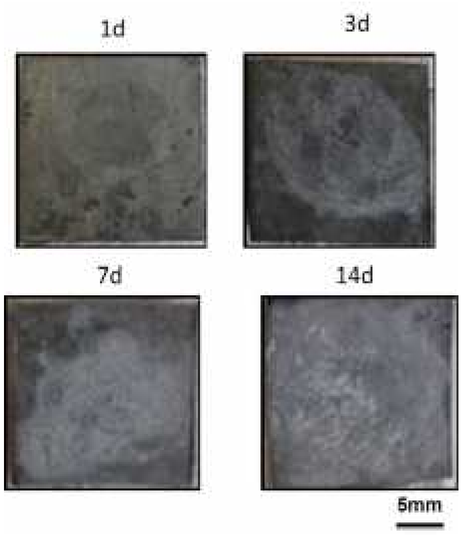

Fig.7b

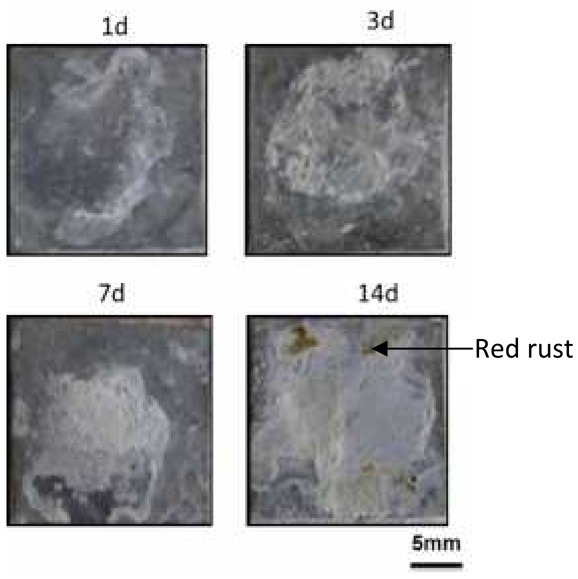

Fig.7c

Figure 7a-c. Photographs of corroded samples in the presence of (a) $(NH_4)_2SO_4$, (b) $MgSO_4$ and (c) Na_2SO_4 solutions

