

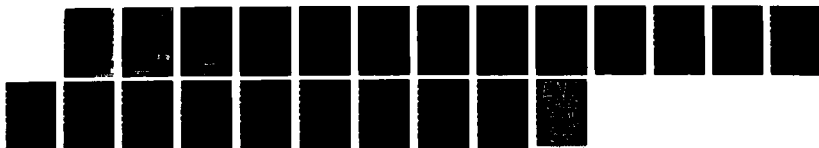
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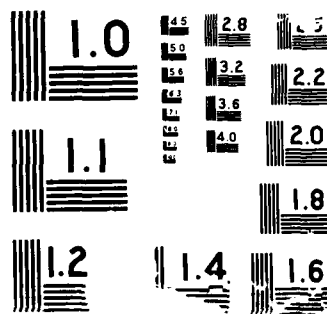
CORROSION OF ALUMINIUM ALLOYS BY IRFNA(U) NOTTINGHAM
UNIV (ENGLAND) DEPT OF CHEMISTRY M F DOVE ET AL
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UNIVERSITY OF NOTTINGHAM

DEPARTMENT OF CHEMISTRY

Corrosion of Aluminium Alloys by IRFNA

R&D 5878-CH-01

First Interim.

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March 1988

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1. Introduction

This interim report gives a brief summary of the work carried out according to the proposal submitted (11 May 1987) for the funding period 1 June 1987 to 31 May 1988. This proposal was subsequently amended slightly, following technical discussions with Dr Barry Allen, in the light of the somewhat reduced level of funding in the contract awarded on 28 September 1987.

2. Part A - Pretreatments

Originally it was proposed that twelve bottom-working electrode cells be pretreated, in the following manner:

A(i) 4 cells (LH/RH/Old IRFNA/New IRFNA) - Water washed and dried (in vacuo)

A(ii) 4 cells (LH/RH/Old/New) - Water washed, dried, PF_5/F_2 treated

A(iii) 4 cells (LH/RH/Old/New) - Water washed, dried, HF/F_2 treated

Of these proposals, A(i) has been carried out. Four cells (BW21, 22, 23 and 24) were set up in March 1987, and incorporate the following pretreatments and features.

BW21 - Water wash/Dry/LH-electrode/IRFNA from SN5208

BW22 - As BW21, but RH-electrode

BW23 - As BW21, but 'Fresh' IRFNA (from R.O.F Westcott)*

BW24 - As BW23, but RH-electrode

These four cells were mounted horizontally (in a temperature-controlled bath @25°C) to prevent any "oil-like" phases interfering with the surface of the working electrode. The results of experiments carried out on these cells are reported in Section 7(i).

A(ii) and A(iii) have been postponed until further investigations into film-thickness and the efficacy of various pretreatment procedures have been carried out. This will involve further surface analysis work (XPS and Auger).

* see Appendix

3. Part B - The Four Working-Electrode Cell

The construction of an electrochemical cell containing four working electrodes, cut from the same region of an oxidiser tank, was postponed to allow for the remachining of cell bodies and lids for Parts A and E of the proposal.

This remachining has been carried out, and the four working-electrode cell has been constructed.

4. Part C - Temperature Cycling

The effect of oscillating-temperature cycles on the corrosion rate of aluminium in IRFNA has been investigated.

Two bottom working-electrode cells, BW13 and BW14 (water washed and dried) were transferred from the constant temperature oil bath (@25°C) to the controlled temperature-oscillation bath (@25°C) on 23 November 1987. The histories of the two cells prior to this date are shown in Table 1.

TABLE 1

<u>Cell Code</u>	<u>Electrode type</u>	<u>Pretreatment</u>	<u>IRFNA supply</u>	<u>Duration</u>
BW13	LH	water wash and dry	R.O Westcott	482.8 days
BW14	RH	"	"	461.1 days

The temperature of the bath was oscillated by $\pm 5^{\circ}\text{C}$ over a 24 hour period. Corrosion potential and corrosion current measurements were determined at regular intervals during the temperature cycle.

It is proposed that temperature cycles of $\pm 10^{\circ}\text{C}$ and $\pm 20^{\circ}\text{C}$ will be carried out. The results of temperature cycling experiments carried out over the $\pm 5^{\circ}\text{C}$ range are discussed in Section 7(ii).

5. Part D - Surface Studies

The original proposal contained three areas of investigation:

- (i) surface characterisation of samples cut from oxidiser tank ring-sections;
- (ii) surface characterisation of working electrodes, fabricated from these ring-sections, after the pretreatments described in part A of the proposal, and again after immersion in (IRFNA)
- (iii) surface characterisation of samples of the machined aluminium alloy used in the fabrication of cell bodies and lids, to look for surface contamination in the machining process.

Following discussions on 15 September 1987, it was agreed to extend this part of the research proposal and include the following:

- (iv) surface characterisation of samples from oxidiser tank SN5144, after
 1. H₂O wash and dry
 2. H₂O wash, dry, ClF₃
 3. H₂O wash, dry, PF₅/F₂
 4. H₂O wash, dry, HF/F₂

Surface characterisation will be by XPS and Auger spectroscopy.

Section (i) of part D has been carried out using the XPS facility at Loughborough Consultants Limited. The results are discussed briefly in Section 7(iii).

6. Part E - 'Doping'

This part of the proposal suggested removal of the IRFNA electrolyte from existing BE-type cells and replacement with samples of acid which have been doped with metal ions and/or water. *was suggested*

Subsequently, the cells would be resealed and placed back on test to observe changes in i_{corr} and E_{corr} .

Following discussions on 15 September 1987, it was agreed that the effect on the corrosion rate of aluminium of water addition to IRFNA is perhaps the most important area for investigation.

Furthermore, it was decided to combine certain aspects of Parts A and E.

Problems have been encountered in the removal of acid from existing BWE-type cells.

On removing the six hexagonal-socket screws which hold the cell lid onto the body, it became clear that the cell lid could not simply be lifted off the cell body. This problem had arisen because the Teflon electrode-guide, through which the platinum reference- and counter-electrode wires pass, had expanded and become tightly lodged in the cell body. Only by cutting the counter electrode wire could the cell lid be removed*.

Progress on this part of the proposal has been limited to the successful removal of acid from one cell (BW18), and replacement with 'fresh' IRFNA (from R.O Westcott)#.

E_{corr} and i_{corr} are being monitored on this cell. The results are reported in Section 7(iv).

7. Results

(i) BW21, 22, 23 and 24 (Part A)

The horizontally mounted cells BW21, 22, 23 and 24 have been 'running' since March 1987.

Corrosion potential and corrosion current measurements have been obtained at frequent intervals. The latter are displayed graphically in Figures 1 and 2.

