

INSTANTANEOUS RATE OF ATMOSPHERIC CORROSION  
OF DIFFERENT METALS BY MEANS OF GALVANIC CELLS AS A  
MEASUREMENT OF THE ENVIRONMENTAL AGGRESSIVENESS

A. CIGADA, B. MAZZA, P. PEDEFERRI, G. RE and D. SINIGAGLIA

Centro di Studio sui Processi Elettrodici del CNR - Istituto di Chimica  
Fisica, Elettrochimica e Metallurgia del Politecnico - P.za L. da Vinci 32

20133 Milano ITALY

Following up a previously undertaken research work, a new type of galvanic macrocouple has been developed for continuous and instantaneous monitoring of the rate of atmospheric corrosion. The macrocouple (fig. 1) consists of a disk and a mesh of different materials. A layer of salts of given chemical composition was interposed between these items. When the relative humidity is sufficiently high, an electrolytic contact is established between the base metal and mesh; hence current flows and with the aid of a zero resistance ammeter the rate of corrosion of the less noble metal can be measured.

The various couplings and intermediate layers investigated are given in table 1.

A first set of tests were carried out by coupling bronze and gold. An artificial patina was used as intermediate layer, consisting of basic copper carbonate with the addition of constant quantities in weight of different salts which were chosen so as:

- to cover a wide range of degrees of hygroscopicity;
- to present different inhibiting properties;
- not to supply ions capable to interfering with the electrode processes by their oxidising or reducing.

Hence magnesium, sodium and potassium chlorides, and potassium sulphate were chosen. These salts have hygroscopic properties which decrease in the order given above and have different activating or inhibiting action on the electrode processes.

The main results from these tests are as follows :

- a) The galvanic current density (table 1) depends on relative humidity and on whether chlorides are present or not in the intermediate layer: current density grows with increasing relative humidity, and becomes appreciably higher (by about three orders of magnitude) if chlorides are present. Furthermore, these results show good reproducibility.
- b) Chloride addition also favours absorption of atmospheric humidity, hence maximum value of galvanic current is rapidly established in the macrocouple. Subsequently (while in the presence of just carbonate, the corrosion process is inhibited as the macrocouple current shows a steep drop in time) the presence of chlorides causes the galvanic current to remain at high and constant values for relatively long periods of time. In the presence of potassium sulphate, instead, absorption kinetics is slower, but the galvanic current, after reaching maximum, drops quite sharply.

c) Anodic and cathodic voltage measurements with circuit both open and closed, show that inhibition is always confined to the cathode. More especially, on allowing the macrocouple to function with an initially non-inhibited cathode, it can be seen that in the presence of carbonates with or without sulphate addition, cathodic inhibition is established within very brief times, while addition of chlorides considerably impairs this tendency.

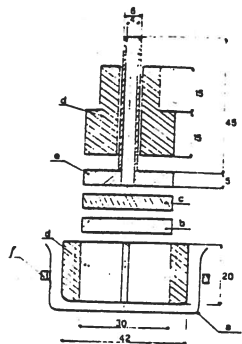
Besides furnishing interesting data concerning the influence of different factors on the corrosion of gold gilded bronze works of art, this method also seems suitable for monitoring atmospheric aggressiveness, in the case of intermediate layers containing chlorides: in fact, the macrocouple then generates sufficiently high and steady currents after a brief initial transient.

The remaining couplings, which used carbon steel and Cor-Ten disks were chosen in order to evaluate application possibilities of couplings with higher driving forces. A practically inert ( $\text{CaCO}_3$ ) and non-hygroscopic patina with addition of  $\text{NaCl}$  or  $\text{K}_2\text{SO}_4$  was used as intermediate layer.

In the tests carried out by coupling carbon steel and Cor-Ten to a cathode mesh (Cu, Au) in the presence of  $\text{NaCl}$ , the galvanic currents essentially coincided and were with an order to magnitude higher than that in the preceding case for bronze. More interesting regarding the selectivity of the method were, instead, the tests with  $\text{K}_2\text{SO}_4$  in which the behaviour of Cor-Ten and carbon steels appears to differ in that the former exhibits lower corrosion currents.

#### References

- Mazza B. et al., *Corrosion Science*, 17, 535-541 (1977)  
Sereda P.J., *ASTM Bulletin*, 228, 53-55 (1958); *ibidem*, 238, 61-63 (1959);  
*ibidem*, 246, 47 (1960)  
Tomashov N.D., *Theory of Corrosion and Protection of Metals*, MacMillan, New York (1966)  
Kucera V. and Mattson E., *Corrosion in Natural Environments*, ASTM STP 558, 239 (1974)  
Mansfeld F. and Kenkel J.V., *Corrosion Science*, 16, 111-122 (1976)



- a) wire mesh
- b) electrolyte
- c) disk
- d) threaded holder
- (Perspex)
- e) copper lead
- f) clip

Lengths, mm

Figure 1 - Testing assembly

DISK	ELECTROLYTE	WIRE MESH	RH (%)	T (C)	$i_{init. max}$ ( $\mu A/cm^2$ )	$i_{24 h_2}$ ( $\mu A/cm^2$ )	BEHAVIOUR
brass	$CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ + $MgCl_2$ 10%	gold	31.5	30	-	$4.3 \times 10^{-3}$	regular
			59.5		-	0.07	"
			85.0		-	0.69	"
			96.25		-	1.7	"
brass	$CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ + $NaCl$ 10%	gold	31.5	30	-	$1.6 \times 10^{-3}$	regular
			59.5		-	0.025	"
			85.0		-	0.88	"
			96.25		-	14.0	"
brass	$CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ + $KCl$ 10%	gold	31.5	30	-	$0.7 \times 10^{-3}$	regular
			59.5		-	0.22	"
			85.0		-	0.25	"
			96.25		-	1.5	"
			100		-	5.8	"
brass	$CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ + $K_2SO_4$ 10%	gold	31.5	30	-	-	regular
			59.5		-	$0.1 \times 10^{-3}$	"
			85.0		-	$0.6 \times 10^{-3}$	"
			96.25		-	$3.9 \times 10^{-3}$	"
C-steel	$CaCO_3 + NaCl$ 1%	gold copper	96	25	470 260	54 58	regular "
C-steel	$CaCO_3 + K_2SO_4$ 1%	gold copper	96	25	0.79 0.14	0.34 0.06	irregular "
C-steel	$CaCO_3 + K_2SO_4$ 10%	gold copper	96 96	25	10 1.3	6 1.2	irregular "
Cor-Ten	$CaCO_3 + NaCl$ 1%	gold copper	96	25	560 320	58 70	regular "
Cor-Ten	$CaCO_3 + K_2SO_4$ 1%	gold copper	96	25	0.24 0.07	0.12 0.05	very irr. "
Cor-Ten	$CaCO_3 + K_2SO_4$ 10%	gold copper	96	25	0.70 0.46	0.39 0.05	very irr. "
ENVIRONMENT: chromatographic air							
Relative humidity over saturated solutions at 30 C $MgCl_2$ 31.5; $NH_4NO_3$ 59.5; $NaCl$ 75.0; $KCl$ 85.0; $K_2SO_4$ 96.25							

Table 1 - Tested couplings and main results