Monitoring of Initial Stages of Atmospheric Zinc Corrosion in Simulated Acid Rain Solution under Wet-dry Cyclic Conditions

Gamal A. EL - Mahdy and Kwang B. Kim

Department of Metallurgical System Engineering, Yonsei University, 134-Shinchon-dong, Seodaemun-Ku, Seoul, 120-749, South Korea

Exposure of zinc samples in simulated acid rain solution (SARS) was investigated under a periodic wet-dry conditions using an AC impedance technique. The periodic wet and dry exposure consisted of the immersion of zinc samples in SARS for one hour followed by exposure to 7 hours drying at 60% RH. Phases of the corrosion products were indentified by X-ray diffraction (XRD). The influence of relative humdiity (RH), temperature, and surface inclination on the atmospheric corrosion of zinc is described. The reciprocal of polarization resistance (1/Rp) decreases rapidly during the initial stages then slowly and eventually attains a steady state as exposure time progresses. The average of reciprocal of polarization resistance per cycle, (ARPR) was calculated and found to decrease as number of exposure cycle increases. An increase of temperature enhances the corrsion rate of zinc. The values of ARPR, of a sample inclined at $30°$ are lower than those for a sample oriented horizontally. The experiment result shows a pronounced dependence of reciprocal of polarization resistance on RH. Exposure in the presence of carbonate anions gives rise to more protective corrosion products than in nitrate anion solution. The corrosion mechanism during the initial stages of atmospheric zinc corrosion under wet - dry cyclic conditions is suggested.

Keywords : *Zinc, AC impedance, Polarization resistance, XRD.*

1. Introduction

The good corrosion resistance of zinc and its relatively low price is the reason for its extensive practical application, particularly in the form of a coating on a steel (galvanizing) and as an alloying element in electrical contacts, connectors and electronic components. The atmospheric corrosion of zinc is accelerated by chloride (Cl) deposition and by gaseous sulfur dioxide (SO_2).[1)-9)] Sydberger and Vannerberger[10)] and Duncan and Spedding[11)-12)] performed a laboratory study on zinc corrosion with more realistic concentrations of SO_2. The deposition of SO_2 is strongly humidity dependent and decreases with time. Sevensson and Johansson[13),14)] reported a laboratory study of the role of O_3 and NaCl induced atmospheric corrosion of zinc in air containing sub-ppm concentrations of SO_2 and nitogen dioxide (NO_2). Corrosion was enhanced by sodium chloride (NaCl) and traces of ozone (O_3) and NO_2. The accelerating effect of O_3 is present both at 70% and 95% relative humidity (RH) while NO_2 is only active at the higher humidity. Falk et al[15)] reported a laboratory study of the atmospheric corrosion of zinc in air containing different concentrations of carbon dioxide. Carbon dioxide slowed down the corrosion rate of zinc.

Mendoza and Corvo[16)] studied the outdoor and indoor atmospheric corrosion of zinc at three sites (coastal, urban-industrial and rural) under different exposure conditions. Runoff and corrosion rates of zinc were investigated after 0.5 , 1,2 and 4 years at seven sites in Switzerland.[17)] Runoff rates differ from corrosion rates depending on the material, the exposure time and the sampling site. The influence of NaCl deposition on the corrosion of zinc in atmospheres with and without SO_2 was studied via quartz crystal microbalance.[18)] The results show that NaCl accelerates the corrosion of zinc.

In a previous publication[19)] in the same journal a mechainsm of zinc corrosion under thin electrolyte layers was discussed as well as the influence of sulfur dioxide gas (SO_2) on the corrosion of zinc. The aim of the present investigation is to monitor the initial stages of the atmospheric corrosion of zinc with varaition of factors such as RH, temperature, surface inclination and the presence of some anions in simulated acid rain solution (sars). The mechanism of the initial stages of atmospheric corrosion will be discussed on the basis of corrosion monitoring under wet/dry cyclic conditions using an AC impedance technique.