BW21 and 22 show a continuing decrease in corrosion current density with time. This trend has been observed using both the cell walls, and the aluminium section from SN5208, as working electrodes.

Corrosion current density measurements for BW23 and BW24 (both bottom working electrode and wall electrode) have remained reasonably constant, as displayed in Figure 2.

* on refurbished cells, the Teflon electrode guides have been reduced in size to prevent this problem recurring.

See Appendix A.

FIGURE 1

BW 21 and BW 22 I_{corr} vs. Time

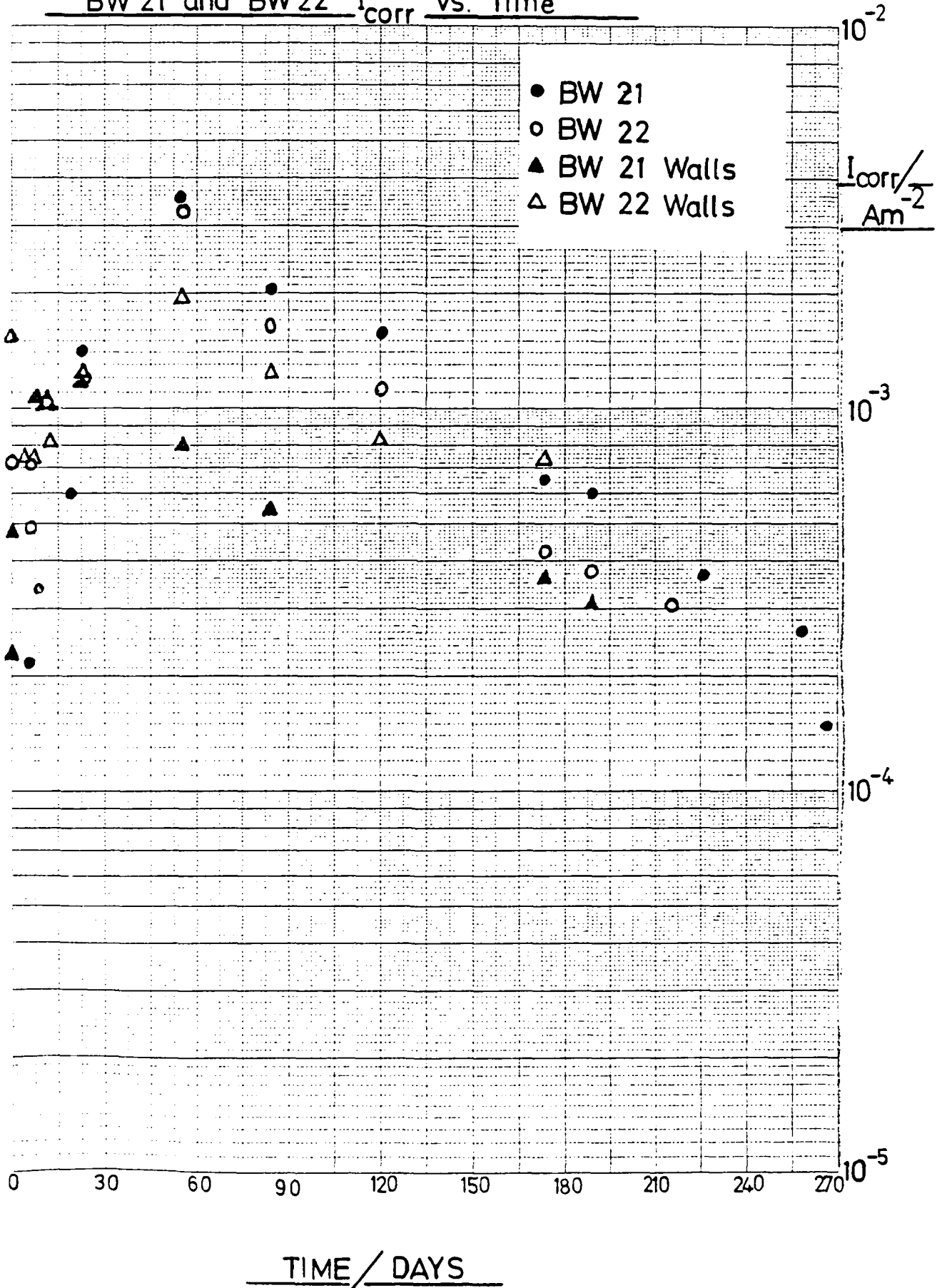
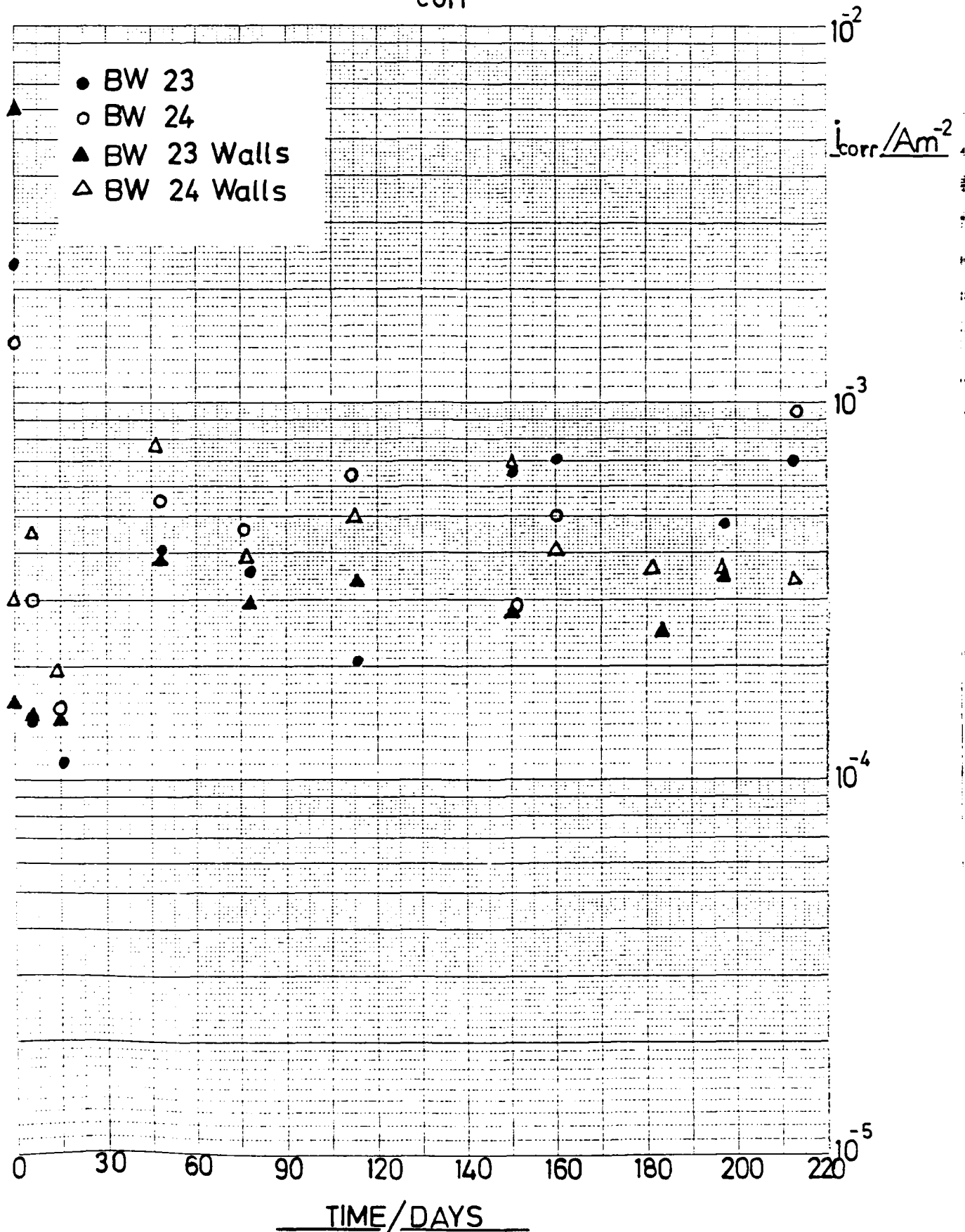


