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The Polarization and corrosion characteristics of ferrosilicon alloys used as a heavy medium

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2.1.2 Masking out of the Test Area and Development of a Suitable Test Cell

Due to the extreme brittleness of the alloy, many specimens showed cracks on polishing for specimen preparation. This made impossible the use of the full rod cross section as a test area as was initially planned. Effective masking out of a test area proved to be exceptionally difficult. Various masking materials were tried, including petroleum jelly, bee's wax, paraffin wax and mixtures of these, coumarone resin, rubber solutions and LACOMIT marking out lacquer. None of these proved successful because penetration of electrolyte under the edge of the screening material occurred in every case. Severe crevice corrosion took place along these edge. ecause of the setting up of a differential aeration cell.

Passivated ferrosilicon would be noble relative to the imperfectly passivated material, with the latter forming the anode under the masking material.

Numerous polarization tests were performed on specimens marked out with the materials mentioned above, using the test cell illustrated in Figure 4. Test curves were not acceptably reproducible.

On account of these difficulties, the test cell shown in Figures 5 and 6 was developed. With this cell, creeping of the electrolyte was eliminated and reproducibility of results was greatly improved. A capillary tube was used for oxygen bubbling. When adjusted from above in the contact tip of the cell, about one centimeter above the specimen surface, it gave "aeration" of the electrolyte close to the test surface. At the same time there was efficient circulation of the electrolyte. The circular area marked out by the line contact of the "TYGON" tubing, had a diameter of 9 millimeters. This test cell made possible the testing of any specimen with the minimum of preparation - only about one square centimeter being required.

2.1.3 Reference and Auxiliary Electrodes

The simplicity of the test cell and its operation, made feasible the concurrent testing of a number of specimens. An electrode assembly containing two platinum wire polarizing electrodes and one silver/silver chloride reference electrode, was constructed as shown in Figure 5, with an insulated cage protecting the electrodes from accidental damage. Movement of this unit from one test cell to another required very little time.

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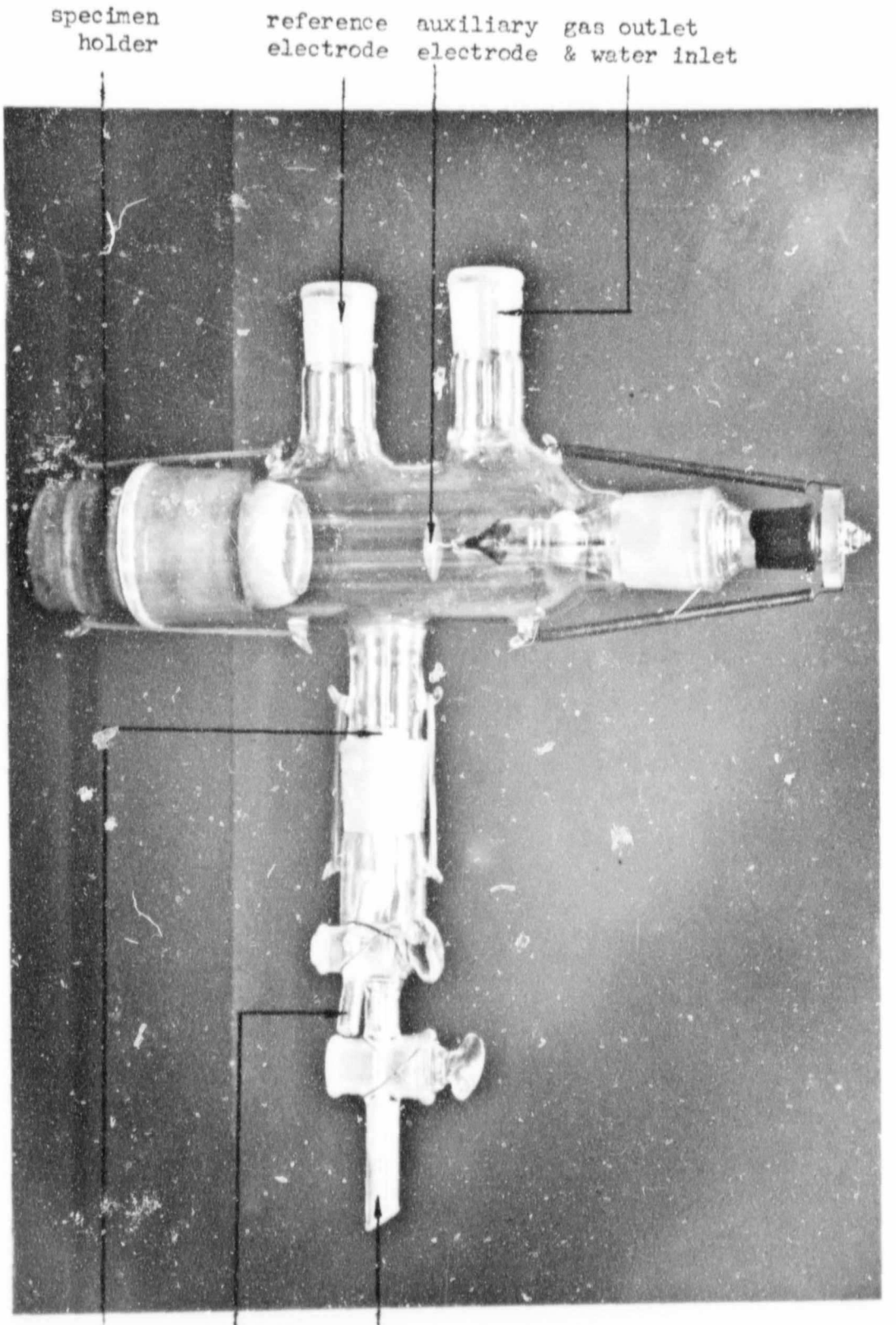

FIGURE 4 : Tacussel type test cell.