Table. 1. Composition of the simulated acid rain (SAR)

Ion	Concentration / mg dm^{-3}
F$^-$	0.098
Cl$^-$	1.0
NO$_3^-$	7.1
SO$_4^{2-}$	11.1
NH$_4^+$	2.3
Na$^+$	0.42
K$^+$	0.11
Ca^{2+}	0.049
Mg^{2+}	0.045

2. Experimental method

2.1 Sample preparation and test solution

The specimen was prepared from a sheet of electrolytic grade zinc (>99.9%). A Pair of two identical metal plates (L=10 mm and W=10 mm) were connected with copper wire using silver paste, then a quick drying epoxy was added to secure the connection. The two metal plates were placed 0.1 mm apart from each other in the epoxy resin holder and an Epoxy resin was poured into the mould with enough thick to cover the copper wire. After 8 hours the resin was cured and the plates were removed from the holder. The electrolytic cell was set on an acrylic vessel placed inside a temperature and humidity controlled chamber. The cell was set with metal surface facing upwards and a bubble leveler was used to ensure the cell was placed horizontally. SARS was prepared from distilled water and analytical grade reagents with a composition shown in table (1) with pH (3.5).[20] SARS was introduced into the vessel from an external tank through an inflow magnetic valve programmed to deliver an enough volume to cover the test specimen. After 1hour immersion, the test solution was drained through an outflow magnetic valve and the amount of the solution remained on the electrode surface was left to dry for 7hours. The specimen was subjected to cyclic wet/dry conditions at 303 K and 60% RH unless otherwise stated. Before exposure, the sample was polished down to #2000 using SiC paper and ultrasonically cleaned in ethanol.

2.2 AC impedance measurements

The impedance measurement was conducted at 10 kHz and 10 mHz using AC Corrosion Monitor with a multi-plexer controlled by a computer through RS-232 interface. Prior to experiment a barrier wall a 0.5 mm thick Mylar

sheet was glued around the electrode to ensure constancy of electrolyte layer remained on the electrode surface at the onset of the dry cycle. The corrosion monitor conducts the measurement continuously when the surface wet and disable to conduct the measurements when the surface became completely dried.

The polarization resistance Rp was determined by subtracting the high frequency impedance at 10 kHz from the low frequency impedance 10 mHz, and the reciprocal value of the polarization resistance was taken as a corrosion rate. The electrical circuit, cell and technique were used as described previously.[19),21)-27)]

2.3 Corrosion products analysis

XRD measurement was conducted after exposure the samples for 72 hours under wet-dry cyclic conditions. Prior to XRD analysis, the sample carefully separated from the epoxy then subjected to XRD measurements for the identification of the chemical composition of the corrosion products using XRD (Shimadzu (Japan) XD-3A).

3. Results and discussions

3.1 Monitoring the poarization resistance of zinc under different RH

The polarization resistance Rp was monitored at two different RH (60% and 95%) at 303 K in sars and the data is shown in Fig. 1. It is the clear that the reciprocal of polarization resistance, which is proportional to the corrosionrate[19),21)-27)] decreases with time. The average corrosion charge (Q) per cycle was calculated from the equation:

$$\text{Average corrosion charge (Q) per cycle} = \int_0^t 1/Rp \, dt \qquad (1)$$

where t is the time of wetness (t$_{TOW}$) per cycle and 1/Rp is the reciprocal polarization resistance.