FIGURE 2

BW 23 and BW 24 i_{corr} vs. Time



The implications of these data are not quite clear. Reducing corrosion current density values (for BW21 and BW22) may indicate a build up of corrosion products on the surface of the working electrode which would inhibit migration of electroactive species to and from the electrode/solution interface, therefore reducing current density.

The electrochemical behaviour of these four cells will continue to be monitored.

7. (ii) Temperature Cycling (Part C)

Procedure

The working electrodes in the cells, BW13 and BW14, selected for this study were made up in July 1986 from LH and RH tank wall samples, whose sole pretreatment had been a wash with water.

The corrosion potentials E_{corr} and corrosion current densities i_{corr} of the bottom working electrodes in these cells, held at a constant temperature of 25°C, were determined periodically in order to establish the random fluctuations in these parameters. The results are presented in Figures 3 and 4.

The same cells were then subjected to a series of 24 hour cycles during which the temperature of the bath around the cells was made to oscillate between 20° and 30°C: the structure of each cycle, depicted in Figure 5, consists of a series of steps of 10 minutes heating followed by 60 minutes at constant temperature. The heating rate used was $0.1^{\circ}\text{C min}^{-1}$. The E_{corr} value of each working electrode was measured automatically at 30 minute intervals over a period of 6 days; the results are shown in Figure 6: i_{corr} values were determined intermittently over the same 6 day period; the values obtained showed some indication of periodic changes, however there were insufficient data for the behaviour to be adequately described. Therefore it was necessary to remeasure E_{corr} and i_{corr} regularly at 70 minute intervals for a full 24 hour cycle. These results are shown in Figures 7 and 8. At no time during this study was there any sign of leakage out of the cells.

Discussion

The E_{corr} and i_{corr} measurements made on the two cells BW13 and BW14 at 25°C were found to agree with one another within 10 mV or $1 \times 10^{-4} \text{ Am}^{-2}$ respectively, see Figures 3 and 4. This agreement was considerably better than had been expected, and can be taken to show that the cells selected had achieved a steady state. The standard deviations for both types of measurements on BW14 are higher than those for BW13 on account of two untypical sets of readings after ca. five days. Similarly satisfactory results were obtained for the E_{corr} values (at 25°C), as measured during the first 6 days of temperature cycling. This is significant because it appears to show that the cell is behaving in a 'reversible' manner rather than showing hysteresis: in fact the general appearance of Figure 6 is remarkably symmetrical with the highest temperature (30°C) corresponding to the most negative corrosion potential and vice versa.

The effect of temperature cycling on E_{corr} for BW13 also shows, see Figure 7, a clear cyclic variation with time, with an amplitude (ca. 15 mV) comparable with that shown in Figure 6. Unfortunately the E_{corr} data for BW14 became highly capricious. The i_{corr} values for the two cells, Figure 8, reflect these results although those for BW14 show signs of a sinusoidal fluctuation. Of particular interest is the observation that the maximum i_{corr} for BW13 occurs at the highest temperature and that the lowest i_{corr} coincides with the minimum temperature: although the results for BW14 are less convincing, they show a similar tendency.

This kind of behaviour (minimum i_{corr} at most positive or noble E_{corr}) is recognised a consequence of inhibition or blocking of the anodic sites, where the reaction is $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^{-}$, by an insoluble corrosion product, such as solvated AlF_3 or Al_2O_3 , as a result of which the anodic exchange current density is diminished. Of itself the regular oscillation of i_{corr} shown by BW13 should not lead to an overall increase in the rate of corrosion, although it will be interesting to see whether the oscillations are truly regular and symmetrical; thus a

Figure 3 : E_{corr} versus Time at Constant Temperature (25°C)

