CHAPTER-III

INSTRUMENTATION TECHNIQUES AND EXPERIMENTAL PROCEDURES

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INSTRUMENTATION TECHNIQUES AND EXPERIMENTAL PROCEDURES

SECTION - I INSTRUMENTATION METHODS :

A) OPEN CIRCUIT POTENTIAL MEASUREMENTS (OCP) :

OCP of carbon steel specimens in different GV solutions was measured by digital multimeter (Aplab instruments) in millivolts versus saturated calomel electrode (SCE). Steady state potentials were noted down, and tabulated to find out shift in OCP with the addition of various inhibitors and at various parameters.

The digital multimeter, which was used for measuring OCP has a high input impedance to the order of 10^{10} Ohms to minimize current drawn from the system during measurements. Sensitivity of the instrument is 1.0 mV over a potential range of 200 mV to 1999 mV.

In some cases, the OCP was continuously measured at regular intervals of time and at increasing temperature and plots were drawn for OCP versus temperature/time.

B) POLARIZATION TECHNIQUE (1, 2, 3) :

Polarization study was carried out using 'Petrolite' Model 4100' instrument. The circuit diagram for the same is given in Figure- 1. After the attainment of steady state potential, the carbon steel specimens in different GV solutions were subjected to polarization scan over a potential range of - 850 millivolts to + 600 millivolts at a scan rate of 10 mV/sec. using 'Petrolite' made 'Potentiodyne Analyzer'.

Aeration of 100 ml/min of air was passed into the system using an electric bubbler as explained elsewhere. Bubbling was carried out away from the test specimen so as not to disturb the electrolytic double layer on the specimen surface.

Polarization was started from a highly cathodic side to obtain (a) a cleaner surface of the specimen, (b) Zonal characteristics in a wider range of potentials (zonal characteristics depicts free corrosion zone, flade potential zone, passivity and transpassive zone), (c) tafel slopes.

Before the polarization experiments were commenced, OCP of the CS in the system was noted down for comparative and confirmatory purpose with the value obtained from DC microvolt meter.

XY plots on semi-logarithmic graphs was obtained and from this plots tafel slopes were derived by extrapolation of cathodic and anodic line of Corrosion potential (Ecorr). Anodic tafel (Ba), Cathodic tafel (Bc) and Corrosion current (I Corr) values were obtained from these lines.

For confirmation of these values and for calculating polarization resistance (Rp) values and corrosion rates, potential and current values on the tafel region were fed to a computer using a programme called Beta Crunch Version 2.0. (4).

From these values % inhibitor efficiency was also calculated.

From the polarization plots, critical current density (icc), passive current density (ip), primary passive potential (Epp) and passive potential (Ep) values were noted down.

Also, the zonal characteristics depicting free corrosion, flade potential and passivity zone potentials were found out from these plots. Different plots were drawn depicting these potentials versus OCP of CS in the system.

C) AC IMPEDANCE TECHNIQUE (5, 6, 7) :

An electrochemical cell can be represented by a purely electronic model since an electrode interface during an electrochemical reaction is analogous to an electronic circuit consisting of resistors and capacitors. This allows, to characterize the electrochemical system in terms of its 'equivalent circuit'.

In a system, where C S Material is passivated by chemical addition, the circuit can be represented as in Figure - 3A :

where

Rp is the polarization resistance at the electrode/ solution interface.

R_Ω is the uncompensated resistance between the working and reference electrode.

Cdl is double layer capacitance at the electrode/ solution interface.

Rp and Cdl can be used to calculate the corrosion rates and inhibitor efficiency.

Once the experiment is complete, the raw data at each measured frequency consists of :

(a) the real component of voltage E' (b) the imaginary component of voltage E" (c) the real component of current I' (d) the imaginary component of current I".

From these data, the phase shift of the response, Θ, and the total impedance, Z, for each applied frequency is found out.

A variety of formats can be used to plot this data :

1) Nyquist plot :

It is also known as Cole-Cole plot or a complex impedance plane diagram. The imaginary component of impedance (Z") is plotted versus the real component of impedance (Z') at each excitation frequency.