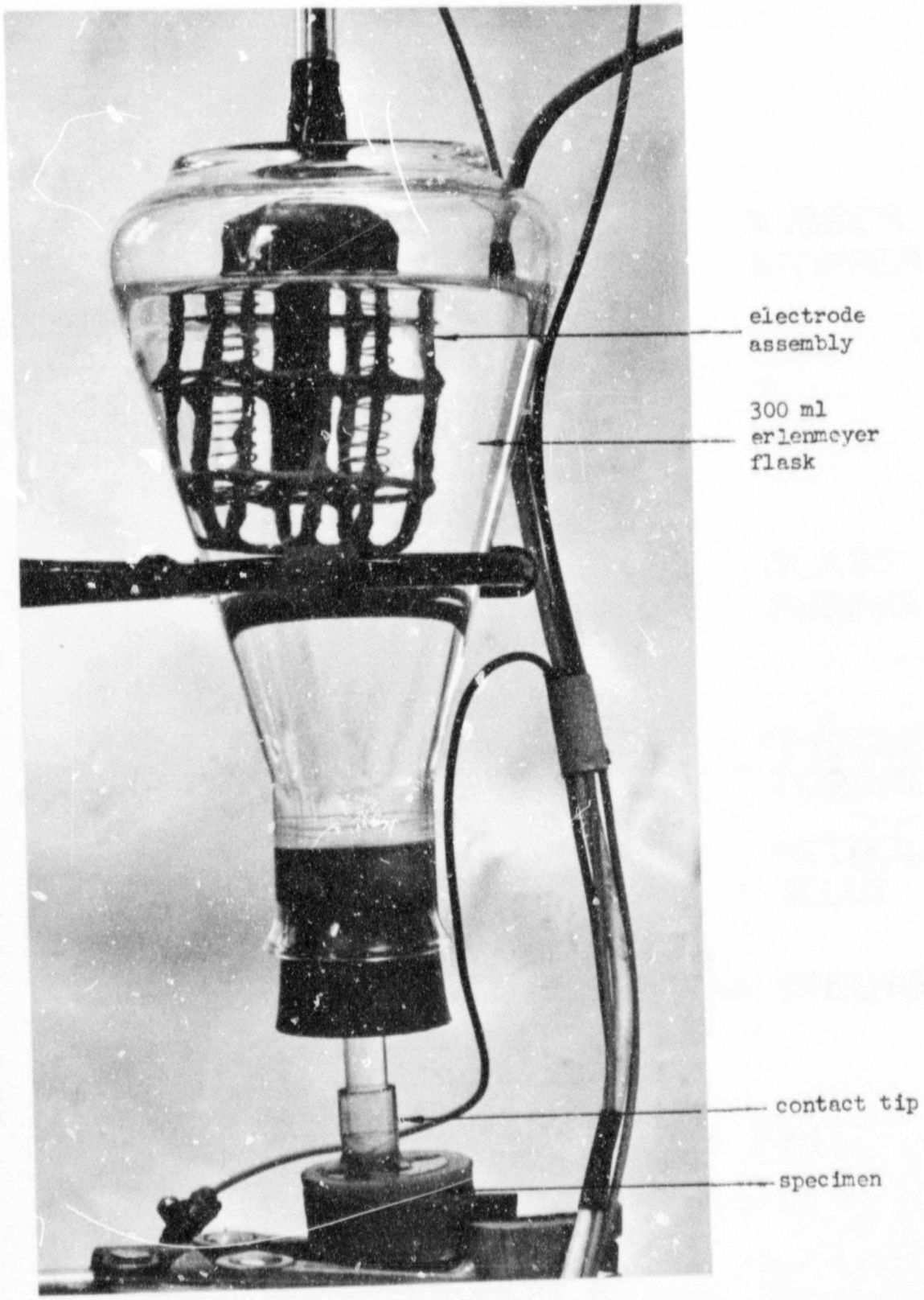

FIGURE 5 : Erlenmeyer flask test cell.

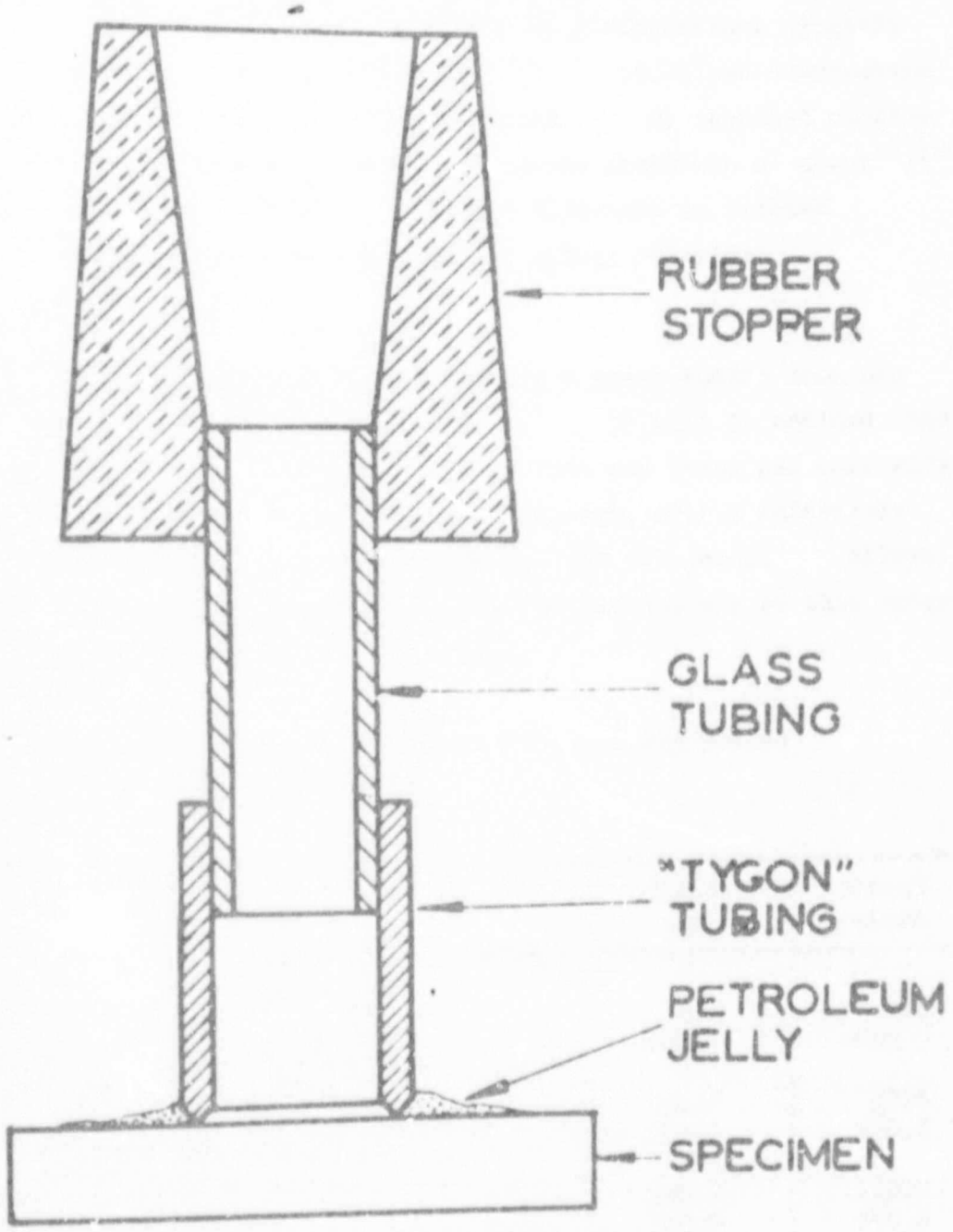

FIGURE 6 : Contact tip of test cell .

The reference electrode[9] which gave satisfactory service, was prepared by coating a twisted platinum wire with a paste of silver oxide and water. The oxide was decomposed to finely divided metallic silver by flame heating in air at a temperature slightly below the melting point of silver (960°C). Localized overheating and consequent sintering probably occurred. By repeated coating and heating a mechanically strong and porous electrode of about 1/4" diameter by 2" long was made. Anodic treatment in diluted hydrochloric acid provided the required silver chloride.

2.1.4 Electrolytes

A typical analysis of water used in a heavy medium iron ore beneficiation unit, is given in Table 4. It will be noticed that this water is not particularly hard and that the principal corrosive constituents are the Cl^- and $SO_4^=$ ions present, with a relatively small amount of the inhibiting phosphates and silicates. Alloys of lower corrosion resistance will corrode excessively in this water and cause service problems on the mine.

TABLE 4 - Typical Analysis of the Water used in a Heavy Medium Iron Ore Beneficiation Unit

	Make up	Slimes return
pH	7.8	7.9
Ionic conductivity Micro Mhos/cm	700.0	800
Total Alkalinity as $CaCO_3$ ppm	91.2	99.6
Total Hardness as $CaCO_3$ ppm	220.0	260.0
Calcium as $CaCO_3$ ppm	100.0	120.0
Magnesium as $CaCO_3$ ppm	120.0	140.0
Sodium as Na ppm	68.0	70.0
Potassium as K ppm	12.0	15.6
Sulphates as SO_4 ppm	42.0	50.0
Chlorides as Cl^- ppm	85.2	99.4
Nitrates as NO_3 ppm	31.0	27.4
Silicates as SiO_2 ppm	20.3	10.1
Phosphates as PO_4 ppm	30.7	-
Total dissolved solids ppm	422.0	553.0

13 / ... ...

Since it is the high chloride and sulphate content of the mine water which makes it corrosive, a synthetic mine water was prepared containing 100 p.p.m. Cl as NaCl and 50 p.p.m. SO_4 as Na_2SO_4. This was used for the total immersion tests of powder and the overvoltage intercept polarization tests. Because of its low ionic conductivity of 460 micro mhos/cm however, "full" polarization curves could not be determined with the existing layout, due to the large ohmic potential drop in the electrolyte at higher current values. This is a difficulty always encountered when low conductivity solutions are used.[16]

An electrolyte containing 1% NaCl and 0.5% Na_2SO_4 and with a conductivity of just over 10,000 micro mhos/cm, gave curves of which Figure 7 is a typical case.