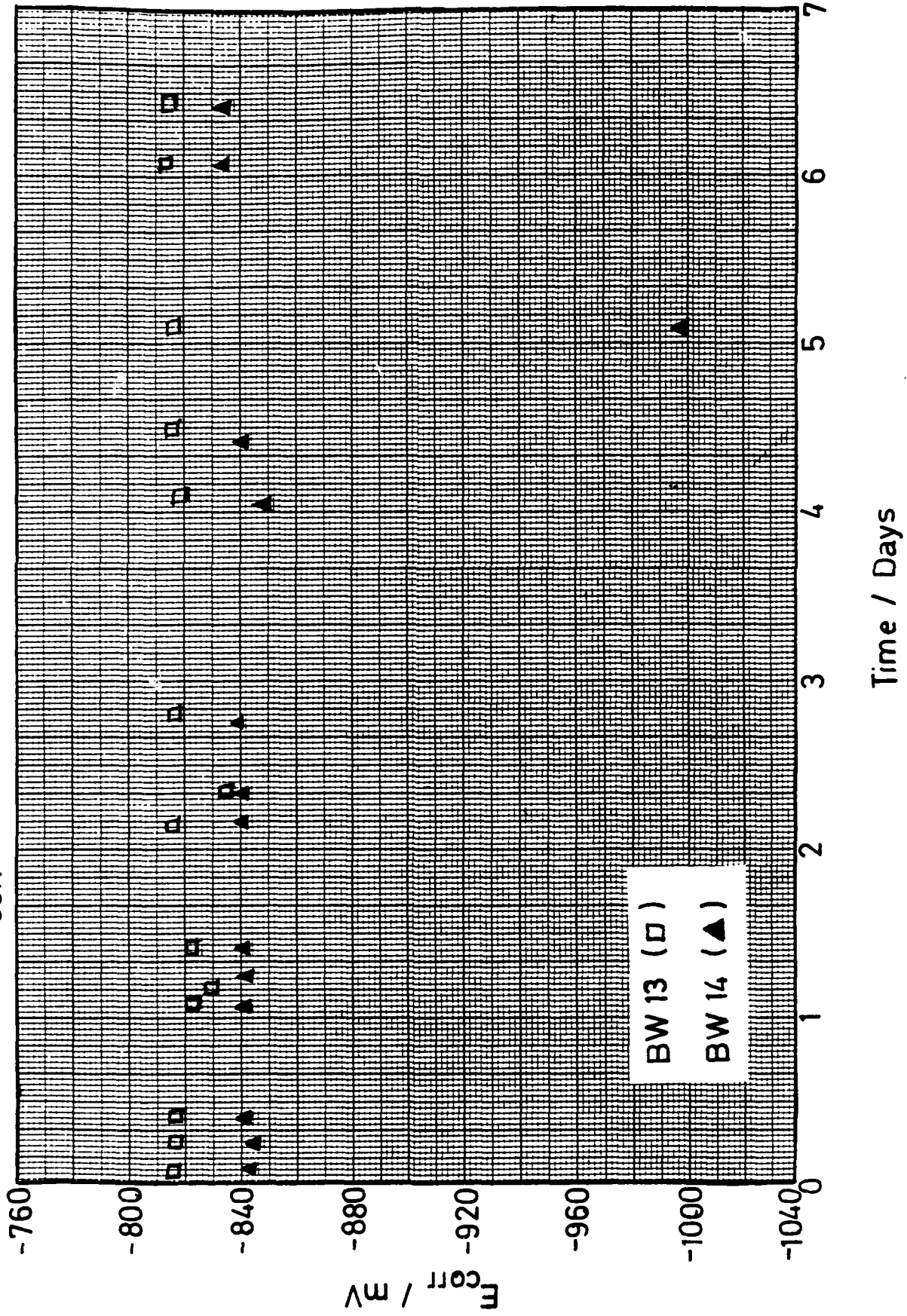


Figure 4 :

i_{corr} versus Time at 25°C BW13 (□) BW14 (▲)

