Evaluation of corrosion inhibition by cerium on aluminium under marine and laboratory environments

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Cerium is considered to be a promising ecological alternative to toxic chromates in the field of corrosion protection. Studies were conducted to evaluate the corrosion inhibition by cerium on aluminium under marine and laboratory environments. The results revealed that under marine environment 1000 ppm Ce treated pure aluminium showed good corrosion inhibition than the Al-Mg alloy M57S. The corrosion rate was significantly high during post monsoon and summer season and cerium treated on pure aluminium showed superior corrosion inhibition in all the seasons. Cerium treated pure aluminium showed better corrosion inhibition as compared to untreated marine grade M57S aluminium. The laboratory evaluation of 1000 ppm cerium treatment on aluminium and its exposure in solutions of different salinity (5 to 200 ppt) revealed 30-66 and 0-92.6% efficient corrosion inhibition in pure and M57S aluminium respectively.

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Chromates are among the common substances used as corrosion inhibitors or incorporated in anticorrosive pretreatments on aluminium and its alloys. However, these compounds are highly toxic and their use produces serious environmental hazards. Lanthanides have been identified as good corrosion inhibitors and have low toxicity and their ingestion or inhalation has not been considered harmful to health. Lanthanide ions form insoluble hydroxides that enable them to be used as cathodic inhibitors. Monazite sand is the best-known mineral containing lanthanides and is available in plenty in Kerala. Among the lanthanides Ce is most abundant rare earth which is easily available and is more abundant than aluminium[1]. Cerium surface treatments on aluminium and its alloys are extensively used for corrosion protection in industrial application. The rare earth metal compounds have been found to have redox characteristics similar to those of chromium(VI). The cerium-based compounds have proved to have very good resistance to pitting in aluminium. The surface analytical technique suggested the formation of hydrated aluminium oxide associated with cerium oxide preferentially deposited on intermetallic particles of aluminium alloys[2]. It is already estab-lished that cerium film formed at local cathodic sites on the alloy surface stifled oxygen reduction thereby limiting corrosion damage[3]. Shaw et al.[4] and Moshier et al.[5] developed Ce – Mo surface treatments on aluminium in three ways. The cleaned aluminium surfaces were (i) immersed in 10mM $Ce(NO)_3$ at 100^oC, (ii) immersed 10mM $CeCl_3$ at 100^oC, and (iii) potentiostatically polarized at +0.5V in deaerated 0.1 M Na_2MoO_4. Aluminium alloy surfaces treated in this manner resisted pitting in aerated 0.5 M NaCl solution.

Aluminium and its alloys are extensively used in the fisheries sector like wooden boat hull sheathing, manufacture of aluminium canoes, aluminium cans for processed fish storage, etc. Use of marine grade aluminium was recommended for wooden boat hull sheathing, instead the fishing boat owners of Kerala extensively used pure aluminium as sheathing material and its life in marine environment is less than one year. The present work was carried out to evaluate the corrosion inhibition for aluminium by cerium under marine and laboratory environments.

Experimental Procedure

Two grades of aluminium were purchased from the market *viz*., pure (type 1100 Al > 99%) (Sample A) and marine grade M57S (Al and Mg 2.2%) (Sample B). The aluminium coupons of size 2.5×5 cm and

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15×10 cm were used for laboratory and field exposure studies. The panels were polished for up to 600 grit using SiC paper then cleaned with water, acetone, again with water and finally rinsed with distilled water. The samples were weighed in a 0.01 mg sensitive electronic balance. Modified method of Hinton and Wilson[6] was used for treatment of Ce aluminium. The cleaned samples were kept for 10 min in a muffle furnace having temperature 200±10°C and hot dipped in 1000 ppm cerium chloride solution and kept as such for 15 min. These specimens were washed with distilled water to remove any soluble $CeCl_3$. The same treatment was followed in the case of 2500 and 5000 ppm Cerium. The treatment was done using 250 mL Ce solution for 8 samples and fresh solutions were used each time whereas in larger sized panels, one liter solution was used for treating eight number of panels. The samples for field exposure were fixed on a steel rack with polyethylene screws and washers without any contact with rack and exposed at the institute test site at Cochin estuary. The water parameters like salinity, pH, turbidity and dissolved oxygen[7] were recorded every week and the exposed samples were retrieved after 28 days. The experiment was repeated in four quarters of the year *viz.* July 2001 (monsoon), September-October (post monsoon), January (pre summer) and April-May (summer) and these seasons are represented in the ensuing discussion as Q1, Q2, Q3 and Q4 respectively. In the retrieved panels the fouling organisms accumulated was removed carefully using fine stainless steel knife, washed thoroughly with water and final cleaning was done with aluminium cleaning solution ($K_2Cr_2O_7$ +H_3PO_4). Final weights of the panel were recorded and rate of corrosion was calculated as per the standard procedures.

