

studied for solar energy conversion.

Based on the investigation, the following composition and operating conditions are recommended:

Nickel sulfate ..	100	g/l
Cadmium sulfate .	15	"
Ammonium thiocyanate	10	"
Coumarin	0,1	"
Formaldehyde ...	0,1	ml/l
pH	4,5-5,0	
Temperature	20-30°C	
Current density	3-4	A/dm ²
Plating time ..	45-60	sec

The deposit immersed in 5% v/v hydrochloric acid for 20 to 30 seconds to develop its full black color. Based on this investigation, a 5 liter solution has been operated satisfactorily.

Further work is necessary to measure absorbance and emittance.

Corrosion studies indicated the stability of the coating. Thermal cycling tests also show the durability of the coating for use in higher temperature applications.

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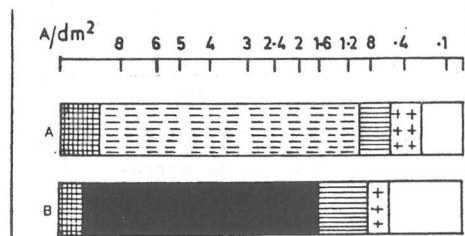


Fig. 8. Influence of acid etching a) before etching; b) after etching in 5% v/v hydrochloric acid 25 sec.

POLARIZATION CURVES OF THE ATMOSPHERIC CORROSION PHENOMENA

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INTRODUCTION

Since atmospheric corrosion is a slow process, natural tests for the direct measurements of corrosion require very long periods of time.

Many researchers have striven to find an alternative electrochemical approach to replace the classical gravimetric procedures. The pioneer works of Tomashov (1) and Sereda (2) regarding the design and use of multilamellar electrochemical cells known as EACM (Electrochemical Atmospheric Corrosion Monitors) are worth mentioning.

A great deal of progress in this line is, nevertheless, due to Mansfeld (3-5) and to Swedish and Norwegian research workers (6-8) who have forwarded an empirical relationship between the current flowing through the cell and the atmospheric corrosion rate.

MATERIALS AND METHODS

With the usual EACM (figure 1a) use is made of the dual electrode technique for determination of the polarization resistance, R_p (9). It is assumed that the imposed polarization, ± 10 mV, is equally distributed between anodes and cathodes, since they are of the same material. For higher polarizations, however, the sharing between anodes and cathodes of the ΔE imposed by the potentiostat is unknown and plotting of polarization curves is impossible. Some additional information is thus lost which could be valuable for a better understanding of the atmospheric corrosion phenomenon.

In an attempt to overcome the limitation mentioned, the design of the usual EACM was modified, a central metal foil is left unconnected to the others, so that it can serve as a reference electrode not polarised by the potentiostat during the measurement (figure 1b). With the new EACM the 3-electrode technique can be used, in order to apply the high polarizations required to obtain polarisation curves.

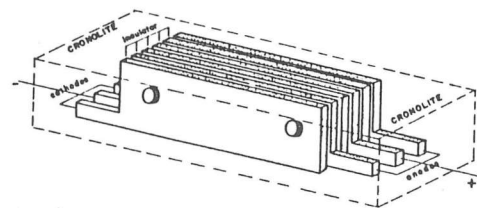


Fig. 1a.- Appearance of usual EACM after assembly.

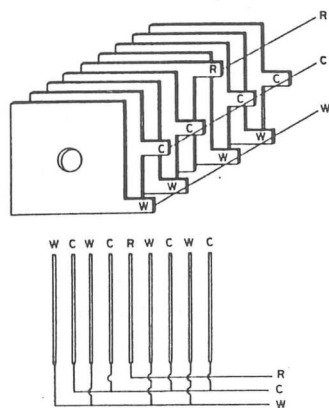


Fig. 1b.- Schematic layout of the new EACM.

R Reference electrode
C Counter electrode
W Working electrode

very rapid reduction in the kinetic of corrosion taking place by the formation of protective layers in some cases (figure 2) and the appearance of rupture potentials with Cu and Zn monitors by medium or high polarizations (figure 3).

The sharply decrease of the corrosion rate in figure 2 is probably due to the formation of protective corrosion products and the environment deactivation caused by SO_4^{2-} removal to form corrosion products.