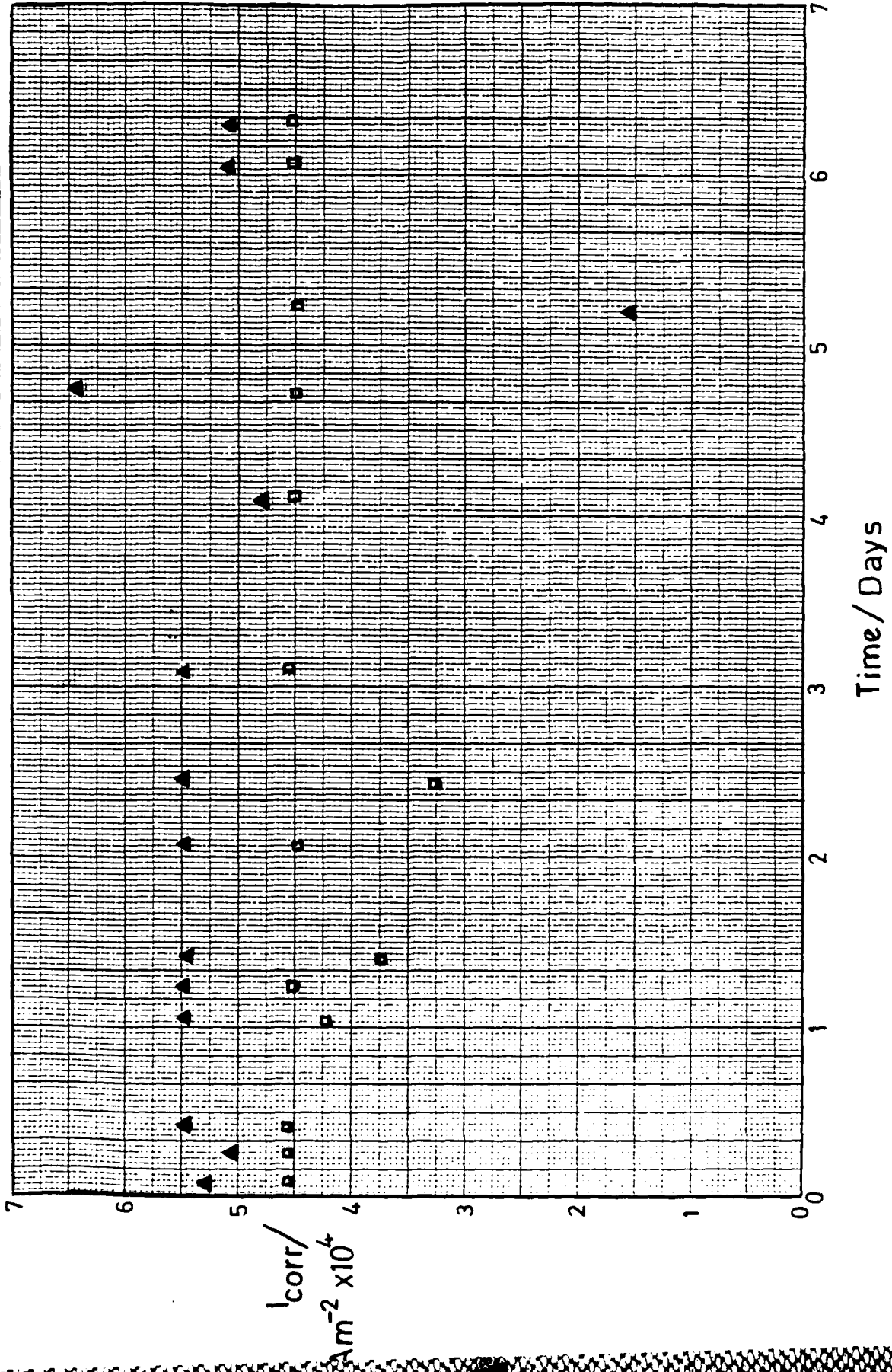


Figure 5: Temperature Cycle for a $\pm 5^{\circ}\text{C}$ Change

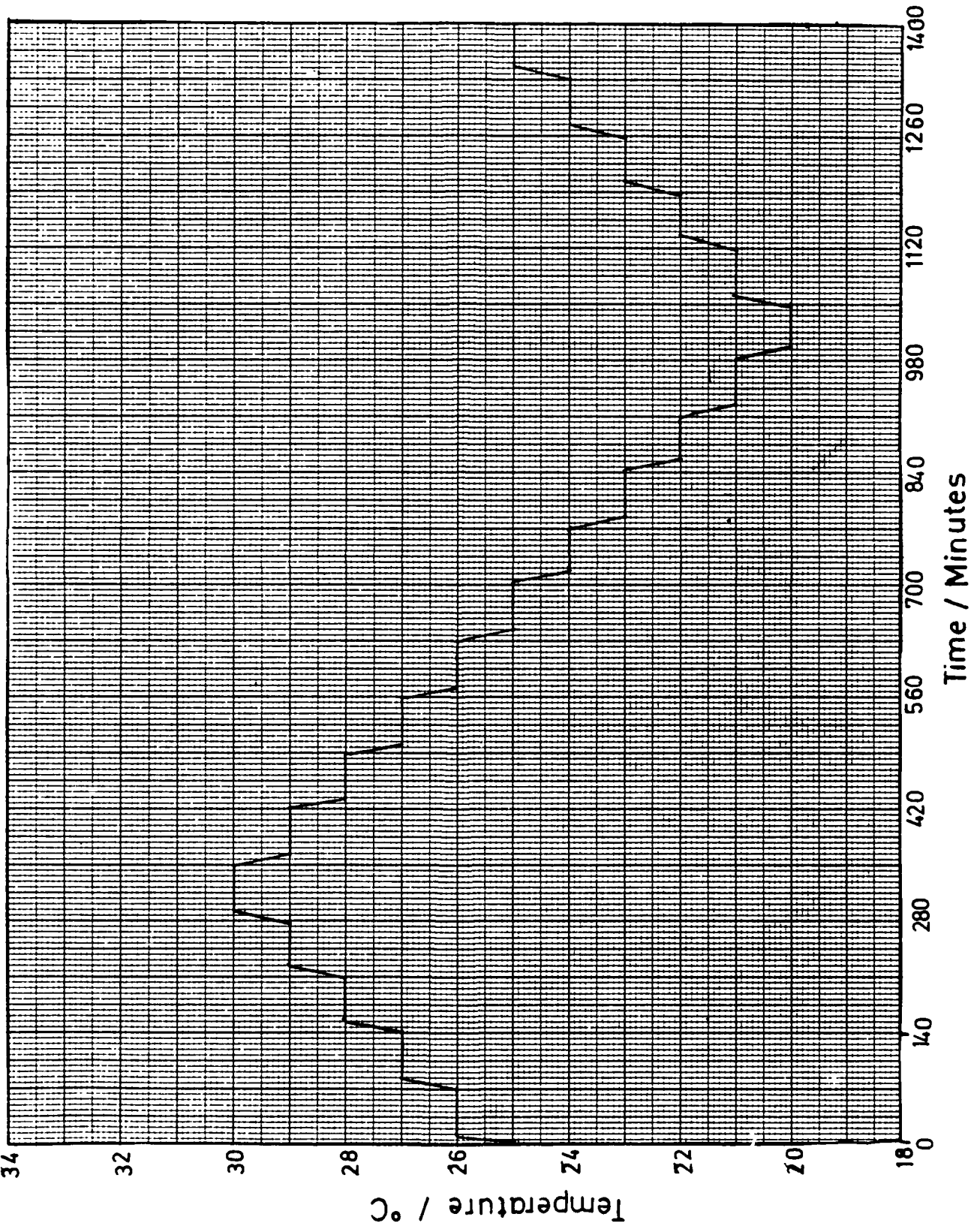


FIGURE 6 ; Variation of Corrosion Potential, E_{corr} , with Time during a $\pm 5^{\circ}\text{C}$ Temperature Cycle. BW 13 (\square) BW 14 (\blacktriangle)