Further "full" polarization tests were carried out in 2.5 wt % HCl and 2.5 wt % H_2SO_4. The conductivity was 230 mhos/cm for the HCl solution and 52 mhos/cm for the H_2SO_4 solution.

2.1.5 Temperature Control

It has been reported that the conductance[10] of a dilute electrolyte increases at a rate of about 2% per ^oC temperature rise, and that polarization currents[22] are even more dependent on temperature. On the basis of the above information it was considered essential that tests should be performed at the same temperature if they were to be compared.

A temperature control unit was designed and installed, maintaining the laboratory air temperature at 25 ± 0.25^oC. The drop in cell temperature due to gas bubbling was of the order of 1^oC. Before test runs, the electrolyte, specimens and other apparatus were allowed to adjust to room temperature overnight.

2.2 THE OVERVOLTAGE INTERCEPT AND POLARIZATION/TIME STUDIES

2.2.1 Introduction

At an early stage of this investigation it became clear that the ferrosilicon alloys have strong self passivation tendencies. High rates of change of the freely corroding potential were accompanied by a long term drop in the corrosion rate.

The determination of polarization curves over a considerable length of time was of uncertain value because the curves were greatly affected by the non-equilibrium behaviour of the specimen which lasted for several days.

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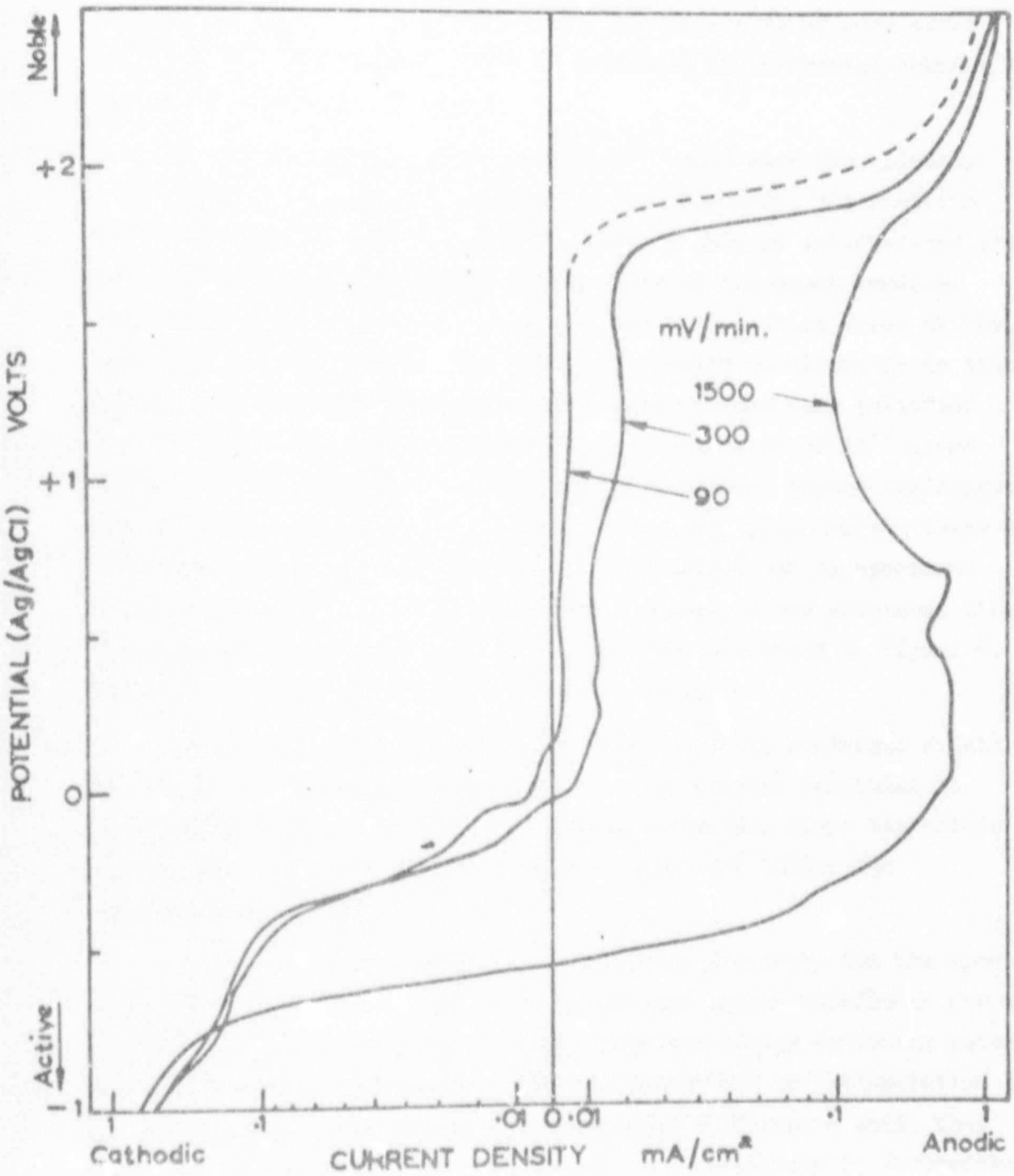

FIGURE 7 : "Full" polarization curves for specimen 6 (12·5% Si, 1% Cu, 2% Cr) in 1% NaCl / 0·5% Na_2SO_4 solution at different potential scanning rates.

It was therefore decided that a study be made of the kinetics of film build-up. This required the development of a test which would least affect the condition of the specimen surface, so that further tests would give a true indication of the ageing characteristics of the material. Furthermore the test should be of such short duration that the natural drift of potential and corrosion current in the test period will be small.

The polarization resistance method[35] would have been ideally suited to this application because of the very small polarization currents employed and the resulting small amount of interference with the electrochemical processes taking place at the metal surface. This method makes use of the slope of the polarization curve at the corrosion potential where the potential-current relationship is linear. Tests indicated that this linear relationship was only satisfied for ferrosilicon for current densities of the order of 10^{-2} micro ampere/cm^2 and smaller. This was unfortunately beyond the sensitivity limits of the apparatus available. Cathodic polarization tests with a potential shift of 100 millivolts were carried out on specimens 1 to 32 (as cast). The curves for a number of the specimens after 24 hours immersion in a $NaCl/Na_2SO_4$ solution are given in Figure 8. These are typical of the curves for the series.

Since these curves essentially maintain their positions relative to one another with changing potential, the current densities at 20 millivolts from the freely corroding potential, place the alloys in the same sequence as do overvoltage intercept values for 100 millivolt tests.

As can be seen in Figure 8, the current densities for the specimens handled, did not exceed one micro ampere per square centimeter for a potential shift of twenty millivolts from the freely corroding potential at that instant. Corrosion currents determined by extrapolation of the straight line portions of the curves of Figure 8 until they meet the freely corroding potential (i.e. m V Relative to Reversible Potential = zero), are of the same magnitude as the 20 millivolt polarization currents. Ideally, the test current density should be less than the corrosion current for negligible disturbance.[18]

It was considered that the relatively small polarization current densities associated with 20 millivolts potential shift, applied to the system for a period of a few seconds and thus supplying to it only a few microcoulombs, would have a negligible effect on the conditions at the metal-electrolyte interface. The reproducibility of test figures showed that this was a justified assumption.