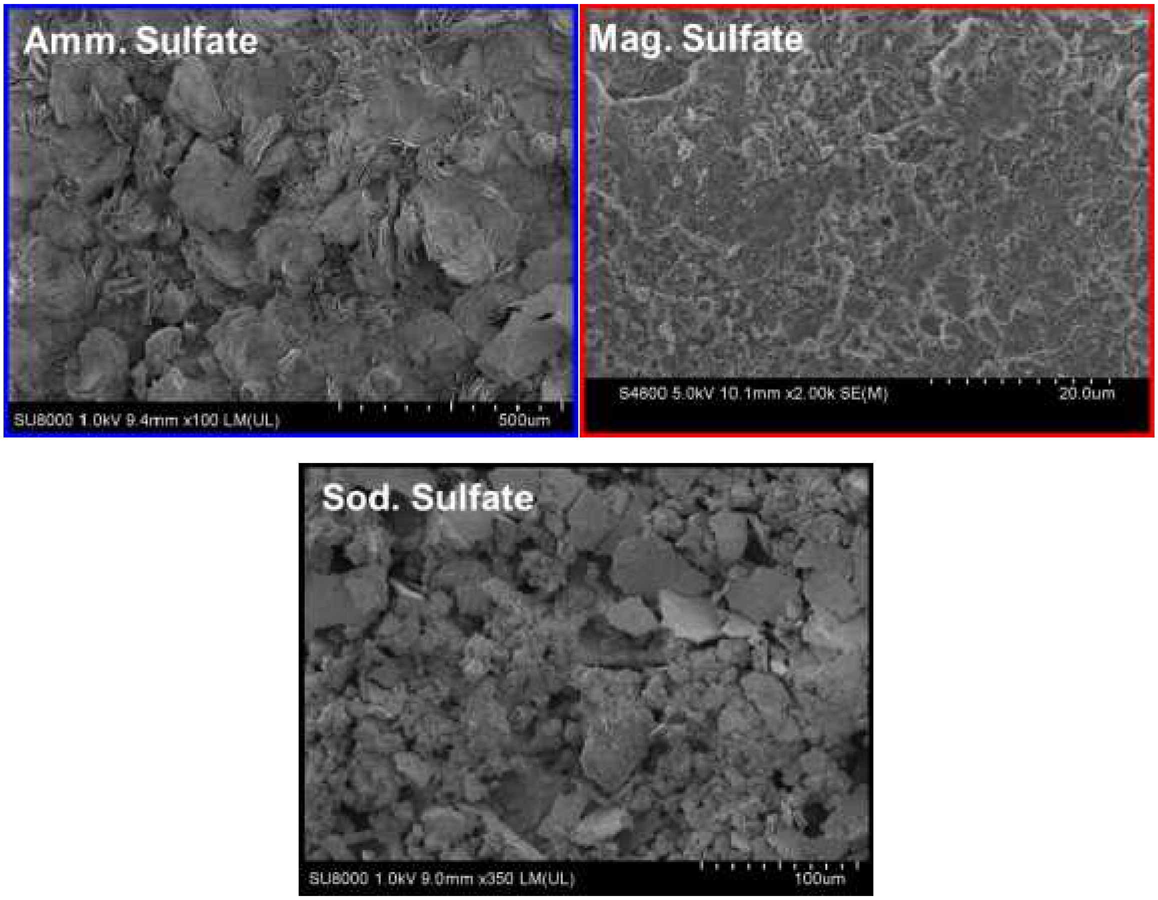

Figure 8. SEM images of samples corroded for 14 days in (a) $(NH_4)_2SO_4$, (b) $MgSO_4$ and (c) Na_2SO_4 solutions.

3.5 Potentiodynamic Polarization

The polarization behaviors of fresh as well corroded galvanized steel samples were recorded in all the three solutions. In all the cases, polarization was started from cathodic potential of about -1.6 V to anodic potential at a scan rate of 1 mV/s. The anodic potential limit was fixed at about 300 mV positive to E_{corr}. Figure 9 shows the potentiodynamic polarization curves of fresh galvanized steel samples in all the three solutions. The polarization was started after corrosion potential was stabilized in about 15-30 min after immersion of the samples.