The anodic polarisation curves were obtained by EACM of Al, Cu, Fe and Zn subjected to the action of 400 μm thick layers of water and 10^{-4} , 10^{-3} , 10^{-2} and 10^{-1} $\text{N.H}_2\text{SO}_4$ solutions. Polarisation curves were also plotted for monitors with adsorbed moisture invisible layers precorroded in the above mentioned solutions.

The R_p values and from these the instantaneous corrosion rate were determined by periodical triangular polarisations at a rate of 10 mV/min (potential increasing during one min., and decreasing the next min., as shown the figure 2).

RESULTS AND DISCUSSION

With the EACM it is possible to study the initial moments of the corrosion phenomenon. So as been shown, for instance, a

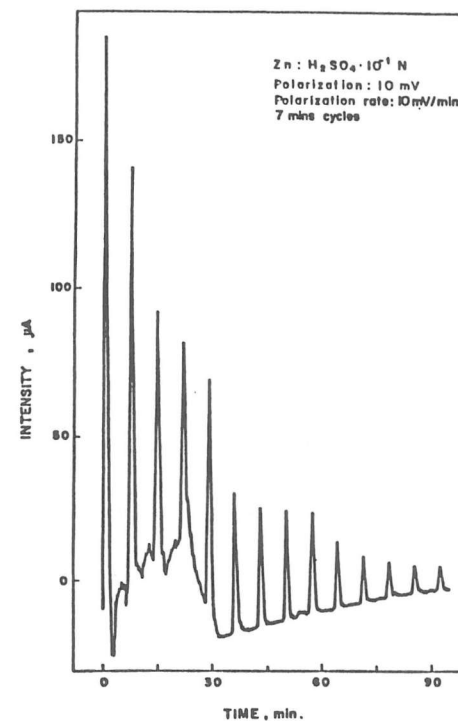


Fig. 2.- Rapid reduction in the kinetic of corrosion by the formation of protective layers.

Rupture potentials as those of figure 3 suggest a more or less perfect protection of the nonferrous metal by the corrosion products and a controlling step of the atmospheric corrosion phenomenon which does not occur directly on the metal surface, but on a more external interphase between two corrosion products substrates, or at the atmosphere/corrosion products interphase.

It is emphasized the existence of some rupture potentials, more or less evident, depending on the conditions, with Cu and Zn EACM's (figure 2). The value of these rupture potentials depends not only of the characteristics of the aggressive medium and the nature of the metal, but also on the exposure time and the thickness of electrolyte layers.

That no E_r potentials are found in the Al EACM may be due to the fact that its passivating layers are more resistant and require higher polarizations than those here applied, of +300 mV. 2/1

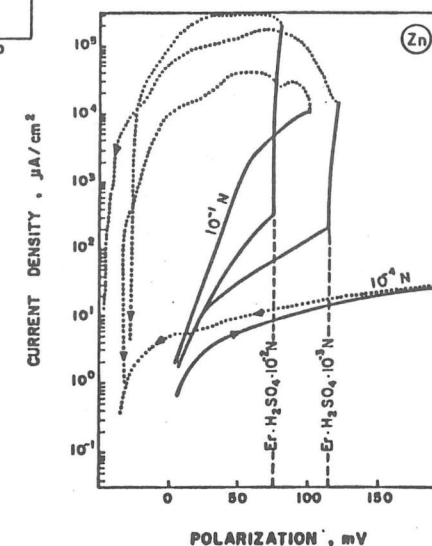


Fig. 3.- Appearance of rupture potentials for Zn monitors with H_2SO_4 400 μm thick solution layers. The E_r appear to increase on decreasing H_2SO_4 concentration.

CONCLUSIONS

Specially designed electrochemical multilamellar cells where a central foil is insulated so that it acts as a reference electrode, have enabled the plotting of polarization curves, representative of the atmospheric corrosion phenomenon.

Due to speed of the measurements, which provide almost instantaneous corrosion rates, the method is ideal for an analysis of each corrosion factor separately, which may provide a valuable guide for a better understanding of the corrosion processes and the establishment of their mechanism.

It is possible to obtain polarization curves with adsorbed moisture layers even in the absence of visible electrolyte layers.

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