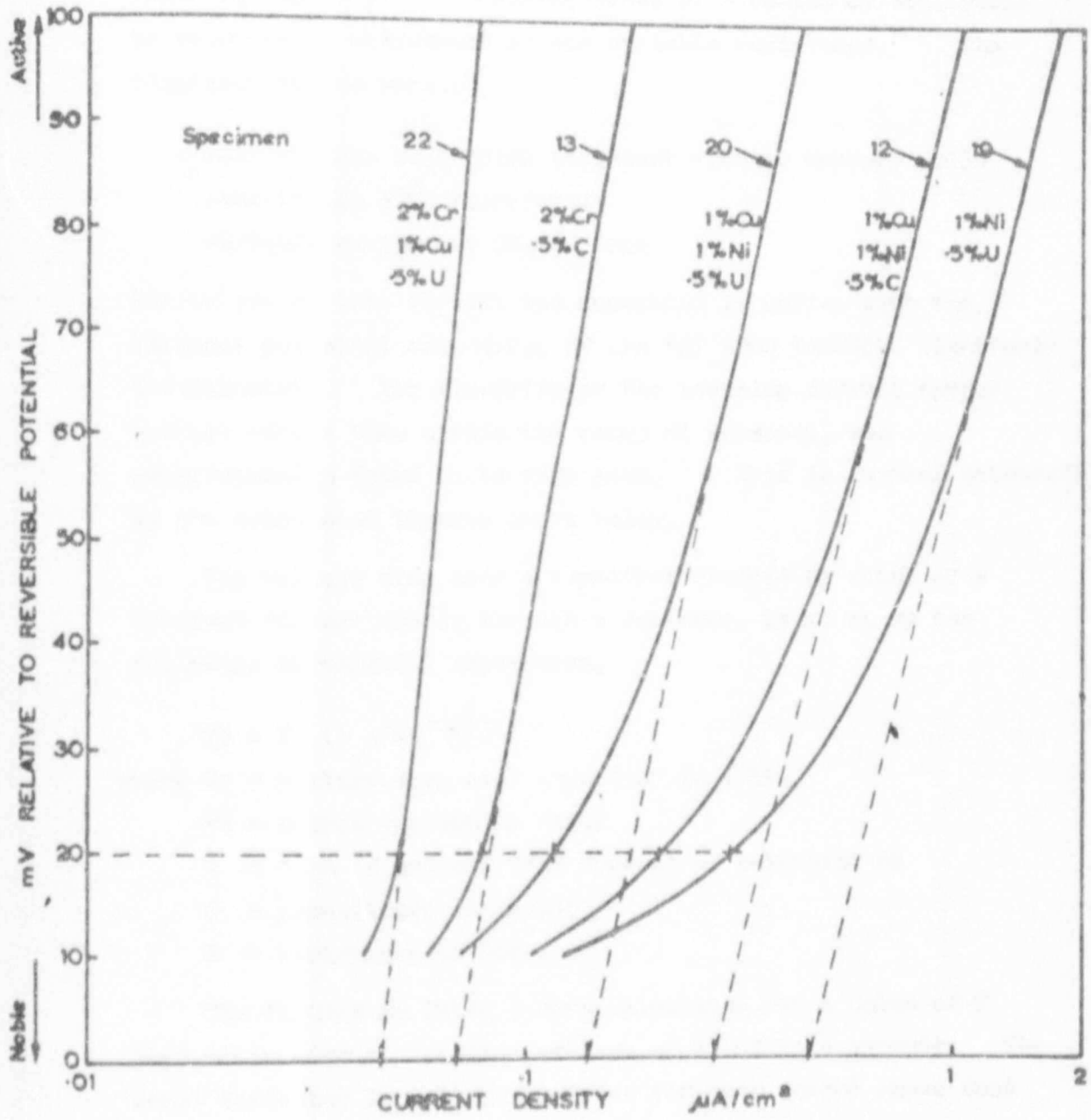

FIGURE 8: Cathodic polarization curves. Electrolyte 100 ppm Cl as Na Cl
50 ppm SO_4 as Na_2SO_4

2.2.2 Apparatus

A schematic diagram of the apparatus used in this test is given in Figure 9. The actual laboratory layout is shown in Figure 10. A perfectly smooth and reproducible scanning voltage was produced with the resistance - capacitance circuit shown in Figure 9. Scanning rates of 3 to 100 mV/sec. could be selected by adjustment of the variable resistance. The component values were :-

cell voltage 1.35 volts (constant voltage mercury cell)
capacitance 5000 Microfarads
variable resistance 50,000 Ohms

The output of this circuit was connected in series with the internal potential controller of the PRT 2000 TACUSSEL electronic potentiostat. The linearity of the scanning circuit output voltage versus time within the range of interest, was experimentally found to be very good. This is further substantiated by the calculated figures shown below.

The voltage drop over a capacitor charged by means of a constant voltage source through a resistor, is given by the following exponential expression,

$$Vc = Vs\ (1 - e^{-\frac{t}{CR}})$$

where Vc = voltage drop over capacitor in volts
Vs = source voltage in volts
t = time in seconds from instant of switching on
C = capacitance in Farads
R = resistance in Ohms.

The figures in Table 5 were calculated for a value of R that would give a capacitor voltage of 20 mV in 4 seconds. The small variation in voltage increase for each second shows that the scanning rate is very nearly constant.

TABLE 5 - The Dependence of Capacitor Charging Rate on Time

Time t seconds	Capacitor Voltage Vc mV	Voltage Increment mV/sec
1	5.03	5.03
2	10.04	5.01
3	15.03	4.99
4	20.00	4.97

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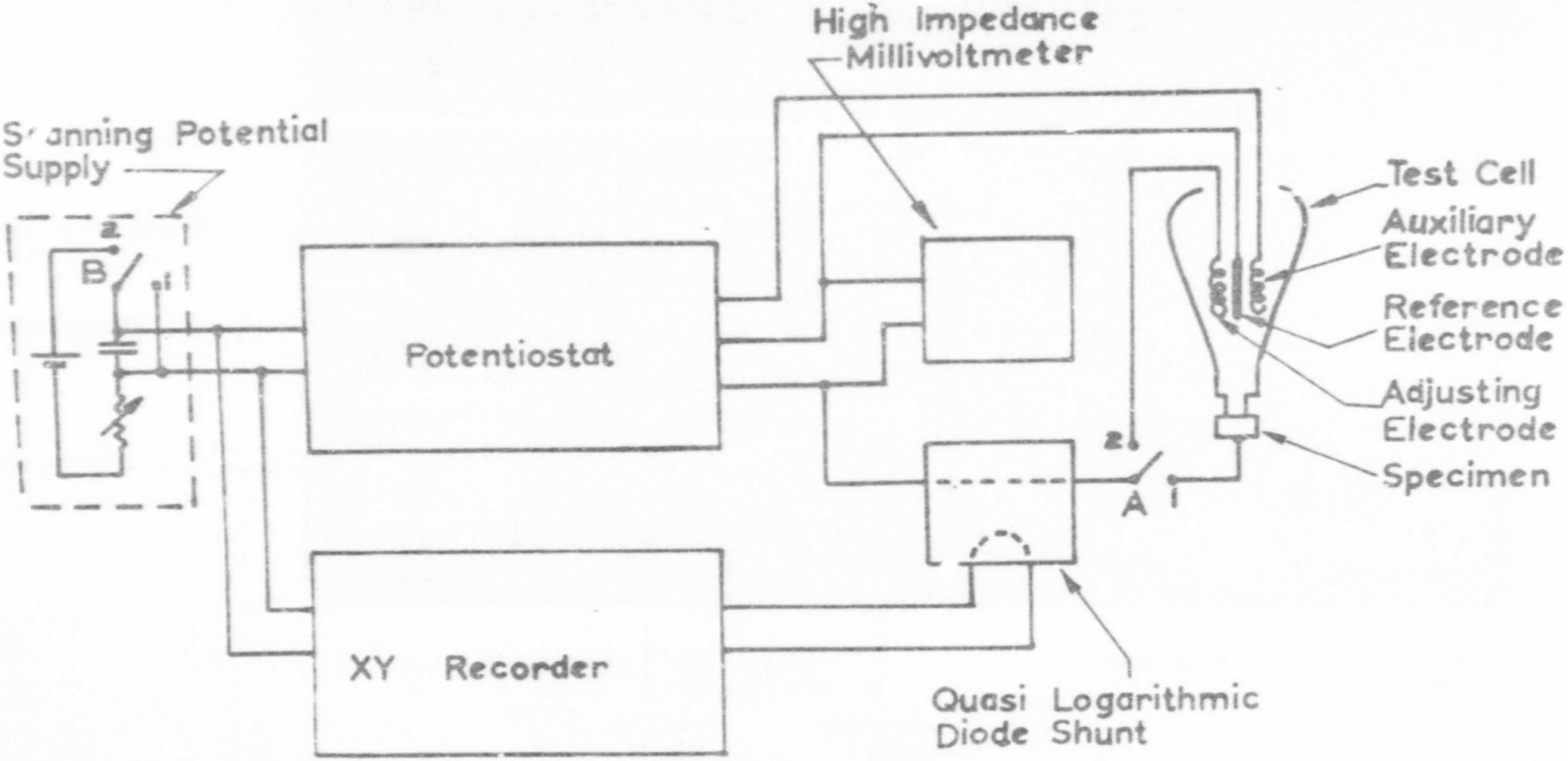

FIGURE 9 : Schematic diagramme of apparatus for current intercept tests.