The Schematic diagram of this plot is shown in Figure - 3B.

2) Bode plot :

In the bode plot, log (absolute impedance, /Z/ is plotted versus log f. At intermediate frequencies, the 'break-point' of this curve should be a straight line with a slope of -1. Extrapolating this line to the log/Z/ axis at w = 1 (log w = 0) yields the value of Cdl from the relationship.

$$/Z/ = 1/Cdl$$

The bode plot is a useful alternative to the nyquist plot to avoid the longer measurement time associated with low frequency Rp determinations. The plot is also desirable when data scatter precludes adequate fitting of the nyquist semi circle.

The schematic diagram of the bode plots is given in Figure-3C.

AC impedance instrumentation :

368-1 model (EG & G, USA) AC impedance system comprises of :

(1) model 173 potentiostat galvanostat (2) model 276 interface plug-in (3) Apple IIe microcomputer and software system was used for the study as detailed in Figure - 2.

These three equipments are used in Fast Fourier Transform (FFT) technique for corrosion studies by low AC frequencies.

In FFT, a mixture of excitation waveforms of varying frequencies is applied to the test system simultaneously. This complex waveform is actually an algebraic sum of many individual waveforms of equal amplitude, each having a different frequency and phase characteristic.

Root mean square value of FFT waveform is approximately 35% of the peak amplitude, (for a simple sine wave it is 70% of the peak amplitude) thus the FFT waveform subjects the electrochemical test system to less severe perturbations than a series of sine waves would. Major advantage of FFT technique is that low frequency data can be obtained faster than with conventional methods, thus minimizing polarization times. At high frequencies, only the uncompensated resistance (RΩ) contributes to the real portion of impedance, while at low frequencies, the polarization resistance (Rp) also contributes to this measurement.

FFT excitation waveform is applied to the test system via the potentiostat and interface module. The interface also functions as a response measurement device. It transmits the raw data in digital form to the Apple IIe for subsequent reduction and display.

The entire experiment, from definition to data display and evaluation is done by Model 368 dedicated software package.

Hard Copy of the plots were taken on a FX-105 printer connected to Apple IIe computer. Data is available in both tabular and graphic form.

Rp, R_Ω and Cdl values were calculated from these plots. In most of the experiments R_Ω was found to be less than 10 Ohms and therefore was neglected. From these values corrosion rate and inhibitor efficiency was calculated using Ba and Bc values from polarization curves.

SECTION - II : EXPERIMENTAL PROCEDURE :

A) SAMPLE PREPARATION (8) :

Carbon steel working electrodes were prepared from a 2.5 cm length of 1.0 cm diameter rod stock. The chemical analysis of the same is given in Table - 1. The specimen was drilled and tapped for fitting into the holder. A leak proof electrode holder was made from proper compression between the electrode, gasket and PTFE coated MS rod. Before experimentation the specimen surface was prepared on a belt surfacer. The adhering mill scales were removed by grinding succesively from 60 to 220 grit paper to achieve a uniform finish. Each specimen was polished till previous coarse scratches were removed. Measurements were taken to calculate the exposed surface area. It was then cleaned with acetone to remove any grease or other impurities and dried by air blower, just before commencement of the experiments.

B) POLARIZATION CELL

b.1) Auxillary electrode :

Platinum electrodes were prepared from a high purity rod stock having 1.0 cm diameter, drilled and tapped for fitting into the holder. Surface of the rod was platinized in order to decrease the hydrogen overpotential and to get increased surface area. A leak proof assembly was obtained by proper compression between electrode and PTFE gasket. Platinizing was accomplished first by cleaning the surface in hot aqua regia, washing and drying and then immersing the electrodes in a solution of 3% platinic chloride and 0.02% lead acetate and electrolyzing at 40 to 50 mA/ cm^2 for five minutes. The polarity was reversed every minute. Occluded chloride was removed by electrolyzing in 10% sulfuric acid solution for several minutes with reversal of electrodes every minute. Electrodes were rinsed thoroughly and stored in double distilled water for further use.

