# INVESTIGATION OF CORROSION BEHAVIOUR OF MAGNESIUM IN AQUEOUS SOLUTIONS

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The paper presents the corrosion data of magnesium metal in different aqueous solutions such as $NH_4Cl$, $NaI$ and $NaClO_4$ of concentrations ranging from 0.1 to 2.0 $M$. Polarisation and optical methods have been used to evaluate the corrosion parameters and surface properties. The dependence of the open circuit potential, corrosion potential, corrosion current and Tafel slopes on the nature and concentration of the electrolytes has been examined. Corrosion current increases linearly with concentration of the electrolyte in all the media. The findings further infer the corrosivity of the anions decrease in the order as $Cl^- > I^- > ClO_4^-$. The nature of the corrosion products formed on the surface as well as morphological features of the specimen obtained from XRD and SEM techniques are also discussed in this communication.

Key words: Aqueous corrosion, magnesium, electrochemical methods.

## INTRODUCTION

In recent years magnesium and its alloys have gained great importance in view of their lucrative properties and multifarious applications in various fields, primarily due to their low weight advantage, four times lighter than steel, two thirds that of aluminium and one fourth that of zinc. Hence the metal production and its consumption have been increased enormously throughout the world and are estimated to be 400,000 thousands tonnes per annum. The increasing demand for magnesium and its alloys in industries by virtue of their attractive light weight and design capabilities, has given the impetus to investigate their electrochemical behaviour under different environmental conditions. Many investigations have been carried out the corrosion of magnesium in various aqueous electrolytes [1-4]. This paper highlights the influence of ions on the corrosion behaviour of the specimen and its variations with concentration.

## EXPERIMENTAL

### Polarisation studies

The metal was turned into small rods and fitted into the electrode assembly by means of copper rod and Teflon sleeves. The working area of the electrode was 0.3 cm$^2$ and had the composition Al 300, Si 400, Fe 300, Cr 60, Zn 40 and Mn 20 in ppm. level. Polarisation experiments were carried out in both anodic and cathodic directions in aqueous $NH_4Cl$, $NaI$ and $NaClO_4$ solutions of 0.1, 0.25, 0.5, 1.0, 1.5 and 2.0 $M$ concentrations by impressing known current, up to 100 mA.cm$^{-2}$ and measured the corresponding potentials. Log I vs E plots were drawn (Fig .1), from which the corrosion parameters such as corrosion potential ($E_{corr}$), corrosion current ($I_{corr}$) and Tafel slopes ($b_c$ and $b_a$) have been evaluated and furnished in Table I.

### X-ray diffraction studies

The surface film formed during the anodic polarisation of the magnesium specimen at 100 mA.cm$^{-2}$ for 30 minutes in 2.0 $M$ solution were subjected to X-ray scattering analysis to identify the nature of the corrosion products (Fig. 2).

### Scanning electron microscopic studies

The magnesium specimen anodically polarised at two different current densities of 10 and 100 mA.cm$^{-2}$ for 15 minutes in 0.25 and 2.0 $M$ solutions, were cleaned using a solution containing 20% chromic acid and 1% AgNO$_3$ [5,6] and subjected to scanning by Jeol electron microscope. The micrographs obtained were furnished in Figs. 3 and 4.

## RESULTS AND DISCUSSION

The anodic and cathodic polarisation plots for magnesium obtained galvanostatically in NH$_4$Cl solution is given in Fig. 1, clearly bring out the applied voltage-current relationships. It is found that corrosion of magnesium in .I$_4$Cl and NaClO$_4$ solutions follow cathodically controlled echanism as inferred from the predominant change of the polarisation curve towards the cathodic direction than to the anodic direction. The same specimen in NaI solution shows only anodic controlled behaviour because anodic polarisation is found to be more than the cathodic polarisation. These behaviours can be confirmed from the higher respective slope values.

### Polarisation data

Table I gives the OCP, E$_{corr}$, I$_{corr}$, b$_c$ and b$_a$ values for magnesium exhibited in all the three solutions at concentrations of 0.1, 0.25, 0.5, 1.0, 1.5 and 2.0 $M$. It is observed from the table that open circuit potential (OCP) increases with concentration in all the solutions, lowest being -1.45 V and highest being -1.81 V in 0.1 $M$ NaI and 2.0 $M$ NH$_4$Cl solutions respectively. This may be attributed to the operation of localised corrosion which becomes more active with increase in concentration [7]. E$_{corr}$ values show that they are negative in all the solutions at all concentrations. The increase in E$_{corr}$ with concentration may be due to the change