Laboratory experiments were conducted using 1000 ppm cerium treated aluminium (samples A and B) and these samples were exposed to different saline solutions *viz.* 5, 10, 20, 25, 50, 100 and 200 ppt for 28 days. After the experiment the samples were thoroughly washed with distilled water and weight loss noted and the corrosion rate calculated. The retrieved aluminium samples were analysed potentiometrically by linear sweep voltammetry using AUTOLAB PGSTAT 30 potentiostat. The potentiostatic measurements were carried out in 0.1M NaCl with Ag/AgCl, SS316 and sample respectively as reference, counter and working electrodes. The electrolyte was deaerated by nitrogen for half an hour. The linear
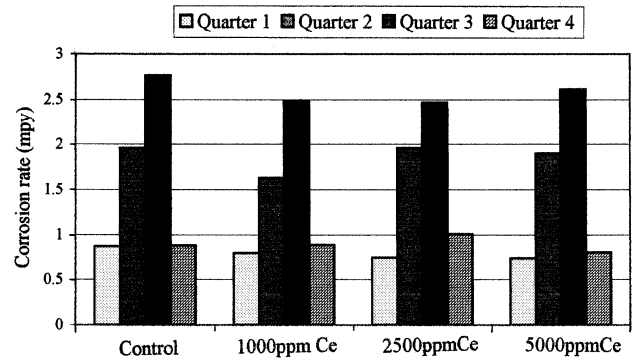

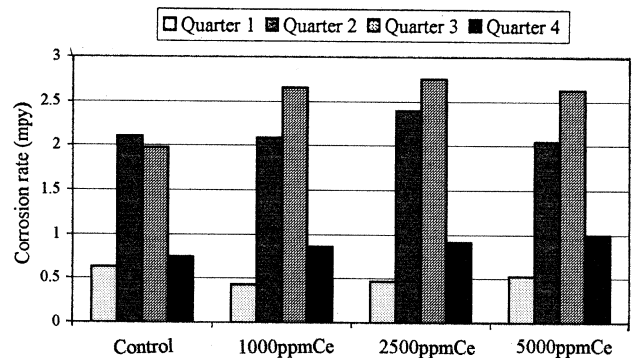Fig. 1—Corrosion of sample A (pure Al) in the marine environment

Fig. 2—Corrosion of sample B (M57S) aluminium in the marine environment

sweep voltammetry was carried out from open circuit potential to ±0.5 Volt. The parameters like E_{corr}, I_{corr}, i_{corr}, R_p and corrosion rates were noted. The statistical analysis was carried out using MS Excel available with Microsoft Office 2000.