b.2) Calomel electrode :

Saturated calomel electrode with a controlled rate of leakage of about 3 microlitre/ hour was used. Potential of the calomel electrode was checked periodically to ensure accuracy. SCE was kept at around 30 Deg. C. by passing water continuously for cooling purpose through the cooling system given in luggin probe.

b.3) Standard polarization cell :

A one litre, round bottom flask, modified by the addition of various necks for introduction of electrodes, gas inlet and outlet and thermometer was used (Figure-4). Luggin probe salt bridge separates the bulk solution from the saturated calomel reference electrode and the probe tip was adjusted to bring it in close proximity with the working electrode.

C) TEST SOLUTION PREPARATION :

c.1) GVSL solution :

Giammarco Vetrocoke (GV) solution for all the experiments was prepared in such a way that the carbonation index is always slightly higher than 1.0. This gives the GV solution a semi lean character and represents the plant GV semi lean solution.

151 gms of A R potassium carbonate, 91 gms of A R Potassium bicarbonate, 50 gms of A R potassium hydroxide and 115 gms of commercial grade arsenic trioxide is weighed accurately on a Sartorius top loading balance up to an accuracy of 0.01 gms. This is dissolved in 700 ml demineralized water in 2 litre beaker at 70 Deg. C.-80 Deg. C. to obtain a blackish tinged solution. A clear solution is obtained when this solution is filtered through Whatman filter paper NO. 41 using a buchner funnel by vacuum filtration which removes

all the black tinge. The solution is made to one litre by demineralized water.

c.2) GVSL solution with antimony trioxide :

Antimony trioxide is scarcely soluble in GV solutions. Hence this solution is prepared in two steps :

a. Preparation of GVSL solution as in c.1 but without potassium hydroxide.
b. Preparation of antimony trioxide in potassium hydroxide solution.

50 gms of A R potassium hydroxide is taken in a 500 ml beaker. Solution is heated to about 70 Deg. C. on a hot plate. Required quantity of A R antimony trioxide is weighed on a Sartorius microbalance up to an accuracy of 0.0001 gms and is added to the hot potassium hydroxide solution. Contents are stirred gently to get a clear solution.

Solution No. (b) is then added to solution (a) and made to one litre using demineralized water.

c.3) Addition of ferric ions to GVSL solution containing antimony trioxide :

Preparation of GVSL solution with antimony trioxide is obtained by following c.2 (a and b) :

35.11 gms of A R ferrous ammonium sulfate is dissolved in distilled water and made to 500 ml in a volumetric flask to get a solution containing 1 ml=10 mg ferrous ions. (A small quantity of concentrated sulfuric acid is added to this solution). This solution will be the stock solution. Required quantity of ferrous ions is taken from the stock solution using a graduated pipette and added to solution c.2 (a and b) and then is made to one litre.

c.4) Plant GV Solutions :

Plant GV solutions were collected on specific dates, a portion of which was analysed for various constituents. Table-2 depicts chemical analysis of the solutions.

c.5) Preparation of GVSL solution containing vanadium pentoxide:

1 gm of A R vanadium pentoxide was weighed accurately and the powder was directly added to the hot GVSL solution (c.1) and made to one litre with demineralized water to get a solution containing 0.1% vanadium pentoxide.

Addition of ferric ions to this solution was carried out by pipetting out required quantity from ferrous ammonium sulfate stock solution and adding it to vanadium pentoxide containing GVSL solution and making it to one litre.

c.6) Preparation of GVSL solution containing potassium dichromate:

7 gms of A R potassium dichromate was weighed accurately and was directly added to the hot GVSL solution (c.1) and made to one litre with demineralized water to get a GVSL solution containing 0.7% potassium dichromate.

Addition of ferric ions to this solution was carried out as done previously.

c.7) Preparation of GVSL solution containing ammonium metavanadate, potassium antimonyl tartrate and tartaric acid :

1 gm of A R ammonium metavanadate, 1 gm of A R potassium antimonyl tartrate and 0.1 gm of A R tartaric acid was weighed accurately and separately and then added one by one to hot GVSL solution (c.1) and made to one litre to get a GVSL solution containing 0.1% ammonium metavanadate, 0.1% potassium antimonyl tartrate and 0.01% tartaric acid.