The t$_{TOW}$ was found to be 2.6 hours /cycle and 8 hours /cycle at 60% and 95% RH respectively. The values of average corrosion charge are traced vs cycle number as shown in Fig. 2. The values of average corrosion charge at 95 % RH is higher than the 60% RH. The results can be explained by on the basis of time of wetness which decreased at 60% RH. The amount of water adsorbed on the Zn surface plays an important role for Zn corrosion and depends on RH and the chemical properties of the corrosion products. During wetting in the first cycle the average corrosion charge is high due to the dissolution of zinc then starts to decrease and reaches a steady state.
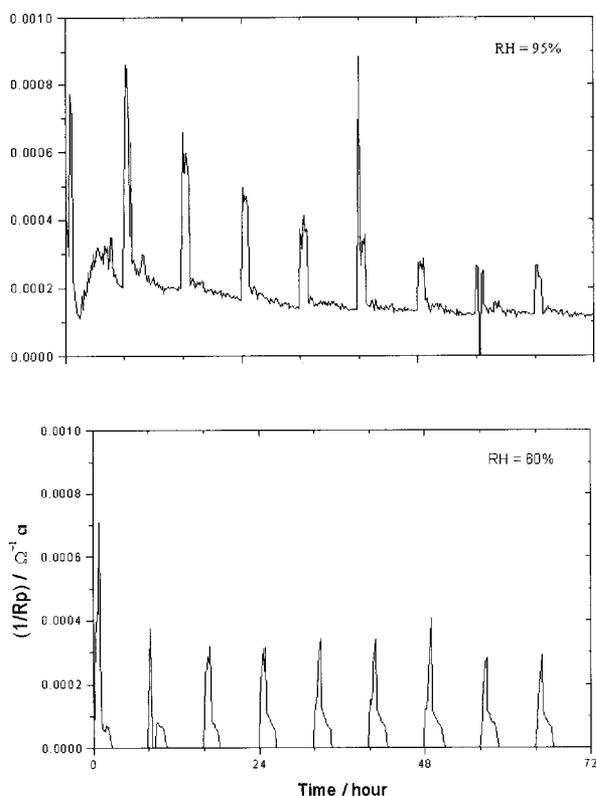
Fig. 1. Changes in the reciprocal of polarization resistance (1/Rp) of zinc with exposure time during wet-dry cycles in sar at 303K and different RH.
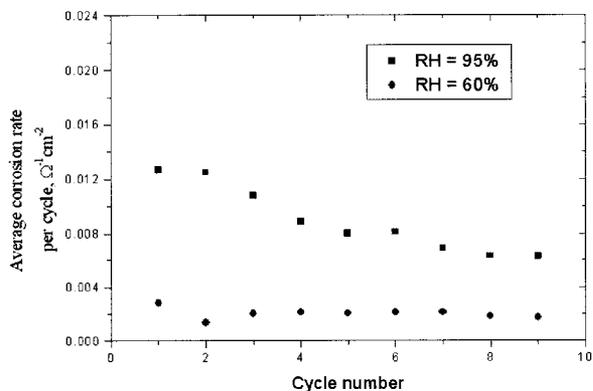

Fig. 2. Effect of RH on average corrosion charge (Q) per cycle.

After draining the solution, the thickness of the sars layer decreases gradually due to the evaporation process. The thinning process is accompanied by a formation of corrosion product at 60% RH. During the next cycle some of corrosion product formed in the preceding cycle is washed off and the other retained on the surface. The latter causes a reduction in Q. The formation of a stable corrosion products reduce the values of Q until reach a steady state gradually. During the drying period the corrosion process

proceeds under thin electrolyte layers and the corrosion process increases owing to an enhancement of the reduction process of oxygen. The zinc surface always wet even during the drying process at 95% RH which causes a continuity of the corrosion process. The zinc surface was covered entirely with the corrosion products leading to a steady state in the last four cycles. The difference in corrosion process may be attributed to the difference in composition of the corrosion products. The results of X-ray diffraction (XRD) indicated the presence of hydrozincite[15),28)-31)] and zinc oxide (ZnO),[20),32)-34)] at 95% RH. The main constituent of the corrosion products formed at 60% RH is zinc carbonate ($ZnCO_3$) which improves greatly the corrosion resistance of zinc. It is obvious that the length of wetting and drying period affects on the corrosion process of zinc.

3.2 Effect of surface inclination

The effect of surface inclination on the corrosion process of zinc has been investigated for samples exposed to a horizontal and mounted to a $30°$ to the horizontal. The experiments were conducted at 1hr immersion in sars containing 1mM Na_2SO_4 and 7hours drying at 60% RH
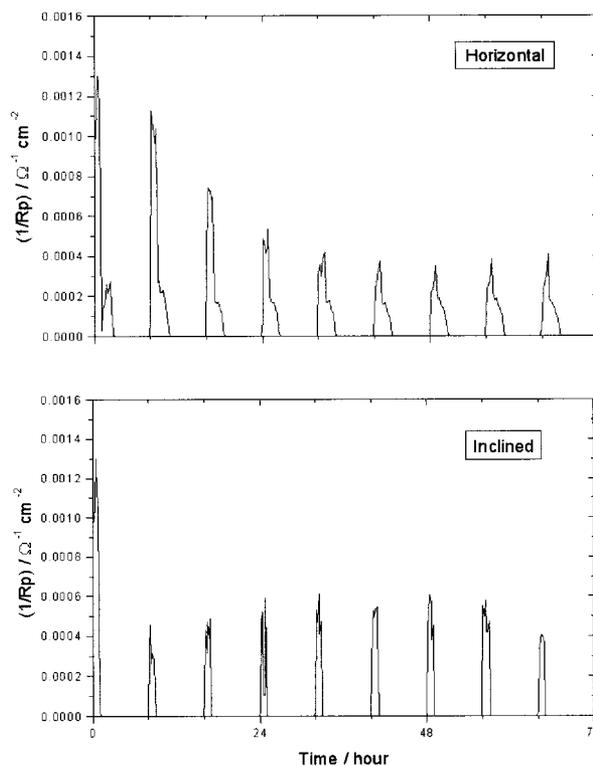