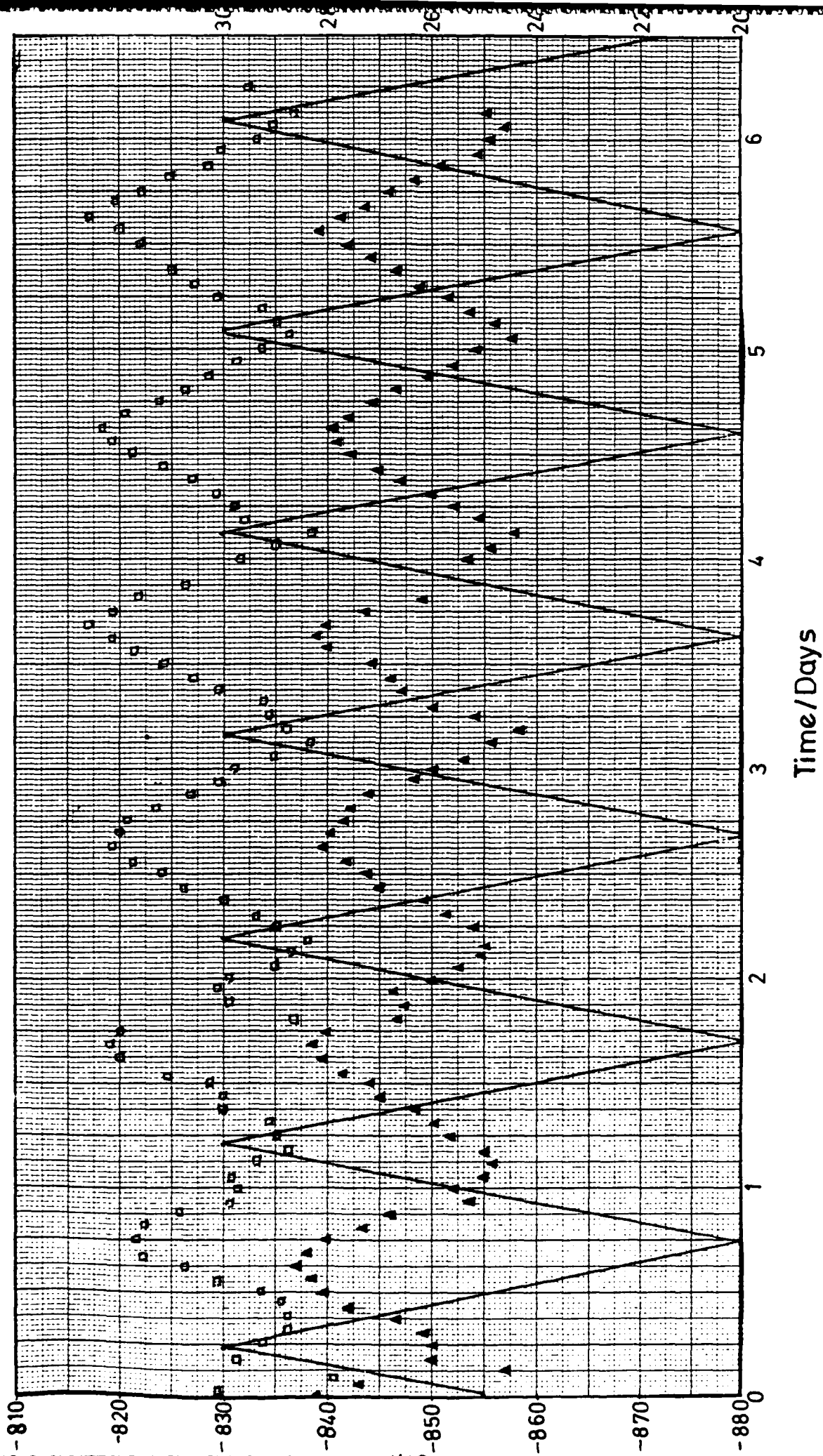


Figure 7: E_{corr} versus Time during a $\pm 5^\circ\text{C}$ Temperature Cycle

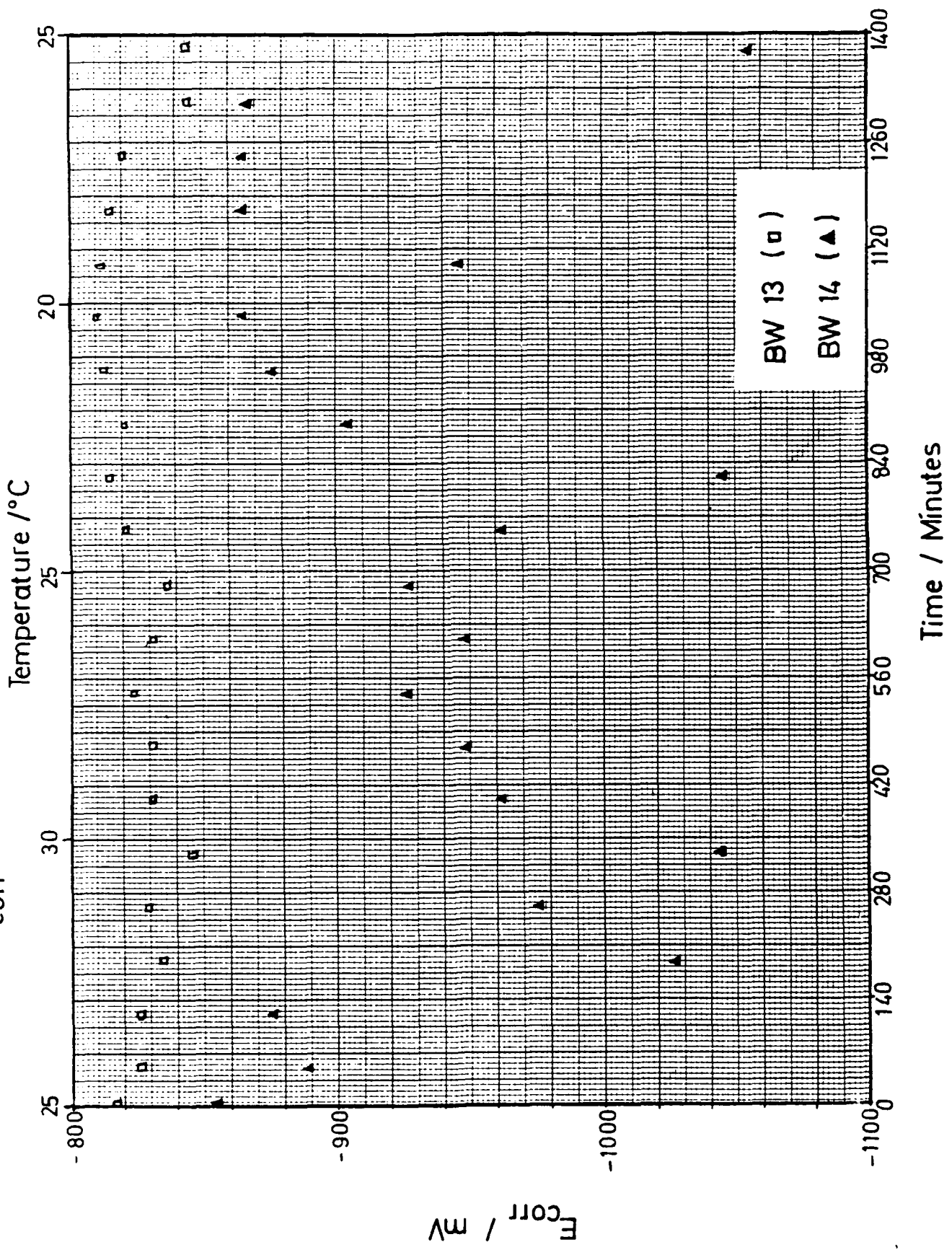
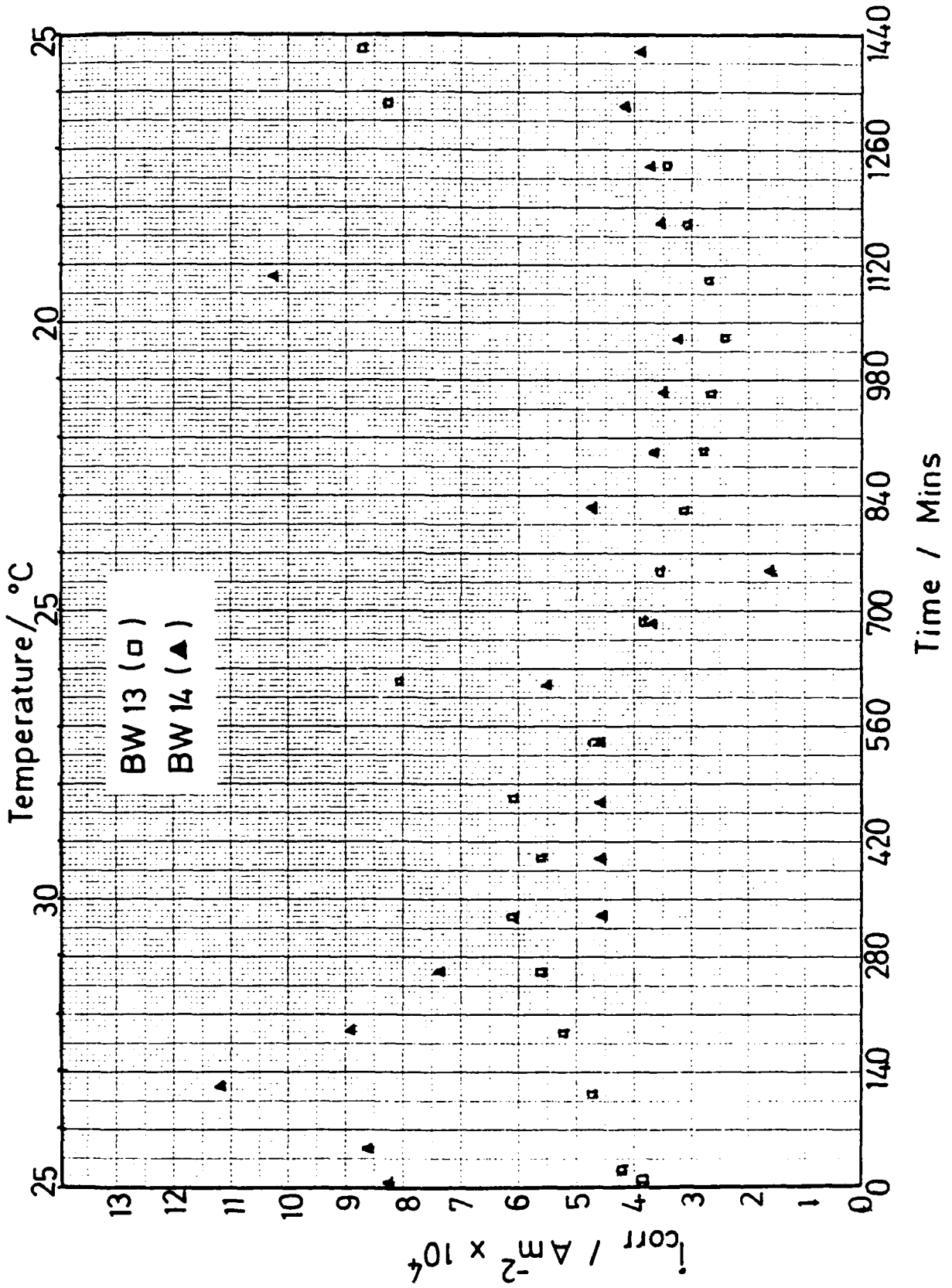