Addition of ferric ions to this solution was carried out as done previously.

c.8) Preparation of GVSL solution containing ammonium metavanadate and sodium nitrite :

1 gm A R ammonium metavanadate and 2.5 gms A R sodium nitrite was weighed accurately and separately and then added to hot GVSL solution (c.1) and made to one litre with demineralized water to get GVSL solution containing 0.1% ammonium metavanadate and 0.25% sodium nitrite.

Addition of ferric ions to this solution was carried out as done previously.

c.9) Preparation of GVSL solution containing sodium silicate and potassium dichromate :

6 gms of A R sodium silicate and 0.2 gm A R potassium dichromate was weighed accurately and separately and then added to hot GVSL solution (c.1) and made to one litre with demineralized water to get a GVSL solution containing 0.6% sodium silicate and 0.02% potassium dichromate.

Addition of ferric ions to this solution was carried out as done previously.

D) AERATION TECHNIQUE :

Filtered air was passed continuously, into the polarization cell, using an electric bubbler, commonly used in domestic aquarium. Bubbling of air was carried out away from the test specimen so as not to disturb the electrolytic double layer on the test specimen surface.

E) PEARLITE LEACHING STUDIES (9, 10) :

e.1) Test specimen :

Carbon steel specimens were prepared from 0.5 M length of 40 mm thickness plate stock. Each specimen was drilled and tapped for fitting into a holder and a leak proof assembly was obtained by proper compression between the electrode and PTFE gasket.

e.2) Surface preparation :

Surfaces of the samples thus obtained were initially taken on belt surfacer to remove hard mill scales with 60 grit carbide paper.

These surfaces were then ground by sequential procedures to 180, 240, 320, 400, 600 and 1000 grit polishing papers and later on up to one micron diamond paste on imported Sclvyt polishing cloth on a lapping machine using kerosene as vehicle. Samples were polished on all edges to maintain uniform surface. Subsequently these surfaces were etched in 2% Nital (con. nitric acid in ethanol). Repolishing was done to remove the disturbed metal in three stages. Final surfaces subjected to GVSL solution were sufficiently polished so as to remove evidences of mild etching during this exposure.

In effect this surface was polished without any passivation layer to study effect of GVSL on leaching of pearlitic phase of the CS material.

e.3) Preparation of GVSL solution :

GVSL solutions taken for study were prepared by the procedure followed in (c.1.2.3).

e.4) Exposure assembly :

Flat bottomed resin flask with one litre capacity having five necked cover was used for exposing the specimens to GVSL solutions. These necks are used for the introduction of air and venting electrode (working) and thermometer. Solution was kept at 85 Deg. C. ± 1 Deg. C. temperature. Twenty days exposure was given to each specimen. The solution was aerated at a rate of 1 ml per min.

After the exposure of 480 hrs the specimens were washed in flowing DM water to remove adhering solution and then with acetone and dried by hot air.

e.5) Microstructure observations procedure :

These specimens were moulded in Araldite leaving one larger surface exposed. Cold mounting was chosen in order to eliminate temperature effects, if any, of hot moulding techniques.

Exposed surfaces were viewed at magnifications ranging from 100-600 times on a wide field metallograph equipment.

Test specimens were designated as follows :

1. Carbon steel metallorgaphically polished up to 0.017 micron using alumina on a lapping disc and etched in 2% nital to reveal general microstructure for metallurgical comparison with GVSL exposed specimens as mentioned below.

2. CS exposed to blank GVSL solution.

3. CS exposed to GVSL solution with an addition of 0.1 wt. % antimony oxide and 0.03 wt % ferric ions.

4. CS exposed to GVSL solution with an addition of 0.15 wt % antimony oxide and 0.03 wt % ferric ions.

Subsequent to viewing in bright field for establishing leaching of a particular phase, if any, and in dark field to establish localised effects of GVSL solution with and without additives on CS, photomicrographs were recorded on a 35 mm Konica camera in coloured print to eliminate recording errors as would be the case in black and white print.