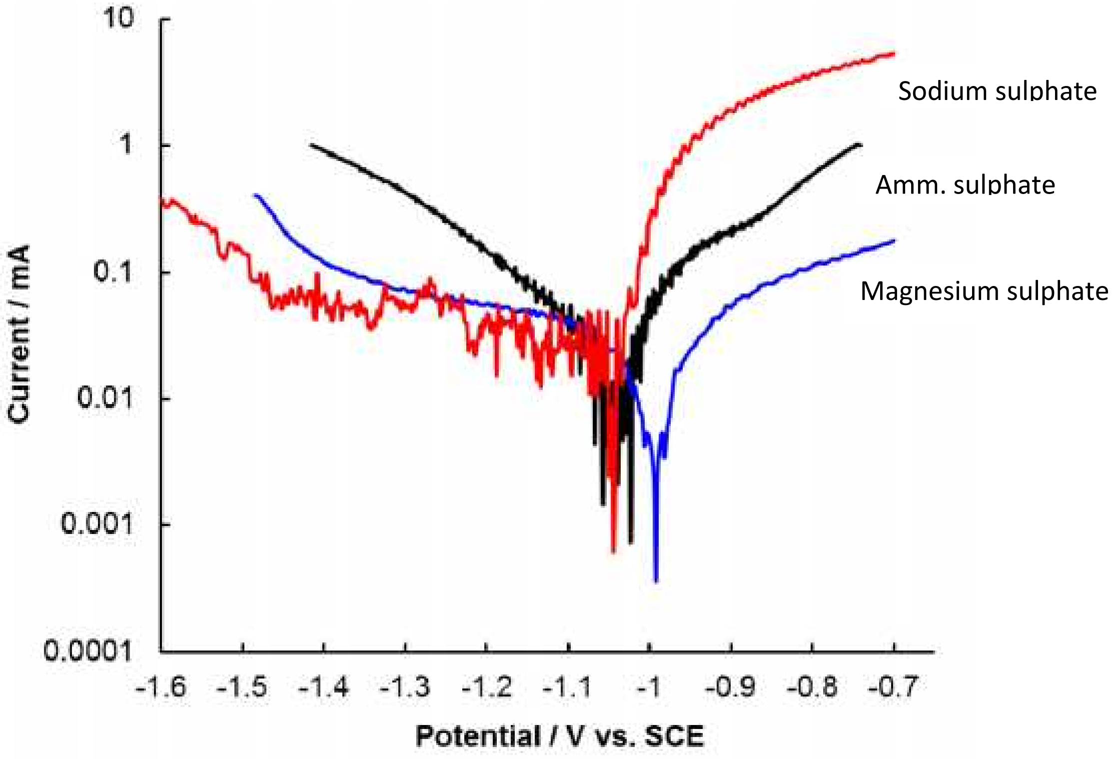

Figure 9. Potentiodynamic Polarization of fresh galvanized steel in 0.5 M solutions of $(NH_4)_2SO_4$, $MgSO_4$ and Na_2SO_4 solutions at the scan rate of 1 mV/s. The polarization was started from cathodic limit of -1.6 V towards anodic direction.

The corrosion potential in magnesium sulfate solution was shifted to noble value by about 100 mV compared to sodium and ammonium ion. Looking at the anodic current values, it was found that the anodic current was lowest in magnesium salt and highest in sodium salt. The anodic Tafel slopes in sodium and ammonium sulfate solutions were about 30 mV/decade which is the typical of galvanized coating [28]. In the case of magnesium salt, the Tafel slope was about 125 mV/decade. The higher Tafle slope showed the inhibition of anodic reaction my magnesium ion. It has been reported that divalent cations get precipitated in cathodic area where high pH exists due to oxygen reduction reaction [36]. The oxide and hydroxide of magnesium have low solubility and therefore form as protective layer.

The cathodic polarization curve shows the diffusion limiting current due to reduction of dissolved oxygen in the case of sodium and magnesium ions. The limiting current was about 35 $\mu A\ cm^{-2}$ which is the typical value obtained for oxygen reduction reaction [14]. In the case of ammonium ion, the cathodic polarization curve was activation control unlike in sodium and magnesium ion solution. The cathodic Tafel slope was estimated to be about 150 mV/decade, which is higher than the value observed for the reduction of hydrogen ion. Therefore, reduction of other species has to be considered together with the reduction of hydrogen ion.

Fedrizzi et al. [47] has considered the reduction of ammonium ion in two distinct path ways. In first case, a direct reduction of ammonium ion to ammonia and hydrogen molecule is postulated as given below:

$$NH_4^+ + e^- \rightarrow NH_3 + H^+$$
$$H^+ + H_3O^+ + e^- \rightarrow H_2 + H_20$$

Its also possible that ammonium ions loses its hydrogen ion and subsequently hydrogen ion is reduced to produce hydrogen molecule.

$$NH_4^+ + H_2O \rightarrow H_3O^+ + NH_3$$
$$2H_3O^+ + 2e^- \rightarrow H_2 + H_2O$$

Baugh et al. [49] has observed that the ammonium ion has the ability to inhibit oxide film formation by lowering the local pH at the zinc surface. Lobing et al. [36] has proposed that the formation of $[Zn(NH_3)_4]^{2+}$ in low pH areas that develop at the anodic sites and release of ammonia at cathode site having high pH. Therefore, the polarization curves of Fig. 9 explain the high corrosion rate in ammonium salt and low corrosion rate in magnesium salt.