Results and Discussion

The samples A and B aluminium was exposed to the Cochin estuary for four quarters of the year. During monsoon the corrosion rate in samples A and B aluminium varied respectively between 0.731-0.863 mpy and 0.427 to 0.625 mpy (Figs 1 and 2). The corrosion inhibition efficiency was highest in 5000 ppm Ce treated pure aluminium panels (14.8%) and lowest in 1000 ppm (9.3%) whereas in M57S, 1000 ppm Ce treatment had shown a corrosion inhibition efficiency of 31.7% and in 5000 ppm it was 16.28%. The average salinity 4.08 ppt, pH 7.2, dissolved oxygen 4.05 mg/L and turbidity 27.5 NTU (Fig. 3) were recorded during the exposure period. In the aluminium panels exposed during second quarter (post monsoon) the corrosion rate increased significantly in both alumi-
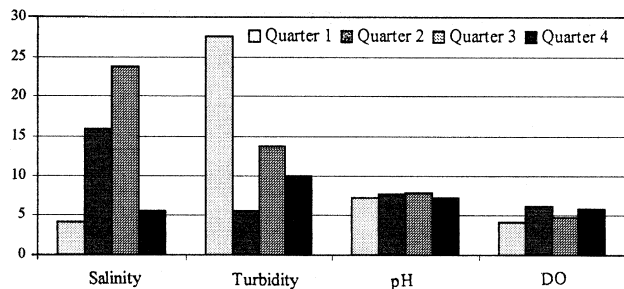
Fig. 3—Hydrographic parameters (mean values); salinity (g/L), DO (mg/L), pH and Turbidity (NTU)

nium which varied between 1.627–1.959 and 2.04–2.39 mpy respectively in sample A and B. The corrosion in sample B was aggressive than sample A and inhibition efficiency varied between 0–2.34%, maximum was with 5000 ppm Ce. The corrosion inhibition efficiency was reduced to 16.82% than previous season in 1000 ppm Ce treated sample A. The corrosion inhibition was absent in 2500 ppm Ce treated aluminium in both cases. The average salinity was 15.96 ppt, pH 7.69, dissolved oxygen 6.05 mg/L and turbidity 5.5 NTU. During the third quarter, Q3, (summer season) higher corrosion rate was recorded and it varied between 2.46–2.767 and 1.971–2.752 mpy in samples A and B, respectively. It is noted that the corrosion in sample B aluminium was very aggressive and in all the cases efficiency was reduced to about 35 % than control during this season. Whereas in sample A the 1000 and 2500 ppm Ce treated panels the efficiency increased by 10% and for 5000 ppm Ce treated panels by 5.5%. The average salinity, pH, turbidity, and dissolved oxygen was 23.77 ppt, 7.88, 13.8 NTU and 4.68 mg/L, respectively. The fourth quarter (pre monsoon) recorded corrosion rates between 0.79 to 1.007 and 0.85–0.997 mpy in sample A and B respectively. The results revealed that the corrosion rate was reduced significantly during this season. None of the treatments were efficient to control the corrosion except 5000 ppm Ce treated sample A (0.787 mpy). The average salinity, pH, turbidity and dissolved oxygen were 5.44 ppt, 7.21, 10 NTU and 5.8 mg/L, respectively. From the above results it is seen that the cerium treated panels gave good corrosion inhibition to a tune of 5.52 to 16.28% under actual field environment. April-May is supposed to be the peak summer season in Kerala, but the current year experienced unusual rainfall and fast changing weather which may be the reason for the reduced corrosion rate. The studies of Hinton *et al.*[8] have shown that higher con-
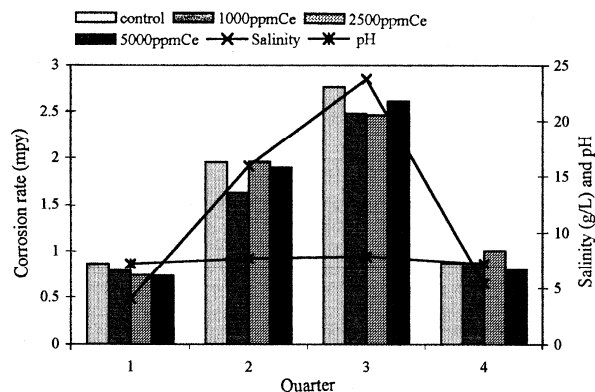