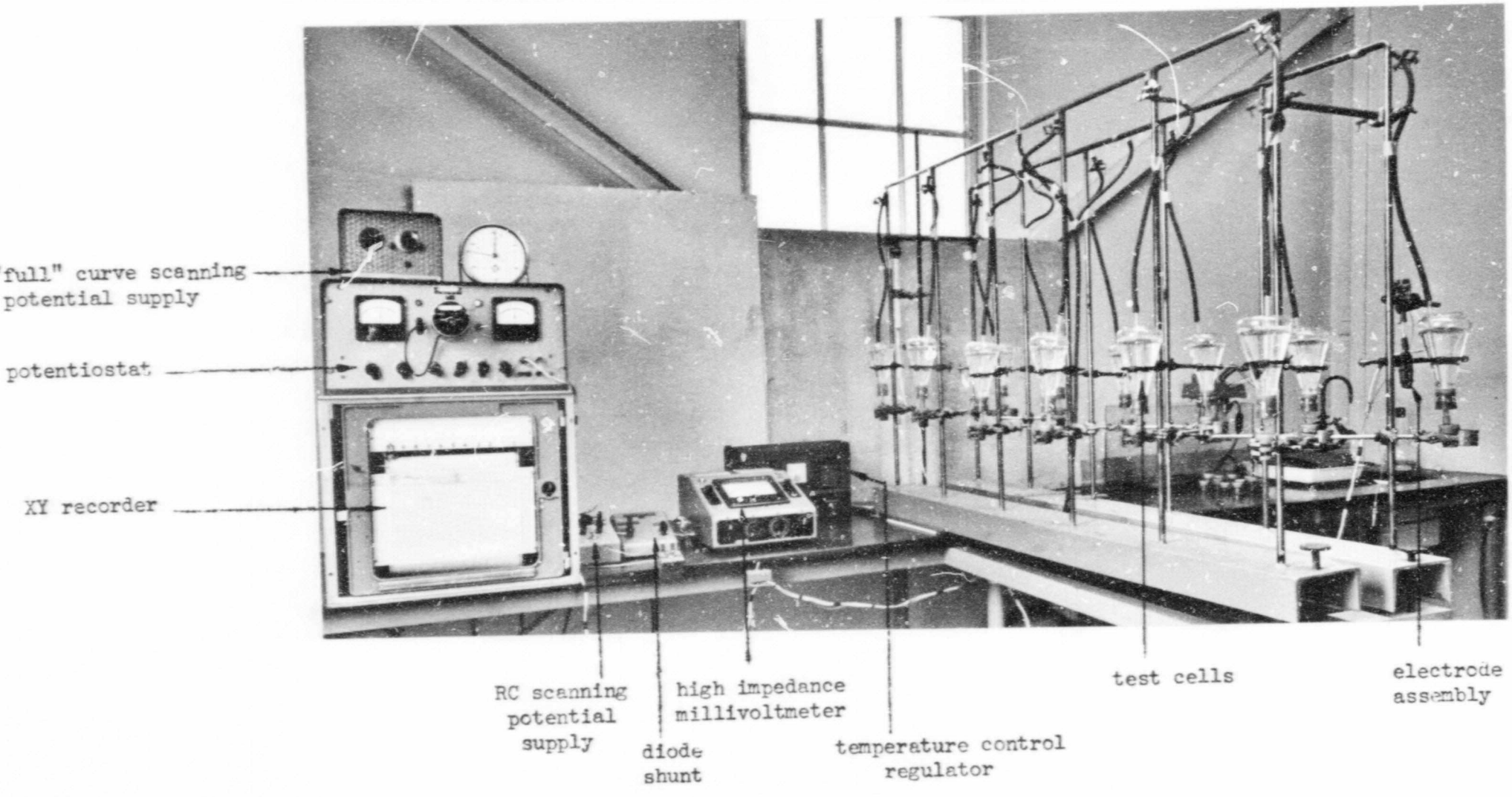

FIGURE 10 : Laboratory layout of equipment.

The TACUSSEL PRT 2000 electronic potentiostat has the following characteristics :-

Output voltage $\pm$ 22V
Maximum deviation from reference voltage $\pm$ 5V
Output current $\pm$ 2A
Minimum time constant 1 to 3 microseconds
Potential stability $\pm$ 15 mV for output variation of 0 - 20 V
Hum and noise insensitivity $\pm$ 2mV

A high impedance - 10^{14} ohms - TACUSSEL voltmeter was used for potential measurements. The WENKING quasi logarithmic diode shunt was used in its linear region for supplying a drive voltage to the PHILIPS XY recorder, with this voltage being proportional to the polarization current. The electrolytic cell and electrode unit shown in Figure 5 were employed.

2.2.3 Experimental Procedure

The one inch diameter cylindrical specimens were polished at one end to a 400 grit finish and liberally washed with ethyl alcohol. The mounting was done as shown in Figure 6 with the "TYGON" tube/specimen joint sealed with molten petroleum jelly. No movement of petroleum jelly onto the circular test area was found to occur. The hole in the rubber stopper was plugged from above with a glass rod before introduction of the electrolyte. All immersion time values were referred to the moment of withdrawal of the glass rod.

Polarization tests were performed after immersions of 1 minute, 5 minutes, 3 hours, and further periods of from 1 to 3 days. Specimen potentials at the time of each test, were recorded.

The following test procedure was followed :-

With reference to Figure 9 -

1. Find the specimen potential with switch A in position 1 and with the potentiostat output switched off.
2. With switch A in position 2, switch on the potentiostat output and adjust the internal potential supply of the potentiostat to give a potential equal to that of the specimen.
3. Switch back to position 1 and finally adjust the internal potential controller for zero external current flow.
4. Throw over switch B from 1 to 2. This allows the constant voltage mercury cell to charge the capacitor through the variable resistor.

17 / ... ...

A gradually changing voltage is thus superimposed by the scanning circuit on to the internal potential controller of the potentiostat. This moves the potential of the specimen through 20 millivolts at a rate of $\pm$ 5 millivolts per second. By means of the XY recorder, the resulting polarizing current is plotted against the shift of potential from the freely corroding value.

2.2.4 Results

Figure 11 is an example of the polarization curves shown by means of the XY recorder. The decrease of current density with immersion time before running the test is apparent.

As explained in 2.2.1, the current densities at 20 millivolts from the freely corroding potential will put the alloys in sequence according to corrosion resistance. The current densities at 20 millivolts were plotted for all specimens as a function of time. The plots for specimens 0, 1, 4 and 5 (as cast) are given in Figure 12. The 1 minute values were omitted because of the influence on the tests of the high rate of potential drift just after immersion.

For comparison purposes the current densities at 10,100 and 1000 minutes were read from these curves. The values are recorded in Table 6.

The reversible potentials (freely corroding) at immersion times of 5 minutes and longer, are shown in Figure 13 as a function of polarization current density at 20 millivolts potential displacement for specimens 0 to 32.