Fig. 3. Corrosion monitoring results (1/Rp) of zinc under alternate conditions of 1h-immersion in sars containing 1mM Na_2SO_4 and 7h-drying at 60% and 303K with exposure time at different surface inclination.
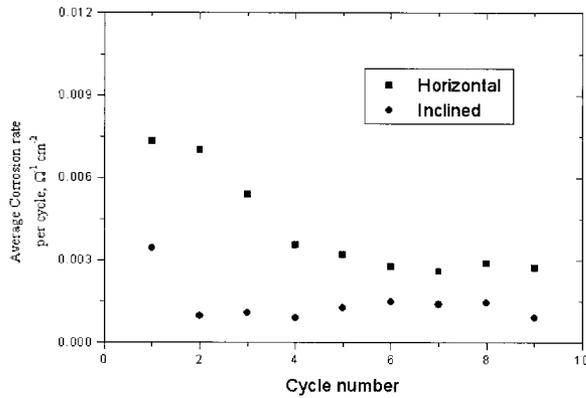
Fig. 4. Effect of surface inclination on average corrosion charge (Q) per cycle.

and 303 K.The results of 1/Rp Vs time is shown in Fig 3. Q, was calculated based on the time of wetness using equation (1) and plotted vs cycle number as shown in Fig. 4. Q, is high at the initial stage of immersion (first cycle) then decreases gradually until reaches a steady state. The time of wetness is only one hour during the immersion period in case of inclined sample and 2.54 hours in case of horizontal one. During the next cycle part of the corrosion products formed washed away from the surface and new corrosion products formed leading to an increase of, Q. At the end of the drying period a stable corrosion product is formed and causes a decrease in Q valuess in both samples. The formation of the corrosion product decreases the values of Q until the surface is completely covered with the corrosion products leads to a steady state. These changes during wet/drying cycle are governed by the wetting period (first flush) during which a large quantity of corrosion products washed away from the surface inclined to $30°$ than those for a horizontal orientation. The thin electrolyte layers retained on zinc surface cause a high corrosion rate in a horizontal oriented sample.

3.3 Influence of temperature

The effect of temperature was investigated in sars containing 0.1 mM sodium sulfate (Na_2SO_4) at two different temperatures (293 and 313 K) and 60% RH. The results of 1/Rp vs. time are depicted in Fig. 5. The estimated Q, values versus the cycle number is shown in Fig. 6. Generally, the value of Q at 313K is higher than at 293K. The results can be explained on the basis of passivating and accelerating effect of temperature. The latter becomes obvious at higher temperature while the former is predicted at a lower one. The results showed that an increase in temperature stimulates the corrosion attack by enhancing the rate of electrochemical reaction as well as the diffusion processes. Also the acid rain temperature affects not only

the composition but also the compactness of the corrosion products. At lower temperature the corrosion products exist as an adherent substance which changes to nonadherent one at a higher temperature. The main constituent corrosion product at high temperature is ZnO as revealed from XRD-diffraction analysis. The oxide film formed in acidic medium was found to be porous and not passivating.
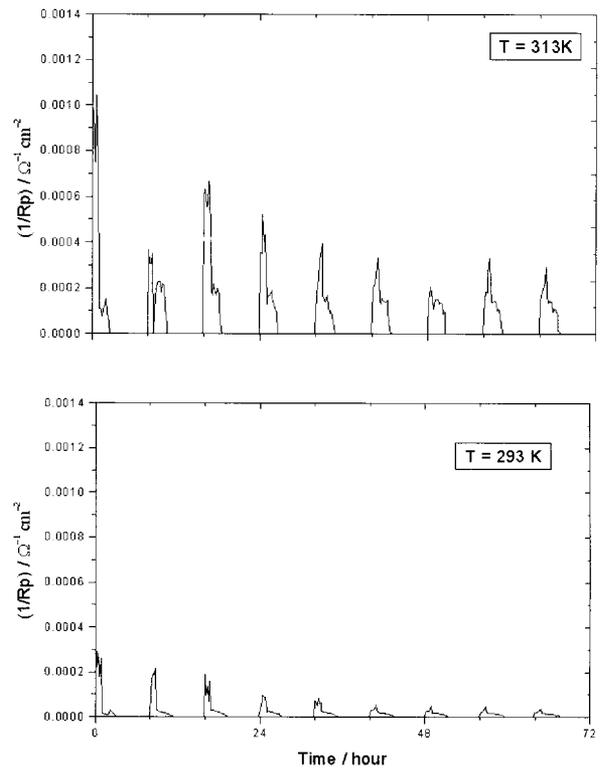