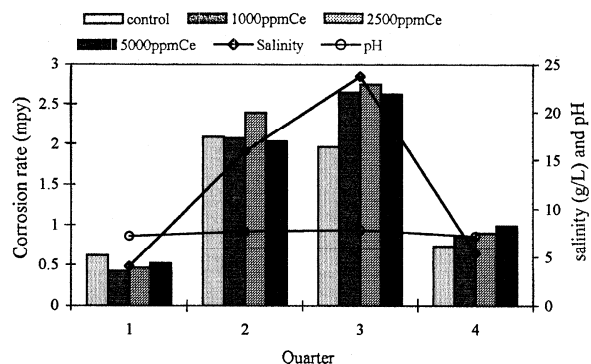Fig. 4—Corrosion rate of sample A and its correlation with salinity (g/L) and pH

Fig. 5—Corrosion rate of sample B and its correlation with salinity (g/L) and pH

centration of $CeCl_3$ does not have much effect on corrosion inhibition and it only produces a stabilization in the rate of corrosion. The studies of Gorman *et al.*[9] revealed that cerium precipitated from solution preferentially onto and around intermetallics suggesting that many of them acted as local cathodes. Ce was also deposited onto the surface as small precipitates containing Ce, Al and O. The studies carried out by Lu and Ives[10] on steel suggested the growth of CeO_2 surface films in both anodic and cathodic active surface areas, leading to corrosion inhibition. The correlation data revealed significant positive correlation with salinity and pH in both the aluminium (Figs 4 and 5). In the control samples the corrosion was aggressive during post monsoon and summer season. Even during these seasons the cerium treatment on aluminium gave very good corrosion inhibition. The results revealed that the higher concentration of cerium treatment on aluminium did not have significant corrosion inhibition. Bethencourt *et al.*[12] in their experiment with 0–10,000 ppm $CeCl_3$ concluded that

higher than 100 ppm concentration of cerium on aluminium can only produce a stabilization in the rate of corrosion and also increased levels of Ce on aluminium will enhance pitting resistance[8]. Cyclic polarization studies conducted by Bethencourt *et al.*[13] and Abelle *et al.*[14] revealed that addition of more lanthanide chlorides leads to an increase of pitting growth resistance.

Laboratory studies

Samples A and B treated with 1000 ppm cerium was exposed in 5, 10, 20, 25, 50, 100 and 200 ppt NaCl solution and the control panels without any cerium treatment also exposed simultaneously for measuring corrosion rate by weight loss method. The corrosion rate in sample A varied between 0.04 to 1.05 mpy and 0.363-1.462 mpy in Ce treated and control panels respectively. The corrosion rate of sample A steadily increased from 10 ppt and reached maximum at 50 ppt and decreased thereafter in both control and treated panels (Fig. 6). The cerium treatment significantly reduced the corrosion rate and it was 30-66% more efficient than the control sample. In the most corrosive medium (50 ppt) the cerium treatment reduced the corrosion rate of about 30.6% with respect to control. The lowest corrosion rate and maximum corrosion inhibition was recorded in 10 ppt NaCl solution. In sample B the corrosion rate varied between 0.126 – 0.200 and 0.056 – 0.509 mpy in control and treated panels, respectively. The higher corrosion rate recorded in control was in the salinity between 10-50 ppt and the cerium treatment on sample B had reduced the corrosion rate significantly in all the treatments (Fig.7) except at 5 ppt. In 5 ppt the cerium treatment aggravated the deterioration than the untreated one. The corrosion inhibition efficiency was maximum in 200 ppt (92.6%) and lowest was in 25 ppt (56.03%). Abelle *et al.*[11] have found that Ce treatment on AA5083, marine grade aluminium, have significant improvement in the behaviour of the alloy against both uniform and pitting corrosion. Comparative evaluation of untreated samples A and B revealed that the former corroded aggressively in the 25-50 ppt media and the latter corroded more in 10-50 ppt but the corrosion rate is lower than the sample A. Comparative evaluation of untreated sample B and sample A against cerium treated sample A (Fig. 8) revealed that the Ce treatment makes the sample A more superior than untreated expensive sample B.
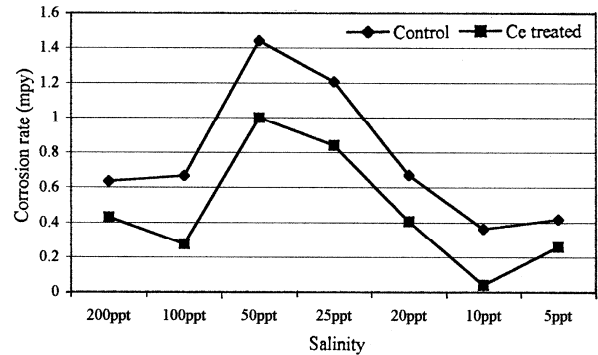