**TABLE I: Galvanostatic polarisation data for Mg in different aqueous solutions**

| Medium | C (M) | OCP (-V) | E$_{corr}$ (-V) | I$_{corr}$ (mAcm$^{-2}$) | b$_c$ (mVdec$^{-1}$) | b$_a$ (mVdec$^{-1}$) |
|---|---|---|---|---|---|---|
| NH$_4$Cl | 0.10 | 1.71 | 1.68 | 3.0 | 220 | 170 |
| | 0.25 | 1.74 | 1.71 | 5.0 | 180 | 160 |
| | 0.50 | 1.75 | 1.73 | 6.2 | 140 | 120 |
| | 1.00 | 1.78 | 1.77 | 7.2 | 90 | 75 |
| | 1.50 | 1.79 | 1.78 | 8.2 | 70 | 60 |
| | 2.00 | 1.80 | 1.80 | 9.6 | 55 | 50 |
| NaI | 0.10 | 1.45 | 1.48 | 1.0 | 200 | 220 |
| | 0.25 | 1.49 | 1.51 | 1.3 | 190 | 210 |
| | 0.50 | 1.50 | 1.52 | 1.6 | 170 | 185 |
| | 1.00 | 1.51 | 1.53 | 1.9 | 140 | 160 |
| | 1.50 | 1.52 | 1.54 | 2.0 | 120 | 140 |
| | 2.00 | 1.53 | 1.54 | 2.3 | 105 | 120 |
| NaClO$_4$ | 0.10 | 1.56 | 1.57 | 1.0 | 200 | 120 |
| | 0.25 | 1.57 | 1.58 | 1.2 | 180 | 110 |
| | 0.50 | 1.58 | 1.58 | 1.6 | 135 | 100 |
| | 1.00 | 1.59 | 1.60 | 1.8 | 115 | 50 |
| | 1.50 | 1.60 | 1.60 | 1.9 | 90 | 40 |
| | 2.00 | 1.61 | 1.62 | 2.0 | 70 | 30 |

in $p$H near the electrode-electrolyte interface[8]. The observed corrosion potentials in all the solutions are found to be nearly 1.0 V nobler than the standard value of -2.37 V vs NHE for magnesium. This is due to the formation of protective film. I$_{corr}$ values indicate that NH$_4$Cl and NaClO$_4$ are the most and least corrosive media for magnesium. The corrosion current is found to be minimum
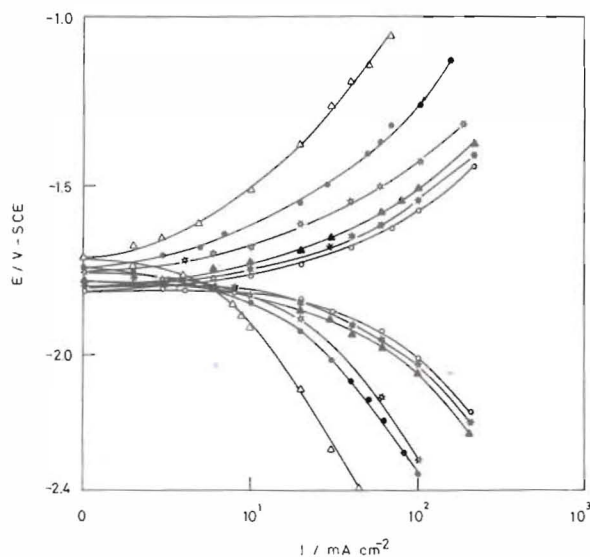


Fig. 1: Galvanostatic polarisation plots for Mg in NH$_4$Cl
($\triangle$) 0.1; ($\bullet$) 0.25; ($\ast$) 0.5; ($\blacktriangle$) 1.0; ($\clubsuit$) 1.5; ($\bigcirc$) 2.0M
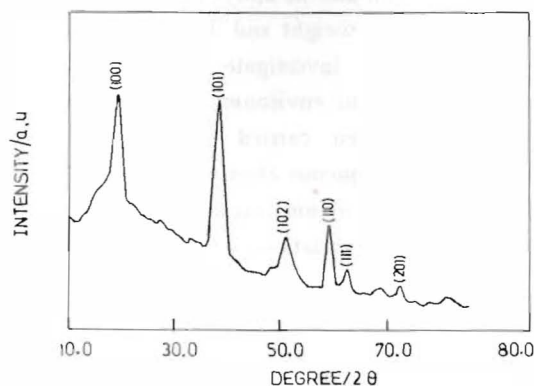


Fig. 2: XRD patterns of the surface film formed on Mg at 100 mA.cm$^{-2}$ in 0.25 M NaI solution

Fig. 3: SEM micrographs of magnesium in 2.0 M NH₄Cl at a) 10 mA.cm$^{-2}$ and b) 100 mA.cm$^{-2}$

in 0.1 $M$, increased with concentration and reached the maximum at 2.0 $M$. For NaI solutions the minimum and maximum $I_{corr}$ values are 1.0 and 2.3 mA.cm$^{-2}$ respectively. On the basis of the $I_{corr}$ values, the aggressiveness of the media follows the decreasing order as NH₄Cl > NaI > NaClO₄. Corrosion of metals by anodic dissolution depends on the anion present in the aqueous solutions [9,10]. The highest corrosion rate of the specimen observed in NH₄Cl is based on its acidity, retardation of the surface films, viscosity of the solution, the preferred size and tetrahedral shape of NH$^{4+}$ ion suitable for association with structure of water. The subdued action of NaClO₄ solution towards magnesium has resulted from the thick film formation which in turn causes passivation arising from the low polarising power of perchlorates.