TABLE-1 : CHEMICAL COMPOSITION OF CS MATERIAL

% C	% P	% Si	% Mn	% S	% Fe
0.20	0.022	0.15	0.60	0.04	Rest

TABLE-2 : CHEMICAL ANALYSIS OF DIFFERENT GV SOLUTIONS

GV Solution	K_2CO_3 g/l	$KHCO_3$ g/l	As_2O_3 g/l	As_2O_5 g/l	KOH g/l	Iron mg/l	Carbonation Index
Lean	290	28	118.3	25.8	-	52	1.06
Semilean	220	59.16	114.7	26.9	-	56	1.15
Rich	102.8	237.39	115.2	24.9	-	43	1.62
Lab Made SL	151.2	91	115	-	50	-	1.00

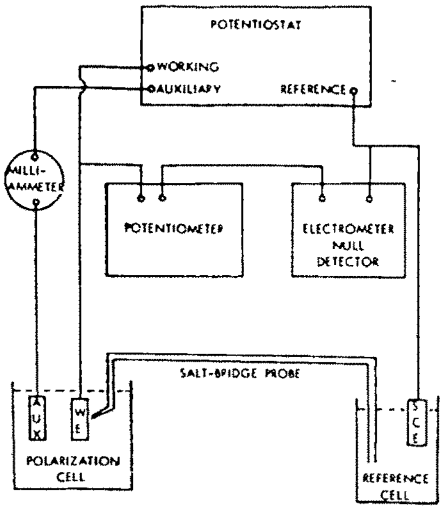


FIG.1 : SCHEMATIC POTENTIODYNAMIC POLARIZATION WIRING DIAGRAM

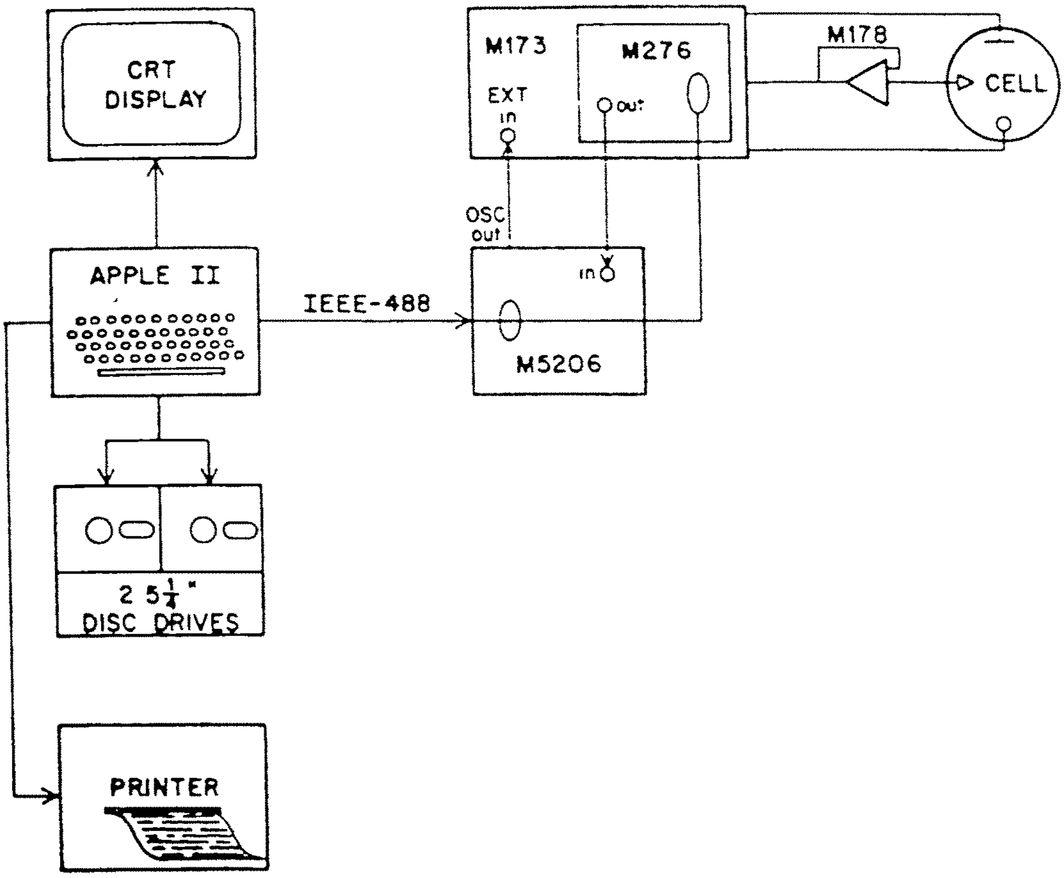


FIG.2 : SCHEMATIC ALTERNATING CURRENT IMPEDANCE WIRING DIAGRAM

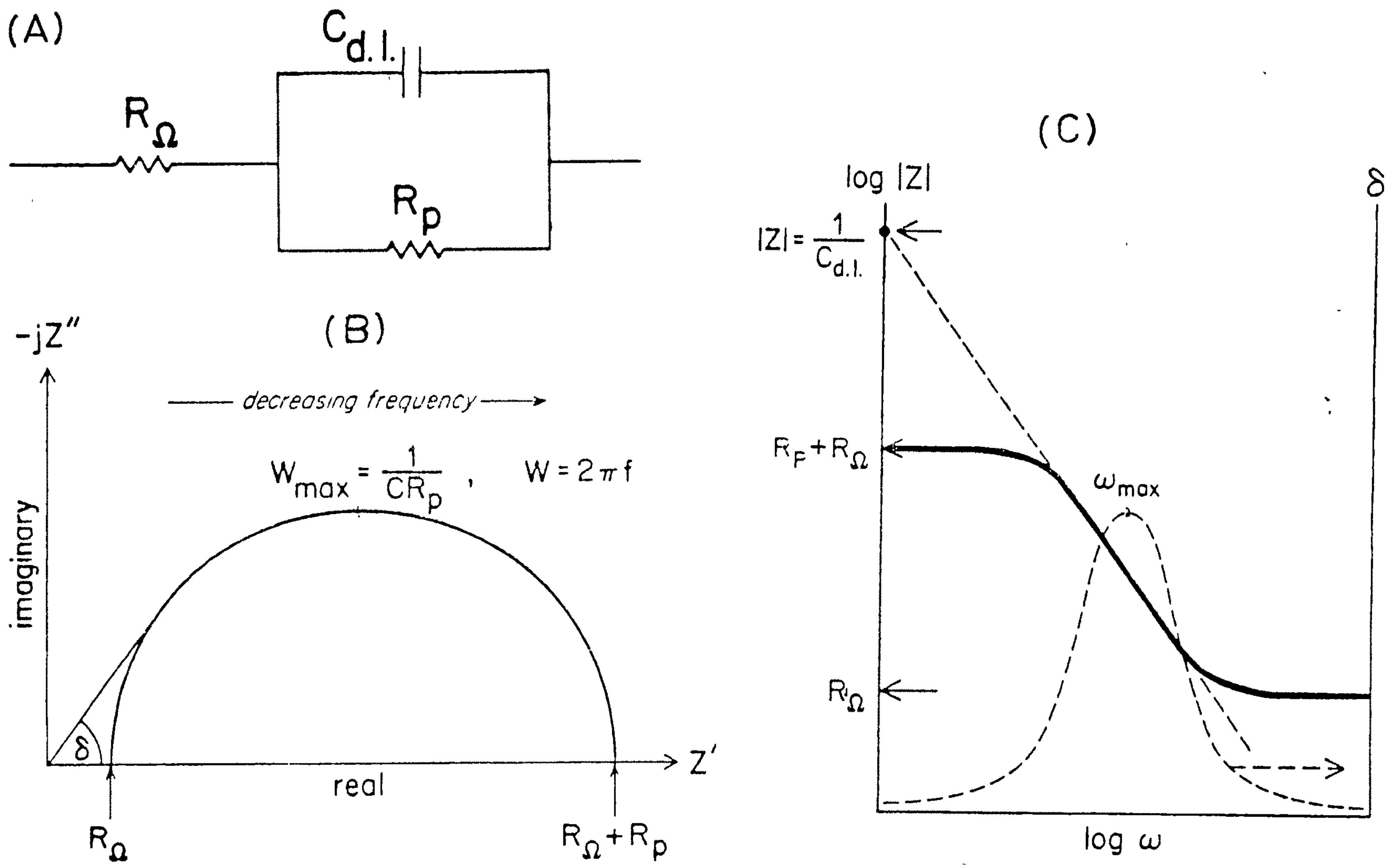
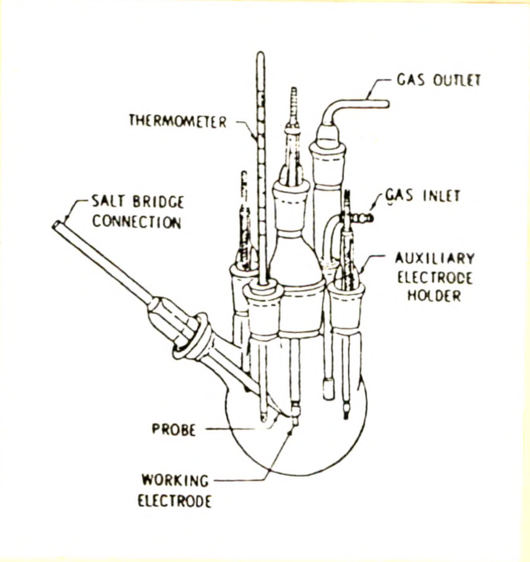