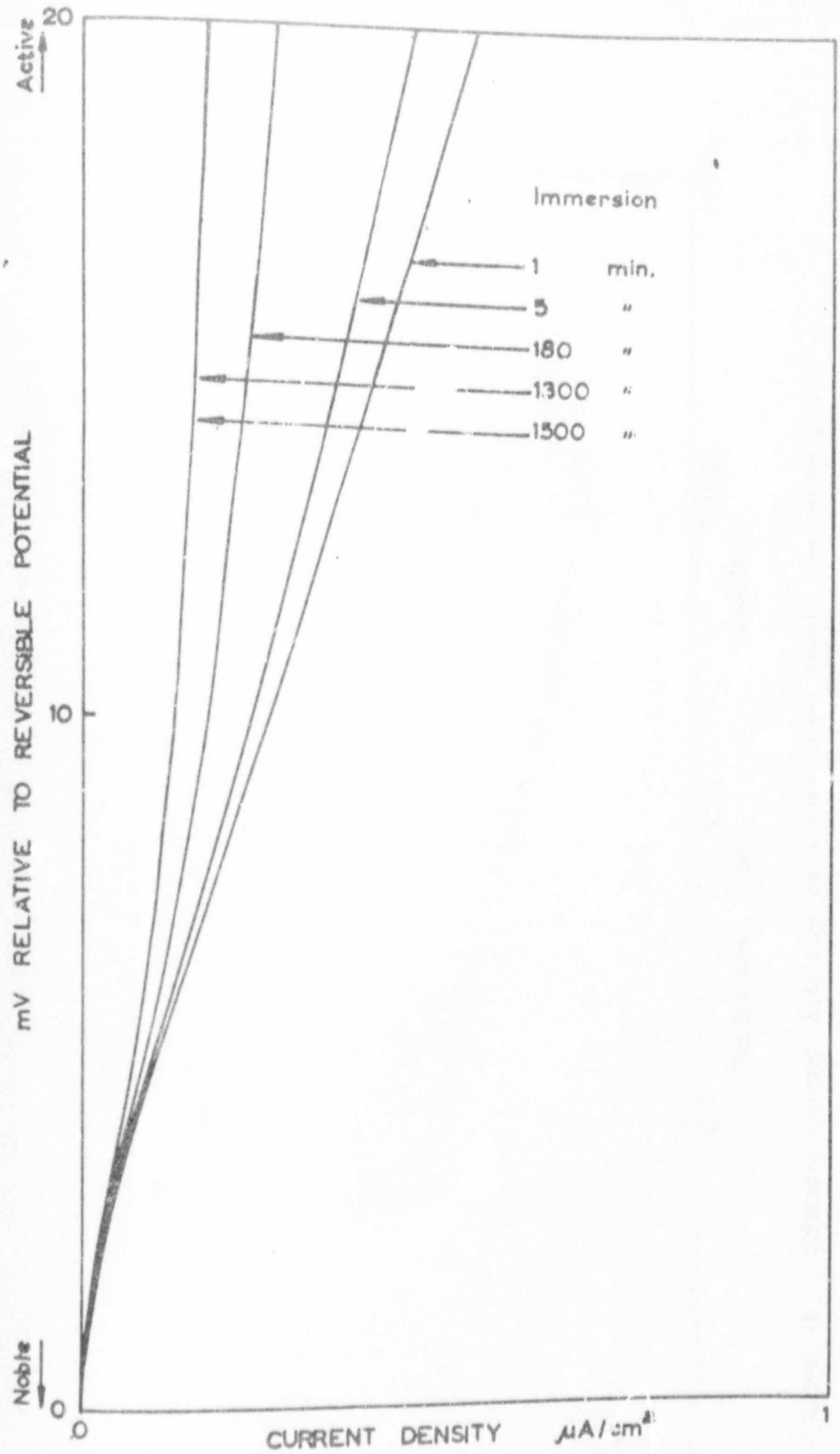

FIGURE 11 : The influence of immersion time of specimen 5 (12-5 % Si, 2% Cr) on the polarization curve close to the freely corroding potential.

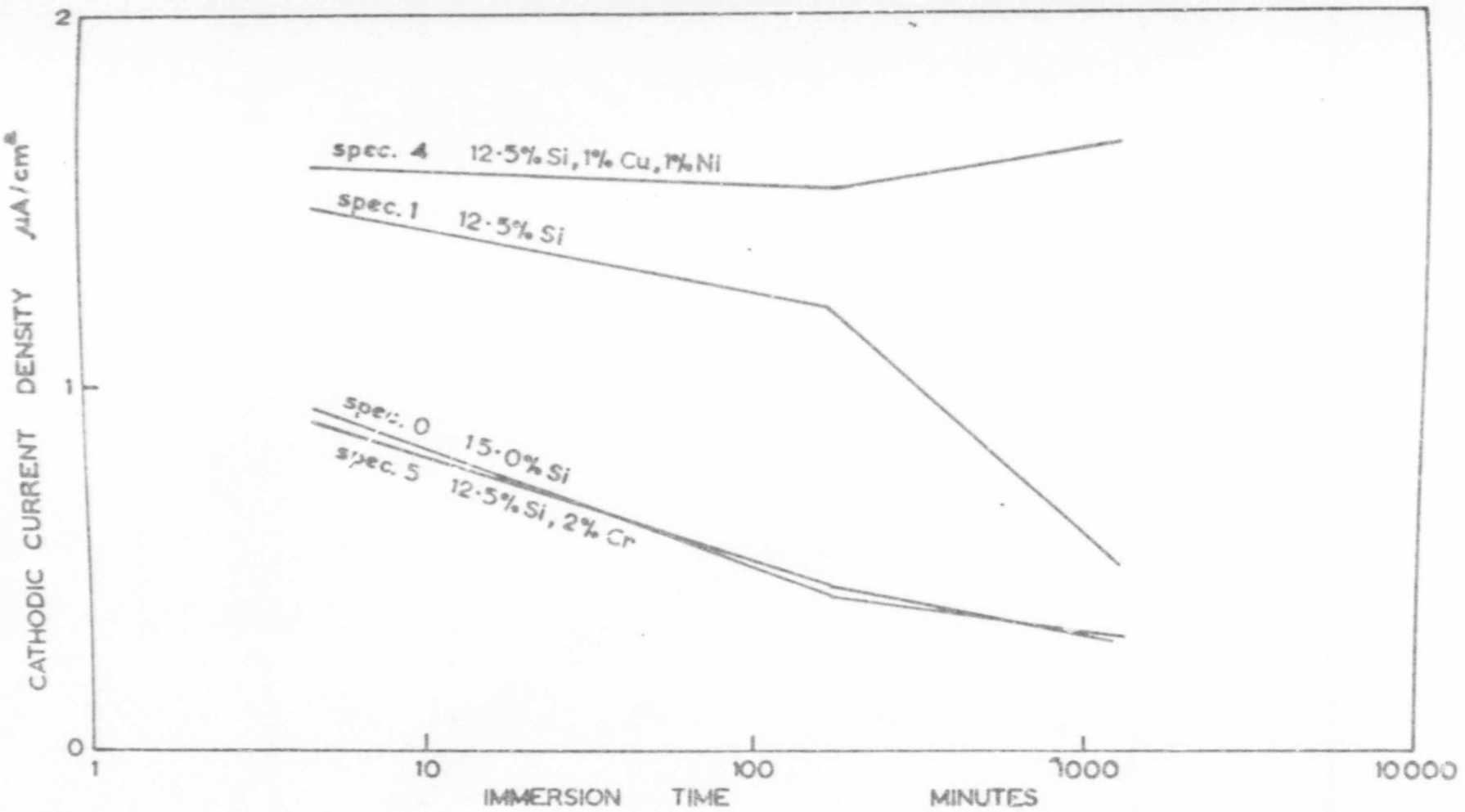

FIGURE 12 Cathodic current densities at 20 mV from freely corroding potential versus immersion time.