Fig. 6—Corrosion rate (mpy) of Ce treated and untreated sample A in different saline solutions
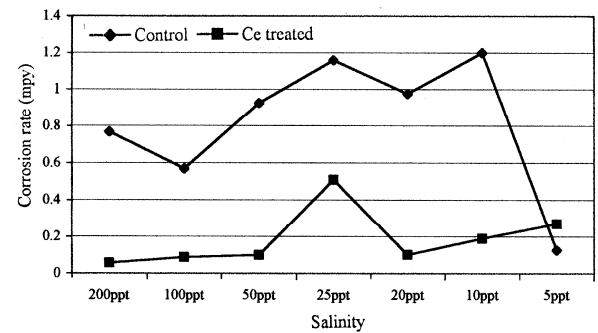
Fig. 7—Corrosion rate of sample B aluminium in different saline solutions
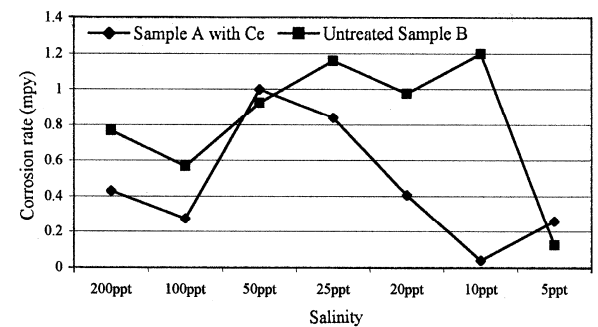
Fig. 8—Comparison of corrosion rate in 1000 ppm Ce treated sample A and control sample B aluminium

Voltammetry of retrieved samples

Several workers have already established the cathodic nature of cerium through polarization measurements[13]. Here an attempt was made to evaluate the changes in linear polarization data after the exposure of aluminium in different sodium chloride concentrations. The cerium treated samples retrieved after the laboratory exposure studies in different salinities were analysed by linear sweep voltammetry. The open circuit potential (OCP) for Ce treated samples A and B

Table 1—Linear sweep voltammetric parameters of retrieved aluminium after the laboratory experiment

Salinity (g/L)	Ce treated		Control	
	Sample A	Sample B	Sample A	Sample B
		OCP (V)		
5	-0.655	-0.708	-0.637	-0.710
10	-0.699	-0.681	-0.672	-0.626
20	-0.664	-0.673	-0.662	-0.647
25	-0.782	-0.656	-0.657	-0.661
50	-0.782	-0.755	-0.676	-0.721
100	-0.782	-0.722	-0.624	-0.641
200	-0.782	-0.702	-0.161	-0.666
		E_{corr} (V)		
5	-0.645	-0.664	-0.574	-0.722
10	-0.647	-0.651	-0.683	-0.604
20	-0.678	-0.654	-0.744	-0.646
25	-0.606	-0.645	-0.665	-0.661
50	-0.616	-0.698	-0.628	-0.705
100	-0.602	-0.712	-0.549	-0.651
200	-0.651	-0.691	-0.232	-0.652
		I_{corr} (A/cm^2)		
5	7.82×10^{-8}	2.92×10^{-7}	2.05×10^{-8}	1.07×10^{-7}
10	1.68×10^{-6}	1.85×10^{-7}	5.37×10^{-7}	3.27×10^{-8}
20	6.63×10^{-7}	1.63×10^{-7}	5.76×10^{-7}	6.06×10^{-8}
25	2.59×10^{-8}	1.31×10^{-5}	3.90×10^{-6}	9.85×10^{-8}
50	2.05×10^{-7}	1.99×10^{-7}	1.05×10^{-7}	2.05×10^{-7}
100	3.15×10^{-7}	1.49×10^{-7}	1.20×10^{-7}	2.74×10^{-8}
200	7.76×10^{-6}	1.57×10^{-7}	1.85×10^{-5}	2.12×10^{-7}
		R_p (Ω)		
5	1.19×10^5	7.78×10^4	4.75×10^5	2.41×10^5
10	2.61×10^4	8.10×10^4	5.49×10^4	5.91×10^5
20	3.50×10^4	3.45×10^4	8.68×10^4	5.94×10^5
25	3.09×10^5	7.72×10^3	1.39×10^4	5.46×10^5
50	1.84×10^5	2.26×10^5	5.82×10^4	2.05×10^5
100	6.85×10^4	4.06×10^5	4.35×10^5	1.63×10^6
200	2.31×10^3	2.95×10^5	7.82×10^3	2.48×10^5
		Corrosion rate (mpy)		
5	0.034	0.126	0.009	0.068
10	0.730	0.080	0.231	0.014
20	0.287	0.703	0.249	0.026
25	0.011	5.644	1.688	0.043
50	0.088	0.086	0.576	0.088
100	0.136	0.064	0.292	0.012
200	3.360	0.068	8.008	0.092