Figure 8 : Variation of Corrosion Current Density with Time during a $\pm 5^\circ\text{C}$ Temperature Cycle about 25°C



disproportionately large increase in i_{corr} during the heating cycle might outweigh the effect of cooling. On the other hand, if two storage sites differ in average temperature by about 10°C our results suggest that the storage tanks at the warmer site could experience approximately twice the rate of corrosion, all other factors being equal. The 'anomalous' behaviour of BW14 which previous as well as subsequent studies have shown to be temporary is perhaps of greater significance. The evidence for this is that most of the deviations in the i_{corr} for this cell lead to higher corrosion rates than would have been expected for a well-behaved cell. The average value for i_{corr} during this 24 hour cycle for BW14 was $5.45 \times 10^{-4} \text{ A m}^{-2}$.

Footnote: The observed change in E_{corr} values is in general made up of two parts, namely absolute changes in the reference potential as well as absolute changes in the potential of the working electrode itself. It is not obvious how to assess the relative values of these changes but it is not too important since the main thrust of the argument depends on the changes in the i_{corr} values.

7. (iii) Surface Studies (Part D)

Samples of aluminium alloy taken from an oxidiser tank wall section (SN5144) were examined by X-Ray Photoelectron Spectroscopy (XPS) using the facility at Loughborough Consultants Ltd.

Samples were taken from the top, middle and bottom of the oxidiser tank section, and were analysed as received and after argon ion etching (to remove the outermost atom layers).

All three samples showed similar O:F:Al ratios. However, the sample taken from the middle of the oxidiser tank wall section had fewer contaminants and was chosen for a more detailed investigation.

The results obtained indicate the presence of both aluminium oxide and aluminium fluoride with possible contributions from hydrated oxide and oxide fluoride species.

7. (iv) BW18 (Part E)

BW18 was set up on 10 September 1986. The aqueous HF pretreated cell was filled with IRFNA (11.821 g), supplied by R.O Westcott*, and placed on test. E_{corr} and i_{corr} have been monitored since that time.

On 24 November 1987, the cell was temporarily removed from test, and the cell lid was removed. The acid electrolyte was removed with an FEP dropping pipette, and replaced with a quantity (11.79 g) of IRFNA from a new batch (R.O Westcott - Drum 3, Lot 67)*. The cell lid was replaced, and the cell put back on test. E_{corr} and i_{corr} have been measured since the cell was originally set up and the data are plotted in Figures 9 and 10.

Figure 9 shows the E_{corr} versus time data. It is interesting to note the corrosion potential at the point in time when the acid electrolyte was replaced (440 days). No significant change in E_{corr} was observed.

Figure 10 shows the i_{corr} versus time data. Here, a change in corrosion current density from ca. $5.4 \times 10^{-4} \text{ Am}^{-2}$ to ca. $1.5 \times 10^{-3} \text{ Am}^{-2}$, is observed at 440 days, corresponding to the change in electrolyte. However, after ca. 466 days the corrosion current density had decreased to a value similar to that observed with the 'old' electrolyte immediately prior to replacement (ie. $< 10^{-3} \text{ Am}^{-2}$).

From these observations we may conclude that changing the electrolyte has not affected the corrosion rate of the aluminium alloy to any significant degree.