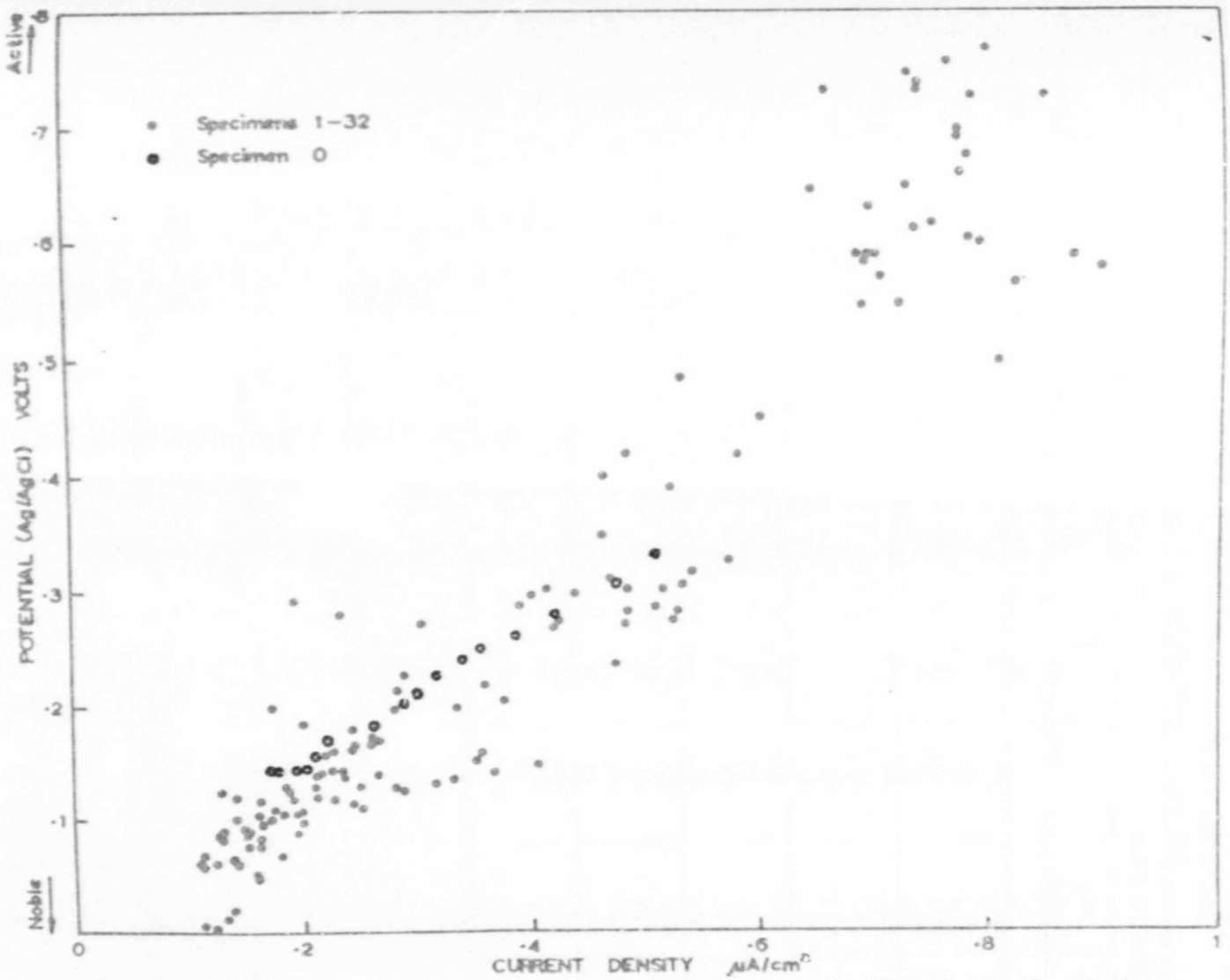

FIGURE 13: Freely corroding potentials versus polarization current densities at 20 mV cathodic to these potentials.

TABLE 6 - Polarization Current Densities after 10, 100 and 1000 Minutes Immersion in $NaCl/Na_2SO_4$ Solution. (100 p.p.m. Cl and 50 p.p.m. SO_4).

Spec. No.	Constituents	POLARIZATION CURRENT DENSITIES in microamperes per cm^2					
		AS CAST			HEAT TREATED		
		10 min	100 min	1000 min	10 min	100 min	1000 min
0	15% Si	.44	.24	.16	-	-	-
1	12.5% Si	.72	.64	.30	.74	.52	.30
2	+ Cu	.76	.62	.36	.64	.54	.46
3	+ Ni	.76	.72	.58	.66	.66	.64
4	+ CuNi	.80	.78	.82	.68	.68	.70
5	+ Cr	.42	.26	.16	.28	.18	.12
6	+ CrCu	.42	.26	.16	.30	.24	.16
7	+ CrNi	.44	.26	.18	.44	.32	.24
8	+ CrCuNi	.50	.34	.30	.48	.38	.22
9	+ C	.62	.50	.28	.60	.42	.24
10	+ C Cu	.70	.66	.72	.66	.64	.72
11	+ C Ni	.70	.66	.70	.68	.66	.68
12	+ C CuNi	.64	.46	.32	.64	.58	.36
13	+ C Cr	.42	.24	.16	.36	.22	.14
14	+ C CrCu	.40	.26	.16	.34	.24	.14
15	+ C CrNi	.42	.26	.16	.44	.28	.18
16	+ C CrCuNi	.42	.28	.14	.36	.24	.16
17	+ U	.70	.72	.72	.66	.66	.70
18	+ U Cu	.64	.42	.26	.60	.42	.32
19	+ U Ni	.66	.58	.60	.70	.66	.70
20	+ U CuNi	.60	.36	.22	.64	.52	.38
21	+ U Cr	.42	.26	.14	.46	.34	.24
22	+ U CrCu	.40	.26	.14	.46	.32	.22
23	+ U CrNi	.42	.28	.16	.42	.26	.18
24	+ U CrCuNi	.44	.28	.20	.48	.36	.26
25	+ UC	.62	.42	.24	.62	.54	.36
26	+ UCCu	.62	.44	.26	.54	.44	.30
27	+ UCNi	.60	.40	.26	.68	.46	.18
28	+ UCCuNi	.62	.42	.28	.54	.38	.22
29	+ UCCr	.40	.28	.18	.40	.26	.14
30	+ UCCrCu	.38	.28	.20	.46	.30	.14
31	+ UCCrNi	.36	.28	.16	.40	.24	.12
32	+ UCCrCuNi	.46	.38	.20	.50	.50	.32
33	+ 2% Mo	.74	.70	.78			
34	+ 4% Mo	.72	.70	.74			
35	+ C 2% Mo	.76	.74	.74			
36	+ C 4% Mo	.72	.70	.74			
37	+ Cr 2% Mo	.52	.46	.40			
38	+ Cr 4% Mo	.64	.64	.62			
39	+ C Cr 2% Mo	.68	.70	.74			
40	+ C Cr 4% Mo	.50	.58	.62			

19 / ... ...

2.2.5 Discussion

In this investigation use has been made of the relationship $\eta = \beta_c \log \frac{ic}{i_{corr}}$ (see 1.4.3) by holding η at 20 millivolts for all specimens and assuming βc to be constant for the purpose of arranging the alloys in the sequential order of corrosion resistance. Under these conditions i_{corr} is directly proportional to i_c and may be used as a measure of the corrosion rate.

It is considered that the corrosion rate of a static body in an electrolyte may be predicted from a knowledge of the polarization characteristics after lengthy immersion - say, 1000 minutes or more. After periods such as this, the protective film is completely formed. For a body in frictional contact with other bodies, i.e. with the protective film being continuously disturbed, the corrosion rate will be more properly given by the polarization current densities at shorter immersion times.

In the case of a heavy medium plant, it could well be that both short term and long term passivation qualities come into the picture. In a heavy medium bath which is continuously stirred, there may be relatively little difference in operation using either an alloy showing a tendency to passivate such as specimen 1 - Figure 12, or an alloy showing no such tendency such as specimen 4. Short term characteristics will be predominant.

On the other hand, a bath which is left unstirred for a day or so (e.g. a week end shut down), may turn into a solid mass when using an alloy with a small passivating tendency. This is a practical consideration which may be of overriding importance.