Fig. 5. Variation of reciprocal of polarization resistance (1/Rp) of zinc exposed to alternate conditions of 1h-immersion in sars containing 0.1mM Na_2SO_4 and 7h-drying at 60% RH and at different temperatures.
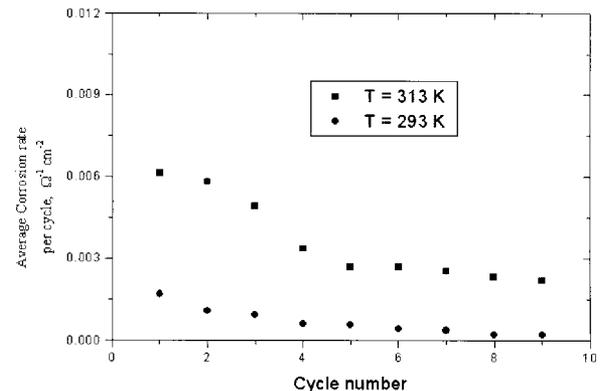

Fig. 6. Dependence of average corrosion charge (Q) per cycle on temperature.

3.4 Corrosion behavior in sars containing carbonate and nitrate anions

The presence of CO_2 and NO_2 gaseous in the atmospheric air led to considerably lower carbonate and nitrate concentrations which play an important role in an atmospheric corrosion of zinc. The latter is a major pollutant and precursor for nitric acid and nitrates, which are no doubt involved, in many chemical process of zinc corrosion. Thus, two experiments were conducted to monitor the polarization resistance in sars containing 1mM sodium carbonate (Na_2CO_3) and sodiun nitrate (Na_2CO_3) anions with immersion time as shown in Fig. 7. Q, was calculated and presented in Fig. 8. The results indicated that the values of Q in carbonate anion are lower than observed in nitrate solution due to the formation of protective corrosion products of zinc carbonate ($ZnCO_3$) which inhibit the corrosion of zinc. The zinc surface covered completely with corrosion products and reaches a steady state after four cycles in the carbonate solution and after six cycles in case of nitrate solution. According to XRD analysis traces of basic zinc nitrates ($ZnNO_3$ (OH). H_2O) and zinc hydroxy nitrate (Zn_5NO_3 $(OH)_8$. $2H_2O$) are formed. The corrosion products formed in nitrate anion containing solution were powdery and easily removable from the zinc surface. Thus, new corrosion products were formed and washed away from the surface during next cycle leading to increase the corrosion loss of zinc in nitrate containing sars.