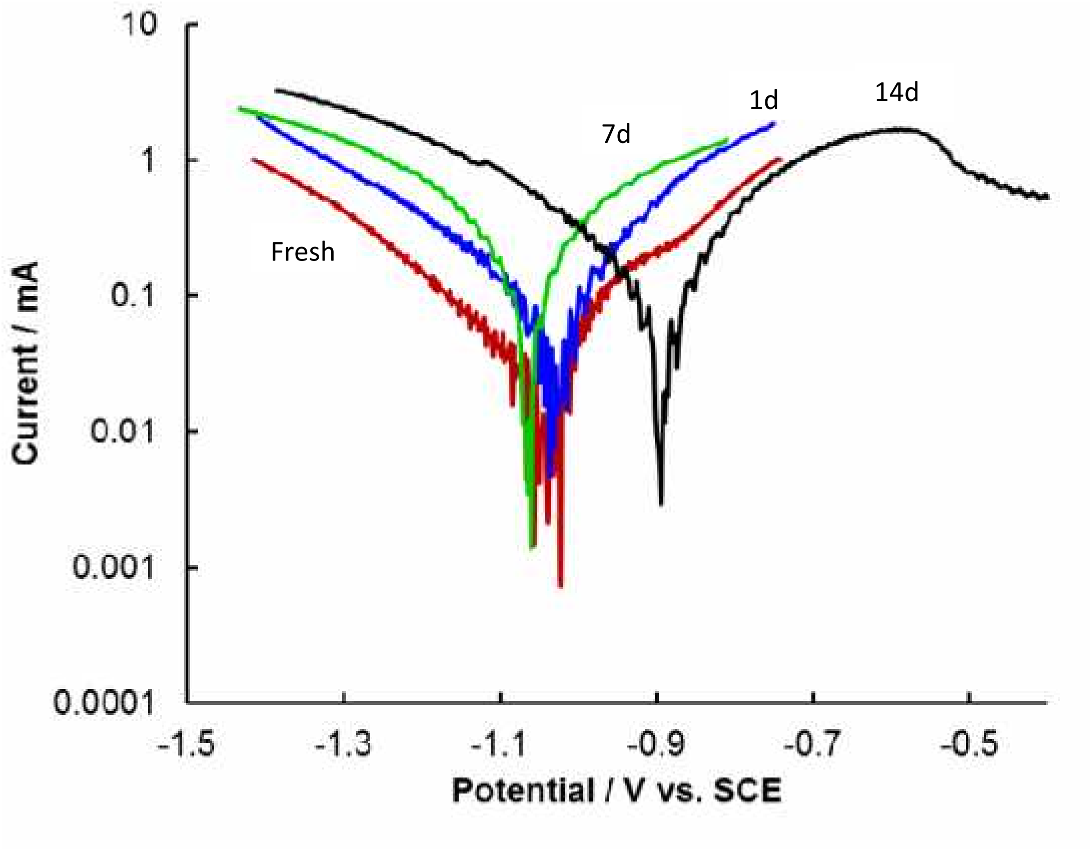

Figure 10a. Potentiodynamic Polarization of galvanized steel corroded in wet-dry cyclic test for 14 days in $(NH_4)_2SO_4$.