Figure 12 shows that passivity is developed at a rate roughly proportional to the logarithm of immersion time. A similar linear-log relationship has been reported for mild steel in ammonium nitrate,[34] and a log-log relationship for 18/8 stainless steel in sulphuric acid.[33]

The dependence of polarization current on time of immersion, is given in summarized form in Table 6, showing that in most cases there is a decrease of polarization current as the immersion time increases from 10 to 100, to 1000 minutes. This drop in the current is a measure of the self passivation tendency of each specimen. Heat treatment does not appear to have had any significant effect on the polarization currents.

20 / ... ...

Figure 13 shows that for the family of ferrosilicon alloys tested, there is a strong linear relationship between polarizing current density and specimen potential. Insofar as the polarization current at 20 mV from the freely corroding potential is a measure of the corrosion rate, the specimen potential can be said to be related to the corrosion rate. Although potential values alone could be largely misleading, in many cases they will place specimens in the sequence of the relative corrosion resistance. Limited use could be made of this finding.

In the series of alloys from 1 to 32, the specimens which showed corrosion resistance closest to that of the 15% silicon alloy (specimen 0), were those containing 2% chromium, viz. specimens 5-7, 13-16, 21-24 and 29-31 (Table 6). This is clearly shown by the polarization current values given in Table 6. Bearing in mind that the polarization current values tabulated, are a measure of the corrodability of the alloys, it is of interest to note that the abovementioned alloys had corrosion rates close to that of the 15% silicon alloy, not only shortly after immersion (10 minute values) but also after more lengthy immersion (100 minutes and 1000 minutes). Furthermore, the decrease in corrosion rate with time, which is a well known property of the 15% silicon alloy, was also found to occur with these other alloys. (Note decreasing current values with length of immersion time).

For some of the other specimens high corrosion rates are indicated by these figures with hardly any or no tendency at all towards passivation. Specimens 4, 10, 11 and 17 show these properties.

Rather surprisingly, the samples containing molybdenum (33 to 40) were found to corrode at a high rate without the tendency to passivate even after relatively lengthy immersion. In the absence of chromium, the addition of carbon improved the corrosion resistance in the presence of uranium - compare specimens 17-20 with 25-28 (Table 6). Copper and nickel proved to be deleterious additions in the absence of chromium - compare specimens 2, 3 and 4 with 1 (Table 6).

2.3 THE "FULL" POLARIZATION CURVE

2.3.1 Introduction

The "full" polarization curve ranging from hydrogen evolution to oxygen ev..ution was used for the study of the electrochemical behaviour of the different specimens in 2.5% HCl and 2.5% H_2SO_4 solutions.

21 / ... ...

2.3.2 Apparatus

Essentially the same apparatus as described in 2.2.2 was used. The scanning potential supply which in this case replaced the potentiostat's internal potential controller, is shown in Figure 14 with the rest of the layout. The circuit component values were :-

Scanning rate controller 5 KΩ
10 Turn potentiometer 5 KΩ
6 Volt battery opposed by 1.5 volt

2.3.3 Experimental Procedure

The specimens were prepared and mounted as described in 2.2.3.

A test procedure which was found to give good reproducibility, was the following :-

Immerse the specimen for 5 minutes - switch on potentiostat output with potential set at - 1.5 volt - hold for 1 minute - scan the potential from - 1.5 volt to +2.5 volts at a constant rate.

Exploratory test runs were done at different scanning rates. The dependence of the shape of the polarization curve on the scanning rate, is illustrated by Figures 7 and 15. For the tests in HCl and H_2SO_4 solutions, a scanning rate of 500 millivolts per minute was adopted.

2.3.4 Results

The anodic parts of the polarization curves for specimens 1 to 32 are given in Figures 16 and 17 for the HCl solution and Figures 18 and 19 for the H_2SO_4 solution. The curves for specimens 33 to 40 are presented in Figure 20. The cathodic parts of all curves were similar with a polarization current density of $\pm$ 12 mA/cm^2 at - 1.5 volts.

In order to compare quantitatively the passivation tendencies of the different alloys, the curve of specimen 4, which shows no passivation, was taken as the reference. (Tables 6 and 8 show that specimen 4 is the least corrosion resistant of all the alloys). The deviation of the curves from this reference was used as an indication of the passivation tendency. To take account not only of the change in current in the passive region, but also the potential spread of this region, the area formed between the curve of specimen 4

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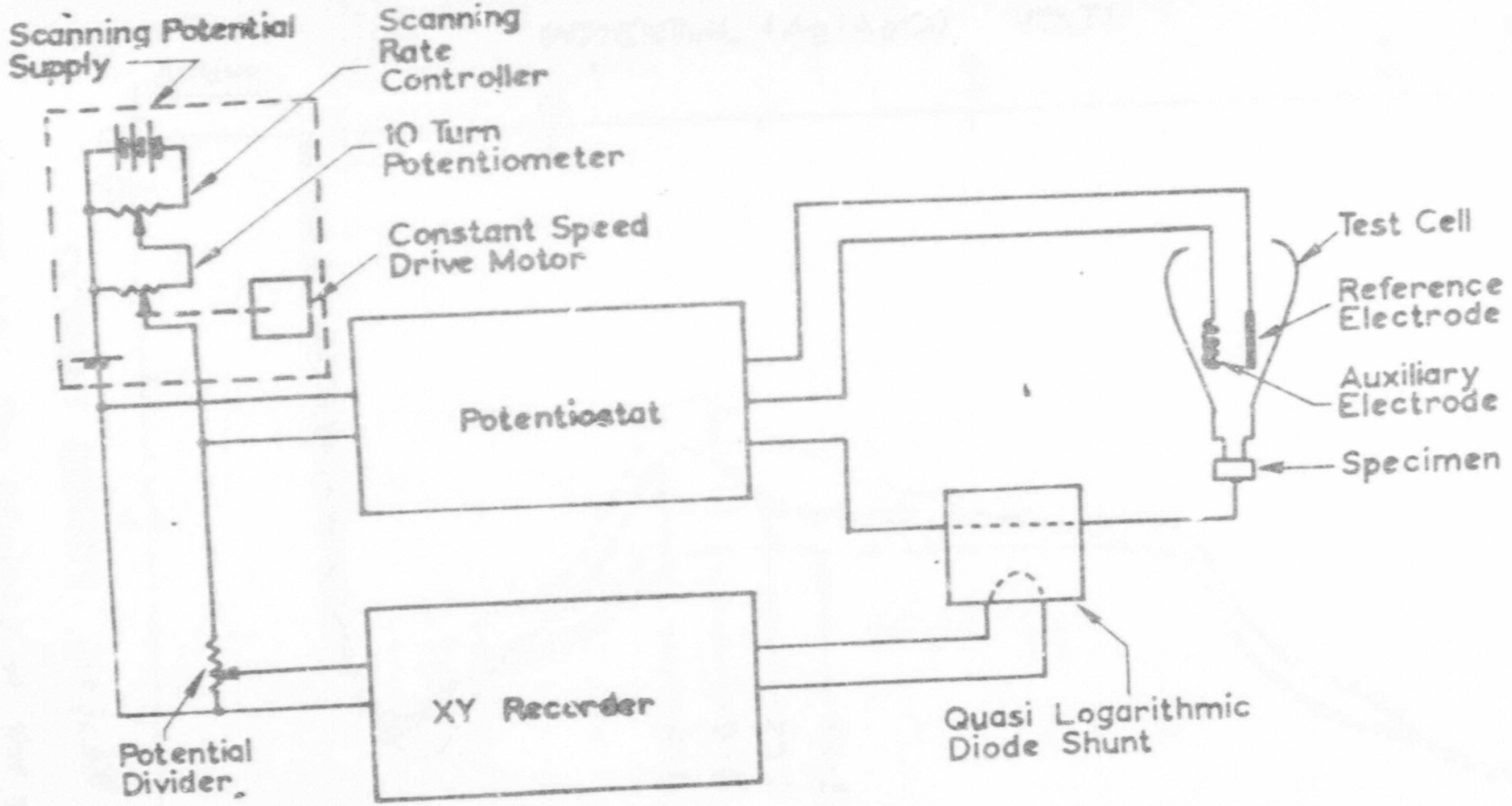

FIGURE 14 : Diagrammatic layout of apparatus used for determination of the "full" polarization curves.

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