### X-ray diffraction analysis

Sharp and well defined XRD patterns consisting of distinct intensity peaks are recorded for the corrosion products formed in all the media. The pattern of the compounds formed on magnesium anode in 0.25 $M$ NaI solution polarised at a current density of 100 mA.cm$^{-2}$ is presented in Fig. 2. The analysis of the peaks show that many of them match with the standard values of Mg(OH)₂ with JCPDS number 70239. A prominent peak found at d value of 4.91 Å does not agree with the standard value of common

compounds of sodium and magnesium. It may be due to the presence of some mixed salts with complex and indefinite crystal structure. All other solutions give brucite only which were identified from the diffraction lines. Maximum intensity peak with $I/I_o$ value 100 has been from the (101) plane corresponding to a d value 2.365 Å and 2θ value 38.2. Second best intensity peak has been from (001) plane for a d value 4.377 Å. Other peaks of comparatively lower intensities have been reflected with the diffraction from (102), (110), (111), (103), (201) and (202) hkl values.

### Scanning electronmicroscopic studies

Figs. 3 and 4 show the morphology of magnesium specimen after the polarisation at two different current densities of 10 and 100 mA.cm$^{-2}$ in NH₄Cl and NaClO₄ solutions. Fig. 3 shows an uneven attack by NH₄Cl which is observed to be an aggressive medium towards magnesium. Certain areas have been affected much, whereas other parts remain unaffected due to low applied current density. But at high current density of 100 mA.cm$^{-2}$ in the same medium a uniform and enhanced corrosion of the specimen are observed as understandable from Fig.3(b). The overall effects of current density, concentration and the nature of medium on the surface morphology of magnesium in NaClO₄ are presented in Figs. 4(a) and 4(b). The specimen at low current density and low concentration is corroded only feebly as seen
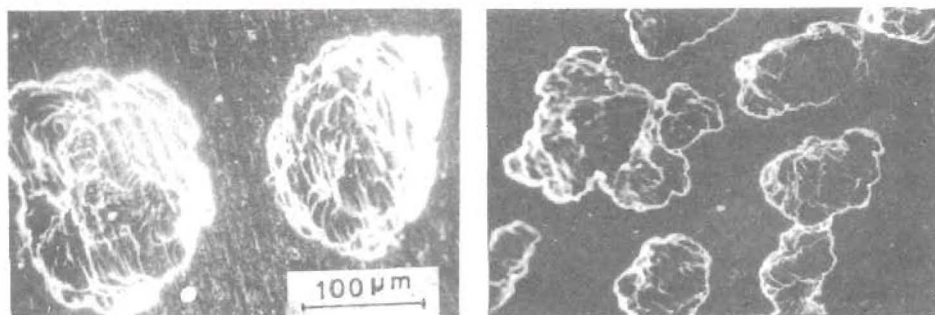


Fig. 4: SEM micrographs of magnesium in 2.0 M NaClO₄ at a) 10 mA.cm$^{-2}$ and b) 100 mA.cm$^{-2}$

from the large area of an uncorroded surfaces in Fig. 4(a). Similarly an increase in current density, enhanced the corrosion of the specimen to a larger extent as can be seen from Fig. 4(b) as more areas have been corroded.

## CONCLUSION

This study has proved electrochemical action of magnesium specimen in a variety of aqueous media. It has been observed that at lower concentration, magnesium corrodes during polarisation at a lower rate which is correlated to the increased passivation at the magnesium surface and can yield better performance in battery systems. The observed corrosion rate at high concentration and at high current density can lead to select alternate electrolytes. This problem can be mitigated by the use of effective inhibitors where magnesium specimens are used.

## REFERENCES

1. A Antonyraj and C O Augustin, *Corrosion Reviews XVI*, **1-2** (1998) 127
2. G Song, A Atrens, S ST John, X Wu and J Nairn, *Corros Sci*, **39** (1997) 1981
3. G L Makar and J Kruger, *Int Mat Rev*, **38** (1993) 138
4. E Gulbrandsen, *Electrochim Acta*, **38** (1992) 1403
5. V M Scepanovic and R Brigham, *Corrosion*, **48** (1992) 780
6. J Gasnesca, C Rodriguez, J Juarez, B Campillo and L Martinez, *Corrosion Reviews XVI*, **1-2** (1998) 95
7. I Nakatsugawa, S Kamedo, Y Kpjima, R Ninomiya and K Kubota, *Corrosion Reviews XVI*, **1-2** (1998) 139
8. C A Nunezlopez, P Skeleton, G E Thompson, P Lyon, H Karimzadeh and T E Wilks, *Corros Sci*, **37** (1995) 689
9. N Sato, *Electrochim Acta*, **41** (1996) 1525
10. N Sato, *Corros Sci*, **37** (1995) 947