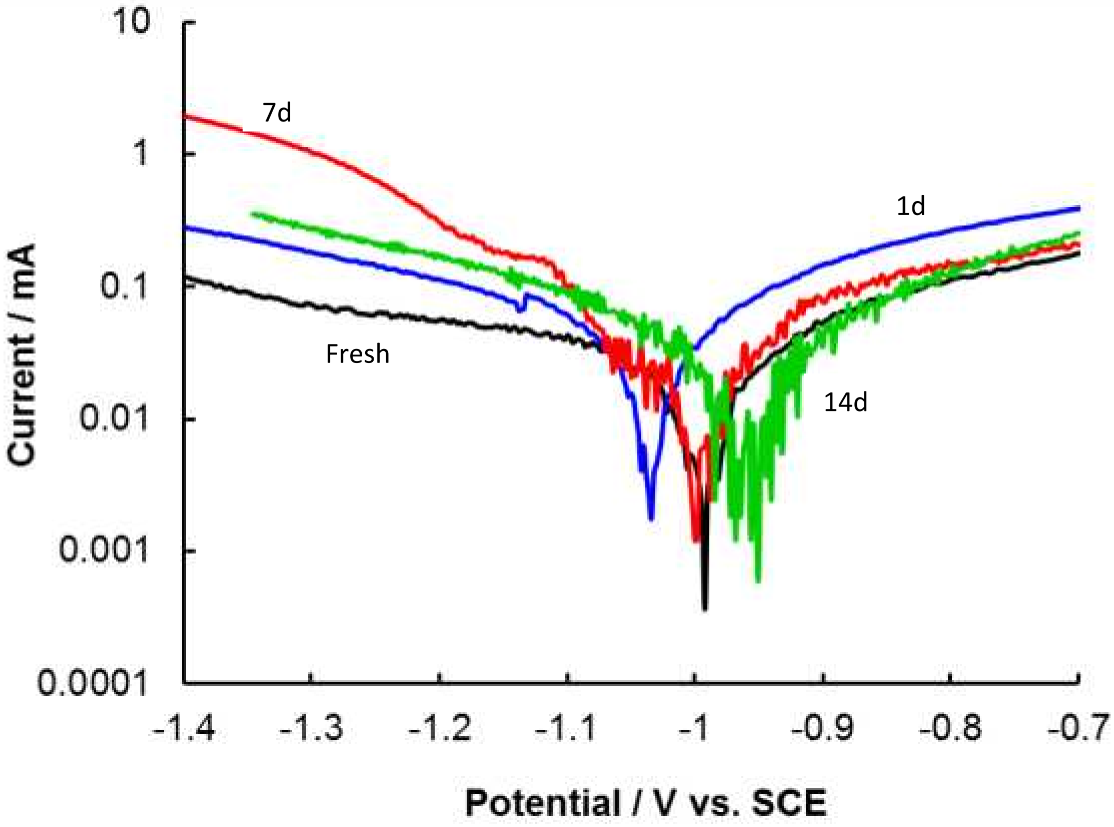

Figure 10b. Potentiodynamic Polarization of galvanized steel corroded in wet-dry cyclic test for 14 days in $MgSO_4$.