3.5 Mechanism of zinc corrosion under wet/dry cyclic conditions

Wet / dry episodes are important in altering the nature of the corrosion products by precipitation, dissolution and changes in the concentration of surface electrolyte layers. In the moist indoor conditions the zinc is oxidized with the formation of zinc hydroxide ($Zn(OH)_2$) which reacts with air constituent forming basic zinc carbonates. The formed zinc hydroxide and basic zinc carbonate formed the so-called zinc patina which protects the zinc surface from attack. The patina either continues to grow or, if exposed to polluted atmospheres may accumulate different anions and eventually transform into other corrosion products. At lower pH such patina formed at earlier periods dissolved leading to high corrosion rate. In the initial stages of wet/dry episodes corrosion of zinc is high due to the dissolution of the air-formed oxide film followed by an active dissolution of zinc causes a high corrosion rate. In case of wetting period (1hour immersion) the corrosion rate of zinc is anodically controlled by zinc dissolution and may be accompanied by an insoluble corrosion products or salt or passivation. During drying
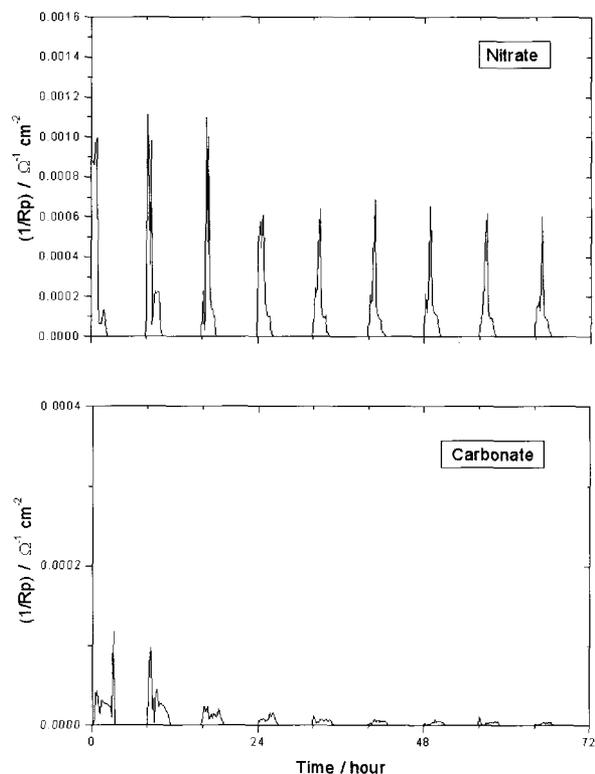

Fig. 7. Monitoring of reciprocal of polarization resistance (1/Rp) of zinc with exposure time in sars contains 1mM carbonate and nitrate anions under wet -dry cycles at 60% RH and 303K.
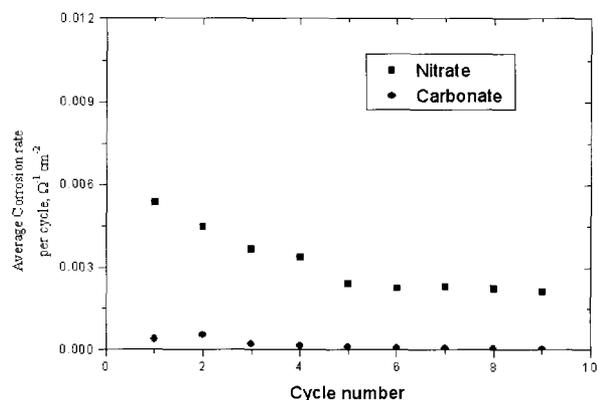

Fig. 8. Effect of carbonate and nitrate anion containing sars on average corrosion charge (Q) per cycle.

process, the electrolyte concentrates, due to evaporation of electrolyte and causes a change in the electrolyte thickness. Thus, if oxygen diffusion is the rate - controlling step the corrosion rate will increases with decreasing the electrolyte thickness under thinning process. After complete dryness of electrolyte, corrosion products will form. The stability and the chemical composition of the corrosion products depend on the length of drying period, RH and temperature and the presence of some anions. Also

The degree of protection of the corrosion products depends on the stability of the amount retained on zinc surface. During next episode, part of corrosion products washed away from the surface and after repeated wet/dry cycles the amount of the retained corrosion products increased and covered the entire surface of zinc leading to decrease the corrosion rate at the final stages of corrosion. At low temperature and high RH the corrosion products formed are gelatnous and adherent substances cause a decrease in corrosion rate. An increase in temperature and lowering RH is accompanied by a definite change from gelatinous form to a granular nonadherent form. The basic zinc corrosion products causes a reduction of the corrosion process.

4. Conclusions

1. The experimental set up used for a monitoring the polarization resistance under wet /dry cyclic conditions is a successful tool for a mecahnisitic study of the initial stages of atmospheric zinc corrosion.

2. An increase of temperature from 293K to 313K and RH from 60% to 95% RH strongly affect the corrosion rate of zinc.

3. The corrosion rate of the inclined sample to 30° is lower than those for a horizontal orientation.

4. The presence of carbonate anion in sars decreases the corrosion rate due to formation of a dense, coherent and adherent film of a protective zinc carbonate.