were varied between –0.655 to –0.782 and –0.656 to 0.755 V respectively and that of control panels was –0.161 to –0.676 and –0.626 to –0.710 V in sample A and B, respectively (Table 1). The OCP was higher in control panels than Ce treated aluminium in both the cases. The corrosion potential E_{corr} varied between –0.602 to –0.678, –0.232 to –0.744, –0.645 to –0.712 and –0.604 to –0.705V in Ce treated sample A, sample A control, Ce treated sample B and sample B control, respectively. No significant difference was found between the different saline environments but there was good variation between the cerium treated and control samples. Higher corrosion current was recorded in cerium treated panels compared to the control. The average values of corrosion current density are 1.532×10^{-6}, 3.39×10^{-6}, 1.63×10^{-7} and 1.06×10^{-7} respectively in Ce treated sample A, sample A control, treated sample B and sample B control respectively. The corrosion current density was 55% lower in treated sample A and in sample B the Ce treated panel recorded average I_{corr} 53% higher than control. These results further reveal that over all the Ce treatment had enhanced the corrosion in sample B panels. Higher corrosion current was recorded in untreated sample A and treated sample B at 25 ppt. At 200 ppt sample A was unstable since both treated and control had high I_{corr}.

The polarization resistance (R_p) was significantly higher in untreated sample B between 5-50 ppt salinity than Ce treated panels (Table 1). This is probably due to the reduced stability of cerium on aluminium in long term exposure. Control sample A recorded low R_p values in all the cases except 5 and 100 ppt salinity. This indicates the stability of cerium on aluminium even after 4 weeks. Among the retrieved panels Ce treated sample B and untreated sample A at 25 ppt showed considerably higher corrosion rate. The corrosion rate varied in Ce treated sample A and sample B as 0.038-3.36 mpy and 0.0644 - 5.644 mpy, respectively. Among control panels sample A recorded significantly higher corrosion rate 0.008 - 8.008 mpy and that of M57S was 0.11 - 0.916 mpy.

The corrosion rate of cerium treated sample B measured through weight loss method and potentiostatic methods was compared and found that both had nearly equal corrosion rate except at 25 and 50 ppt where instrumental corrosion rate was very high.

In the case of cerium treated sample A there was an irregular behaviour and potentiostatically highest corrosion rate was with 200 ppt.

Conclusion

The results obtained in the study suggest that cerium behaves as a cathodic inhibitor. It acts by blocking the cathodic sites in the metallic alloys. During the inhibition process, protective surface films incorporating the lanthanide element are formed. The cerium treatment on pure aluminium has significant corrosion inhibition under aggressive marine and laboratory environment. The cerium treated M57S was good under laboratory environment and highly susceptible to corrosion under marine environment. The pure aluminium with cerium is superior to untreated expensive marine grade M57S aluminium and can be used for marine purposes.

Acknowledgments

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