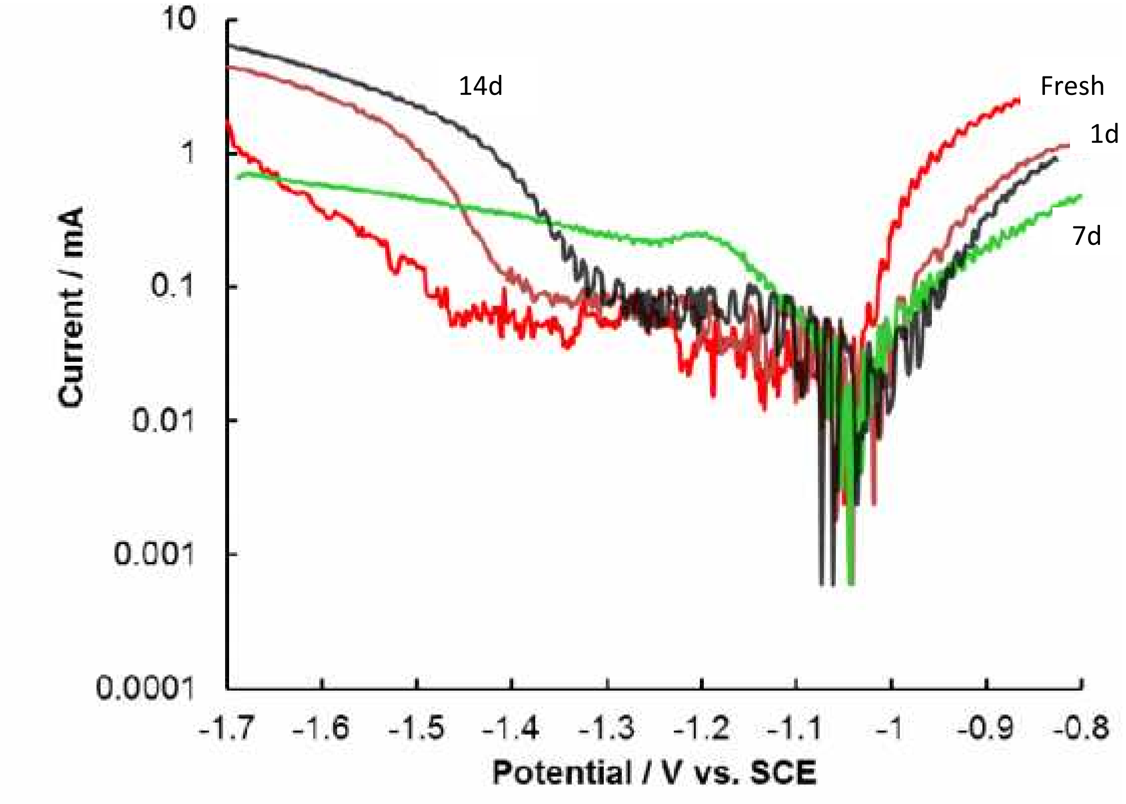

Figure 10c. Potentiodynamic Polarization of galvanized steel corroded in wet-dry cyclic test for 14 days in Na_2SO_4.

The effect of rust layer formation on the corrosion rate can be explained by considering the polarization curves of corroded samples in the three different solutions. Figure 10a-c shows the potentiodynamic polarization curves of samples corroded for 1d, 7d and 14d together with the fresh sample for comparing the nature of the curves. Of the three most obvious effect of rust layer formation on the Tafel slopes can be seen in the magnesium salt, which shows increasing of anodic and cathodic Tafel slopes in accordance with the lowing of corrosion rate. The effect of red rust is obvious in ammonium sulfate solution with the increase of both anodic and cathodic current but the slopes in both the cases are higher due to deposition of rust layer.

Conclusions

This study was done with aim of investigating the effect of cations on the corrosion behavior of galvanized steel sheets locally produced in Nepal. The three different cations used as corrosive medium were $(NH_4)_2SO_4$, $MgSO_4$ and Na_2SO_4. The electrochemical test, wet-dry cyclic test and weight loss were used to assess the effect of these three cations on the corrosion behaviors of galvanized steel sample. The following conclusions were made from the obtained data:

1. The corrosion rate was highest for the samples corroded in ammonium sulfate solution and lowest in magnesium sulfate solution. The corrosion rate was estimated to be 0.1 $mm.y^{-1}$, 0.03 $mm.y^{-1}$ and 0.06 $mm.y^{-1}$ in $(NH_4)_2SO_4$, $MgSO_4$ and Na_2SO_4 solutions, respectively at the end of 14th wet-dry cycle. The corrosivity of the three ions decreased in the order $NH_4^+ > Na^+ > Mg^{2+}$.
2. The corrosion potential in magnesium sulfate solution was nobler than in ammonium and sodium salts. This indicated the formation of protective surface film in magnesium sulfate solution. The corrosion potential in ammonium salt showed most noble value at the end of 14th wet-dry cycle due to appearance of red rust.
3. The surface observation of the samples showed least corrosion in magnesium salt solution and highest corrosion in ammonium salt solution, which corroborates the corrosion rate data. The rust layer was found to be very porous in ammonium salt followed by sodium salt and a compact and thin rust layer was observed in magnesium sulfate solution as revealed by SEM image.

4. The potentiodynamic polarization curves showed the inhibition of both the cathodic and anodic reaction by magnesium ion, while the ammonium ion changes the cathodic reaction from diffusion limiting current due to oxygen reduction to activation control reduction of ammonia and hydrogen ions. The anodic Tafel slopes in sodium and ammonium ion was almost similar. So the difference in the corrosion rate can be assigned to change in cathodic reaction, which increase the pH and therefore favors the formation of less protective corrosion products. On the other hand, at anodic site lowering of pH inhibit the formation of oxide.

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