* see Appendix

FIGURE 9

BW18 E_{corr} vs. Time

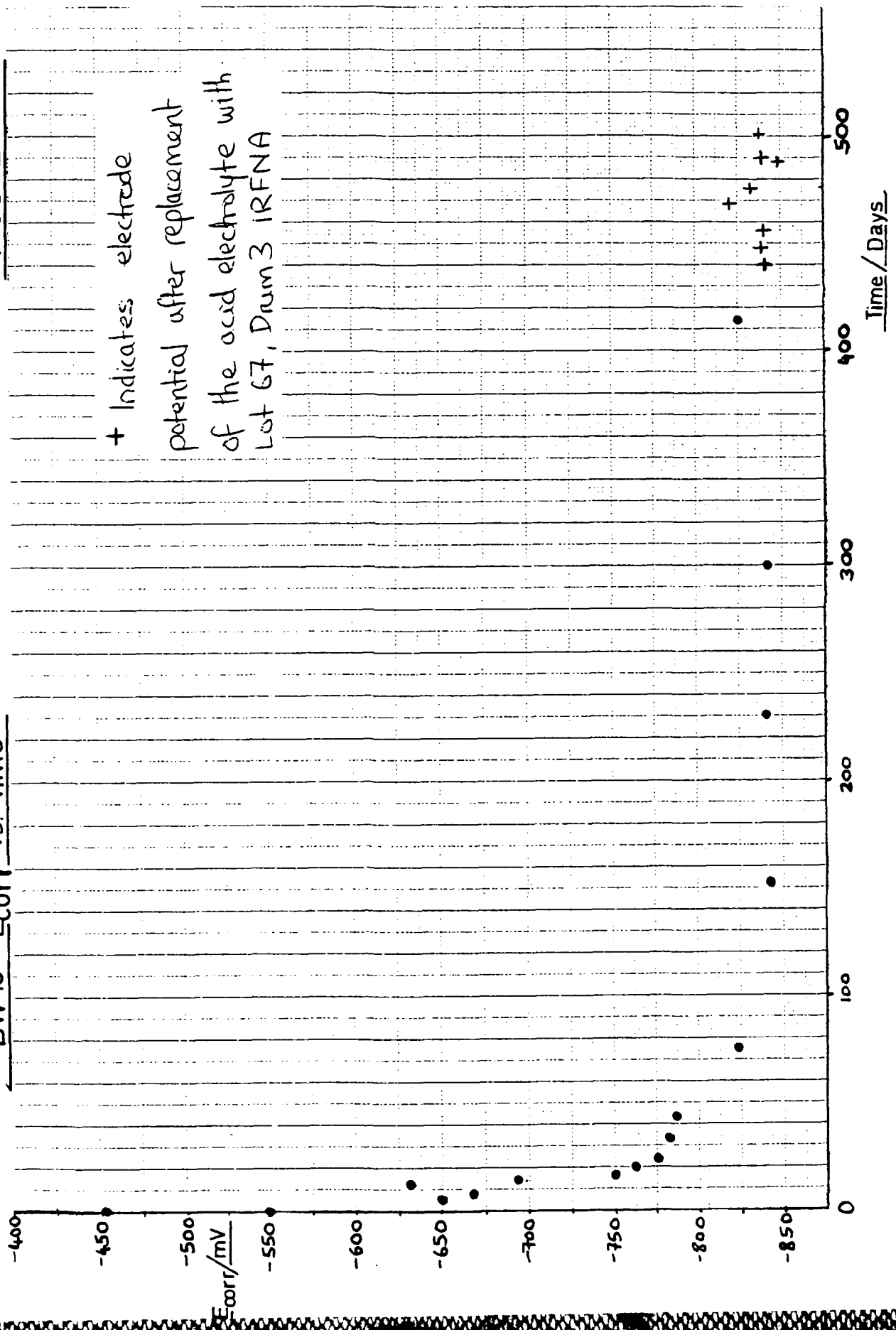
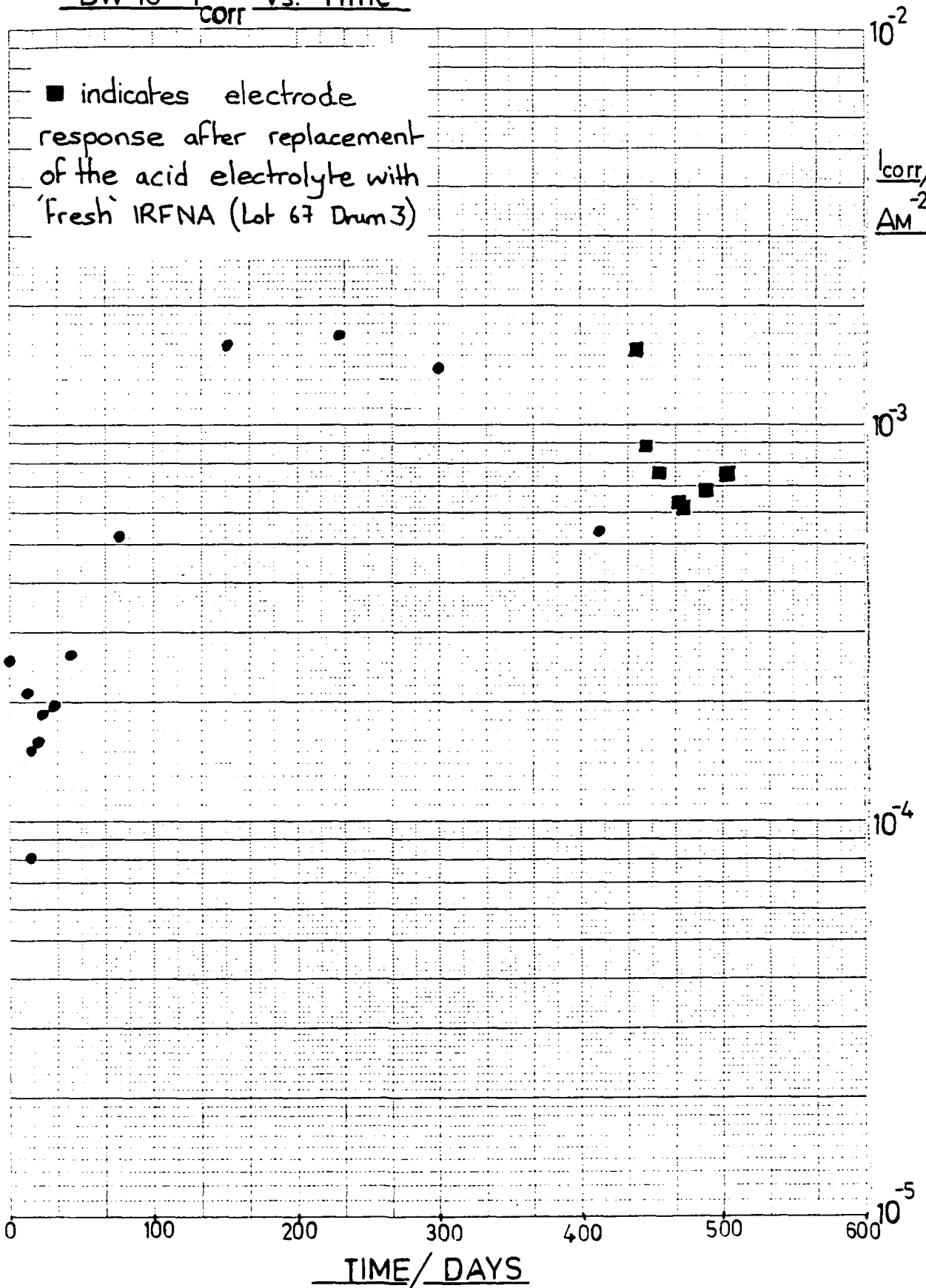


FIGURE 10

BW 18 i_{corr} vs. Time



8. Appendix Composition of IRFNA

Composition of IRFNA supplied by R.O Westcott and used in cells P/BWE to BW20 inc.*

HF	0.55 wt %	(Nottingham analysis)
Al	170	wppm
Cu	4.3	wppm
Fe	151	wppm
Cr	34.1	wppm

* with the exception of BW2 (IRFNA ex SN5208)

Composition of IRFNA supplied by R.O Westcott (Lot 67, Drum 3; October 1987) and used to refill BW18.

HF	=	0.55 wt %	(R.O Westcott analysis)
HF	=	0.52 wt %	(Nottingham analysis)
H ₂ O	=	2.0 wt %	

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