References

1. S.Cramer, J.P.Carter, P.M.J.Linstrom, and D.R.Flinn, *The Degradation of Metals in the Atmosphere*, ASTM STP 965 (Eds. S.W.Dean and T.S.Lee). p.316, *American Society of Testing and Materials*, Philadelphia (1988).
2. F.H.Haynie, *ibid.*, p.282 (1988).
3. M.Bernarie and F.l.Lipfert, *Atmos. Env.* 20, 1947 (1986).
4. S.D.Cramer and L.G.McDonald, *Corrosion Testing and Evaluation*: Silver Anniversary Volume, ASTM STP 1000 (eds. R.Baboian and S.W.Dean) p.241, *American Society of Testing and Materials*, Philadelphia (1990).
5. J.W.Spence and F.H.Haynie, *ibid.*, p.208.
6. F.H.Haynie, J.W.Spence, F.l.Lipfert, S.D. Cramer, and L.G.McDonald, *ibid.*, p.225 (1988).
7. B.S.Skerry, J.B.Johansson, and G.C.Wood, *Corros. Sci.* 28, 721 (1988).
8. M.G.Gusto and M.G.S.Ferreira, *ibid.* 34, 533 (1993).
9. L.A.Farrow, T.E.Gradel, and C.Lygraf, *ibid*, 38, 2181 (1996).
10. T.Sydberger and N.G.Vannberger, *ibid.* 12, 775 (1972).
11. J.R.Duncan and D.J.Spedding, *ibid*, 13, 993 (1973).
12. R.Duncan and D.J.Spedding, *ibid.* 14, 271 (1974).
13. J.E.Svensson and L.G.Johansson, *ibid.* 34, 721 (1993).
14. J.E.Svensson and L.G.Johansson, *J. Electrochem. Soc.* 140, 2210 (1993).
15. T.Falk, J.E.Sevensson, and L.G.Johansson, *ibid*, 145. 2993 (1998).
16. A. R .Mendoza and F.Corvo, *Corros. Sci.* 42, 1123 (2001).
17. A.U.L.Minger, M.Faller, and P.Richner, *Mater. and Corros.* 53, 157 (2002).
18. Q.Qu, C.Yan, Y.Wan, and C.Cao, *Corros. Sci.*, 44, 2789 (2002).
19. G.A.EL-Mahdy, accepted for publication in *Corrosion NACE* (in press).
20. S.Magaino, M.Soga, K.Sobue, A.Kawaguchi, N.Ishida, and H.Imai, *Electrochim. Acta* 44, 4307 (1999).
21. EL-Mahdy, A.Nishikata, and T.Tsuru, *Corros. Sci.* 42, 183 (2000).
22. G.A.EL-Mahdy, A.Nishikata, and T.Tsuru, *ibid*, 42, 1509 (2000).
23. G.A.EL-Mahdy, A. Nishikata, and T. Tsuru , Proc., *4th International Conference on zinc and zinc alloy coated steel*, p.421, Tokyo, Japan (1998).
24. G.A.EL-Mahdy, A. Nishikata, and T. Tsuru, Proc., of *the Joint International Meeting on Corrosion and Corrosion Control in Saltwater Environments*, Honolulu, Hawaii, (USA) October 17-22, 97 (1999).
25. A. Nishikata, Y.Ichihara, and T.Tsuru, *Corros. Sci.* 37, 897 (1995).
26. A.Nishikata, Y.Yamashita, H.Katayama, T.Tsuru, A.Usaami, K.Tanabe, and H. Mabuchi, *ibid*, 37, 2095 (1995).
27. R.P.Vera Cruz, A. Nishikata, and T.Tsuru, *ibid*, 38, 1397 (1996).
28. I.Odenvall and C.Lygraf, *Corros.Sci.*, 34, 1213 (1993).
29. V.Ligier, M.Wery, Jean-Yves Hihn, J.Faucheu, and M.Tachez, *ibid.*, 41, 1139 (1999).
30. W.Feitknecht, *Chem. Ind.* 5, 1102 (1959).
31. H.E.Townsend and J.C.Zoccola, *Mater. Perf.* 18, 13 (1979).
32. R.Grauer, *Werk. und Korrosion* 31, 837 (1980).
33. E.Johansson and J.Gullman "*Corrosion Study of Carbon Steel and Zinc - comparison Between Field Exposure and Accelerated Tests*" Atmospheric Corrosion, ASTM STP 1239, W.W. Kirk and H.Herbert Lawason, Eds., Philddelphia, p.240, (1995).
34. T.E.Graedel, *J. Electrochem. Soc.* 136, 193C (1989).