FIG.3 : A) EQUIVALENT CIRCUIT FOR CORROSION OF STEEL IN INHIBITED AQUEOUS SOLUTION
B) A TYPICAL NYQUIST PLOT
C) A TYPICAL BODE PLOT



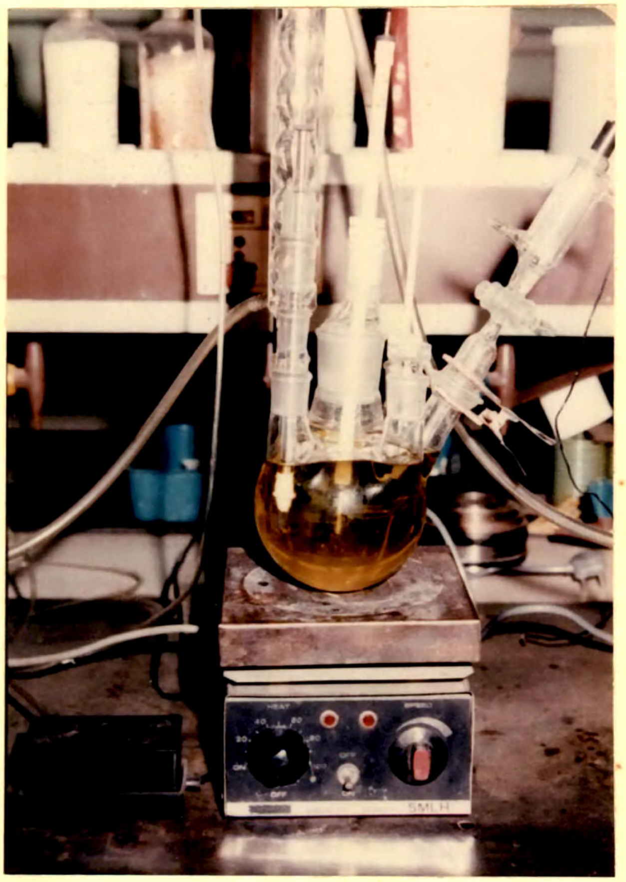


FIG &
PLATE 4 : STANDARD POLARIZATION CELL - EXPERIMENTAL SETUP USED IN POLARIZATION AND AC IMPEDANCE STUDIES.

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